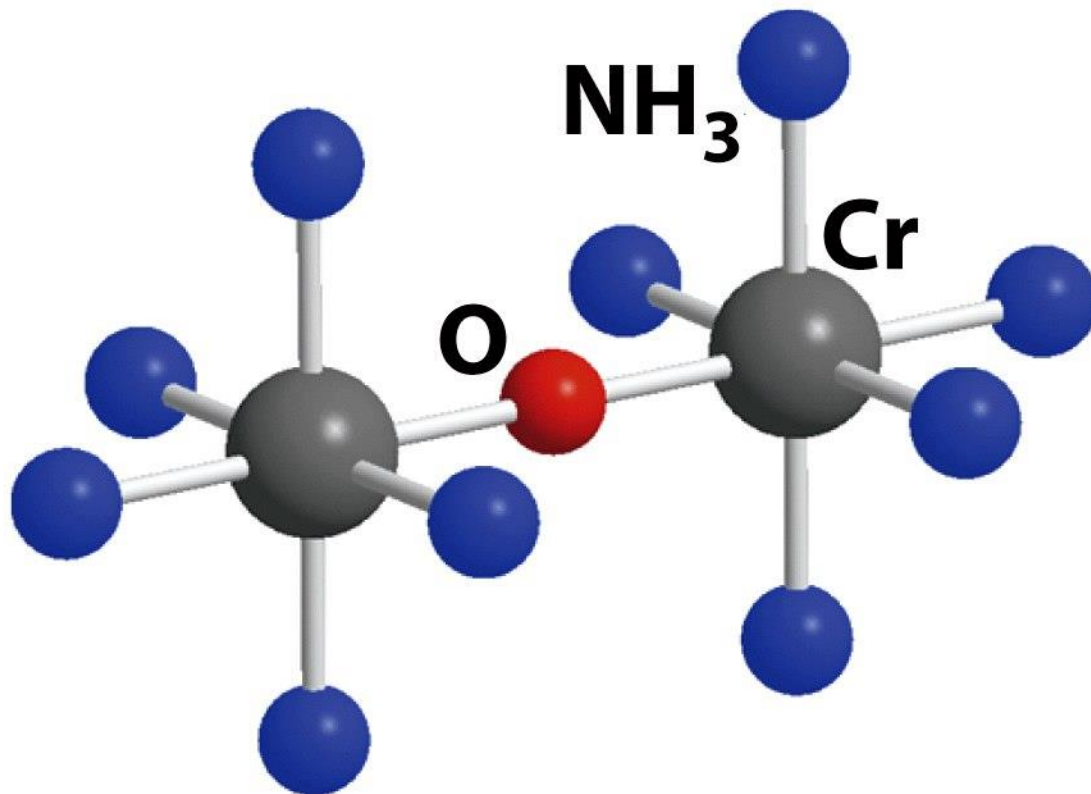


$[\text{Co}(\text{NH}_3)_6]^{3+}$ esaamminocobalto(III)

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

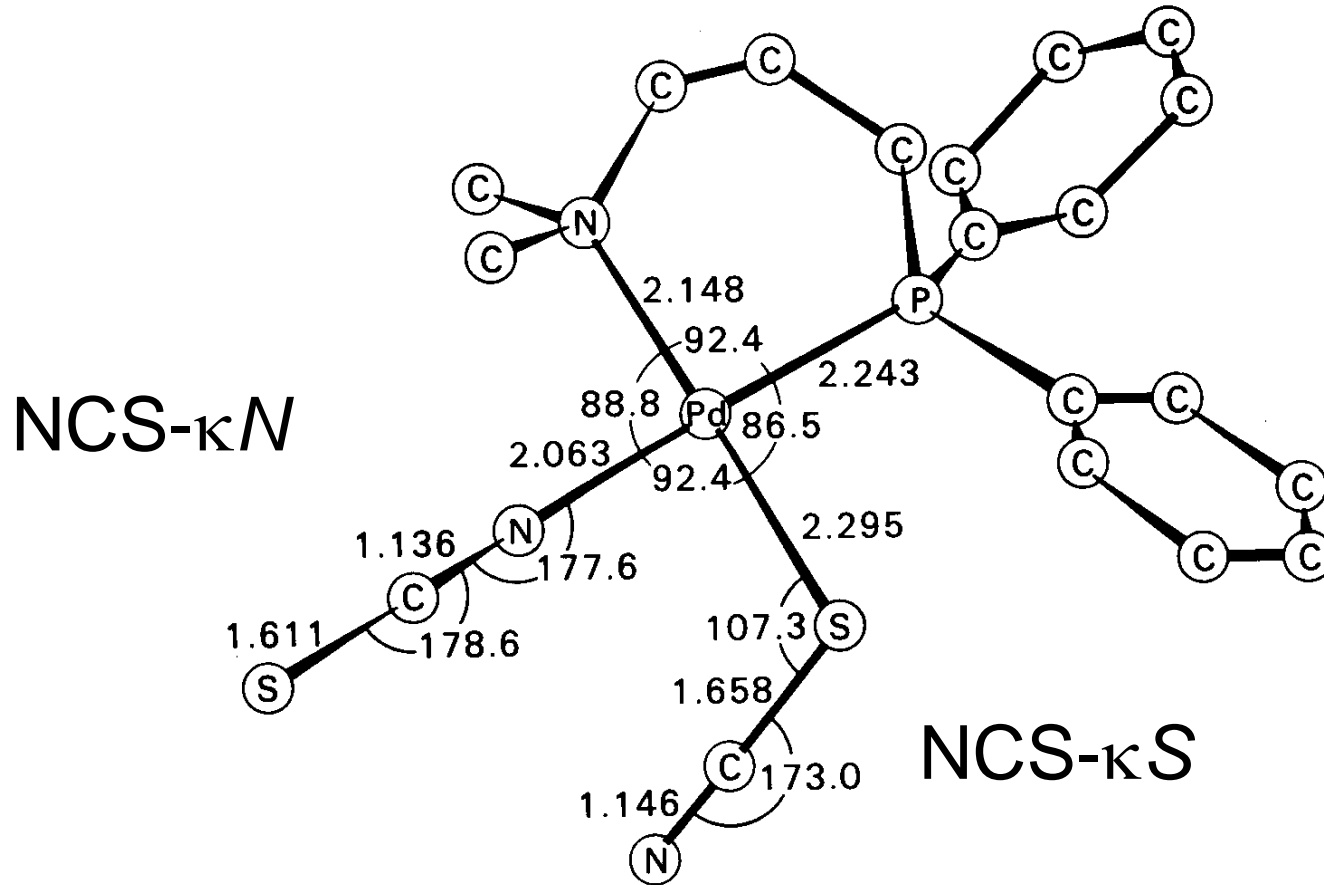
$[\text{PtCl}_4]^{2-}$ tetracloroplatinato(II)

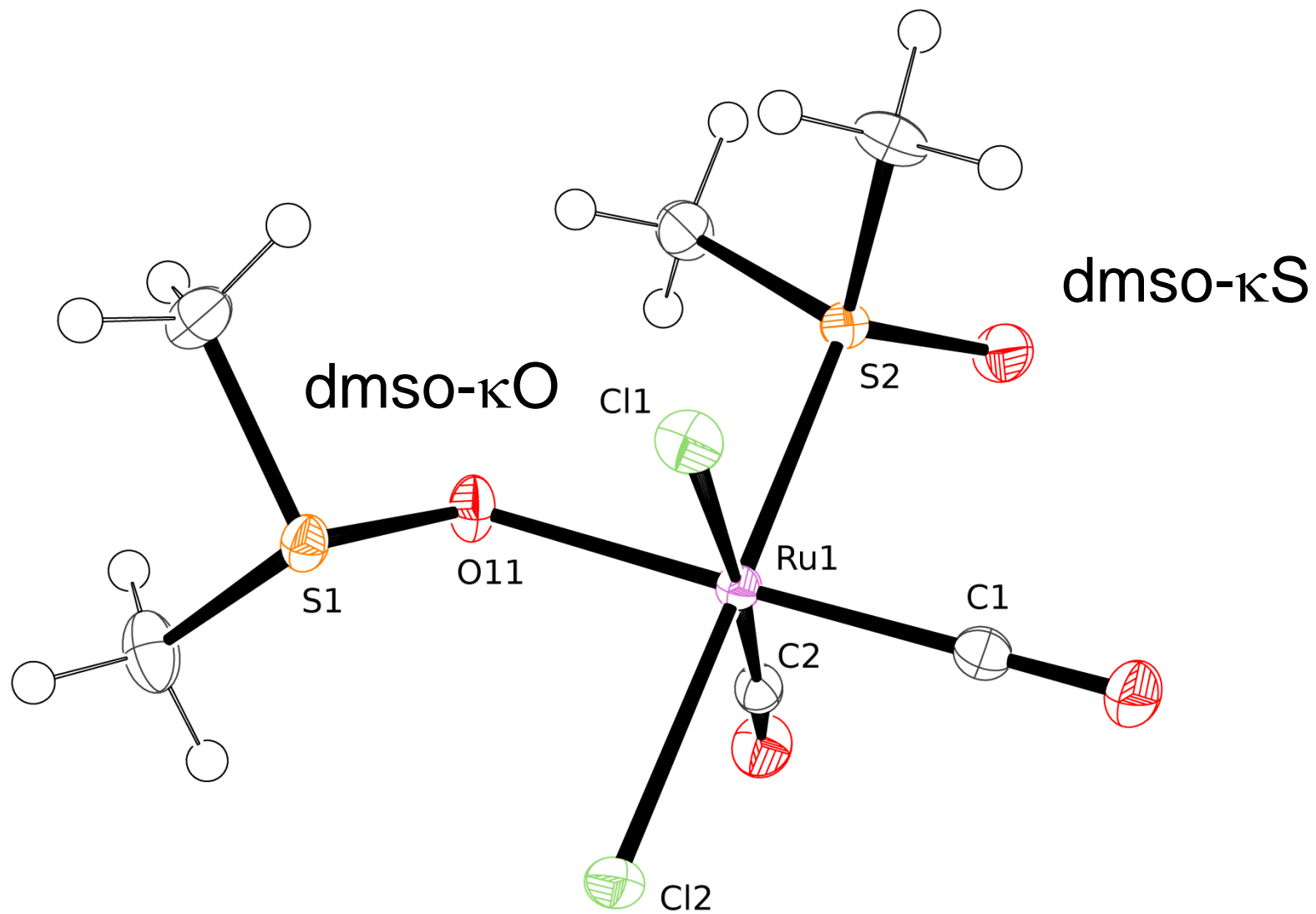


μ -osso-bis(pentaammino)cromo(III)



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)

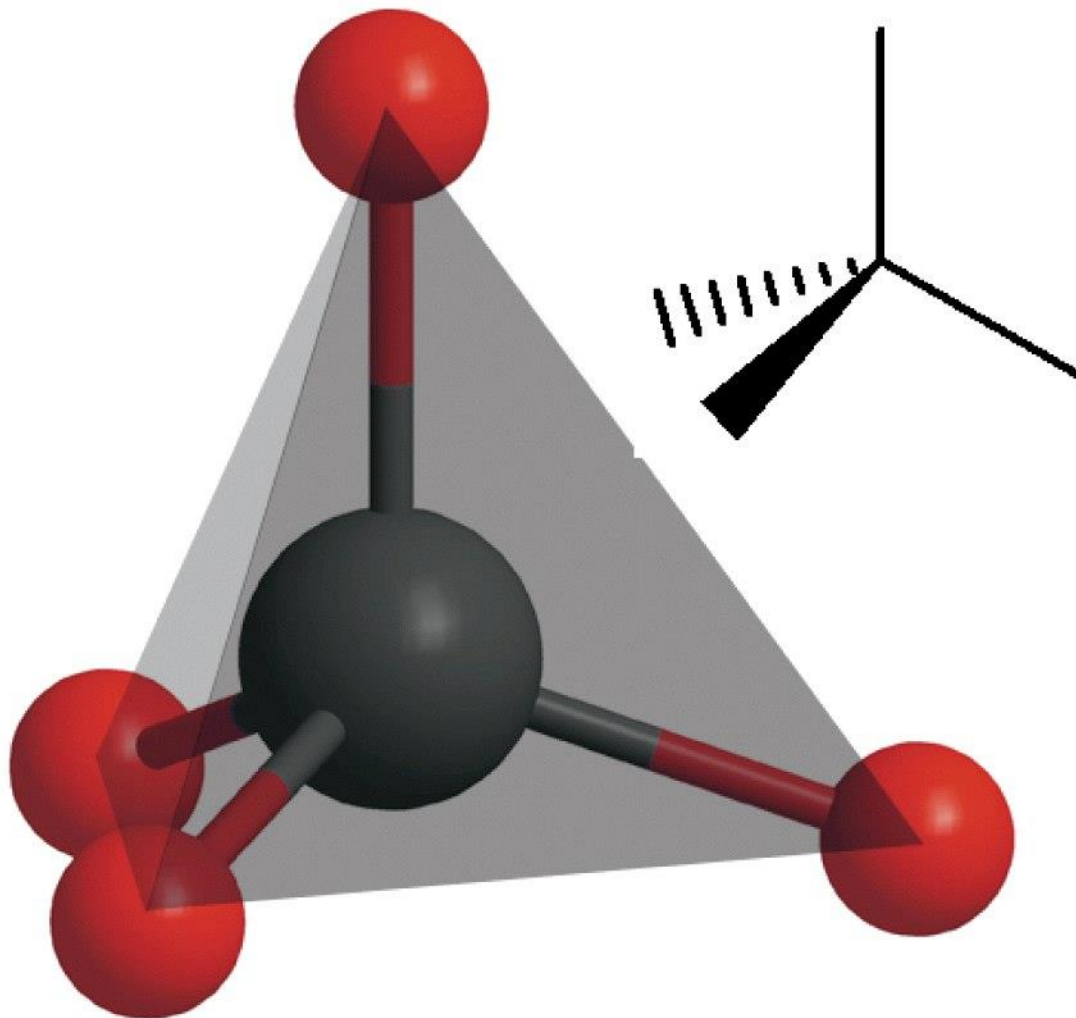


Numero di coordinazione 3 geometria trigonale planare

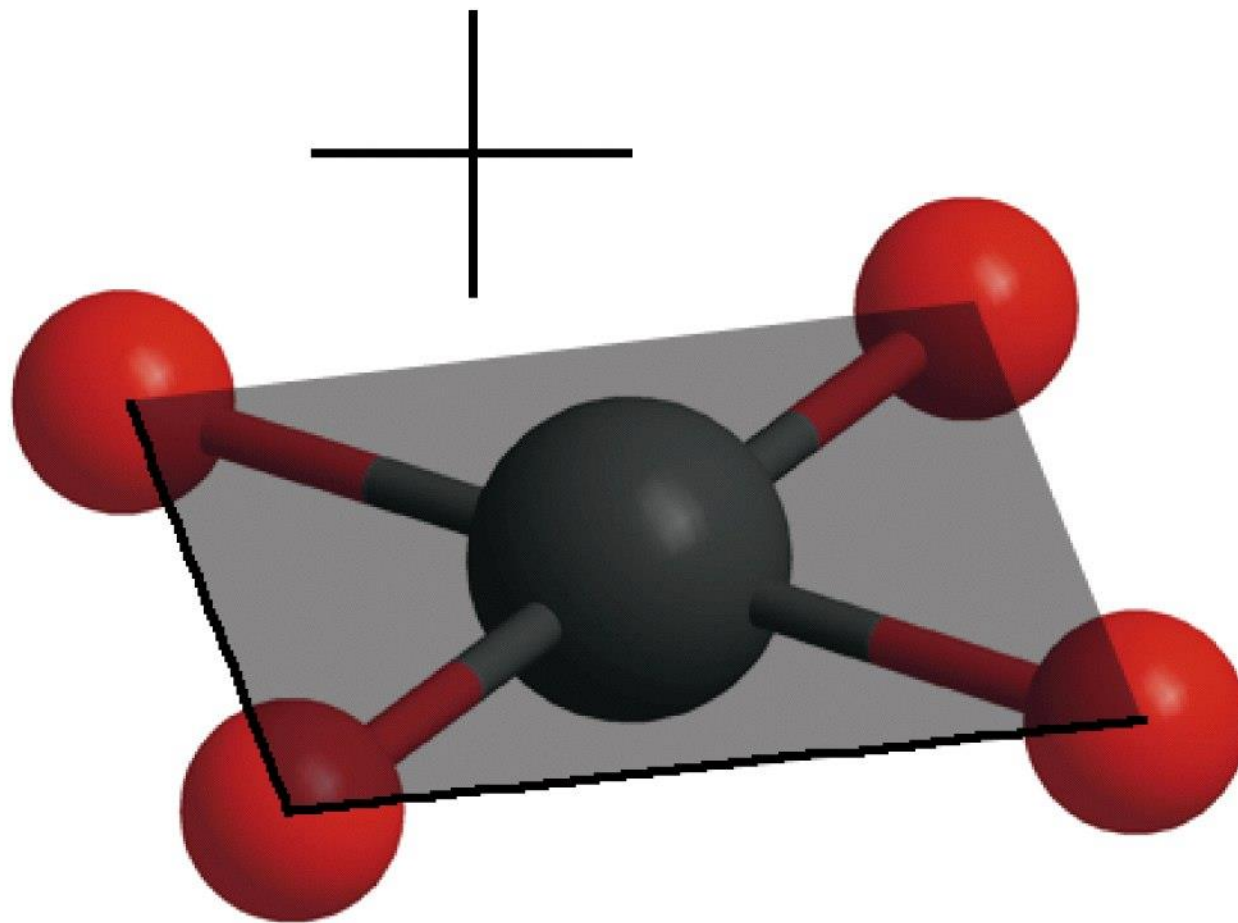
Ioni d^{10} : Cu(I), Au(I), Pt(0)



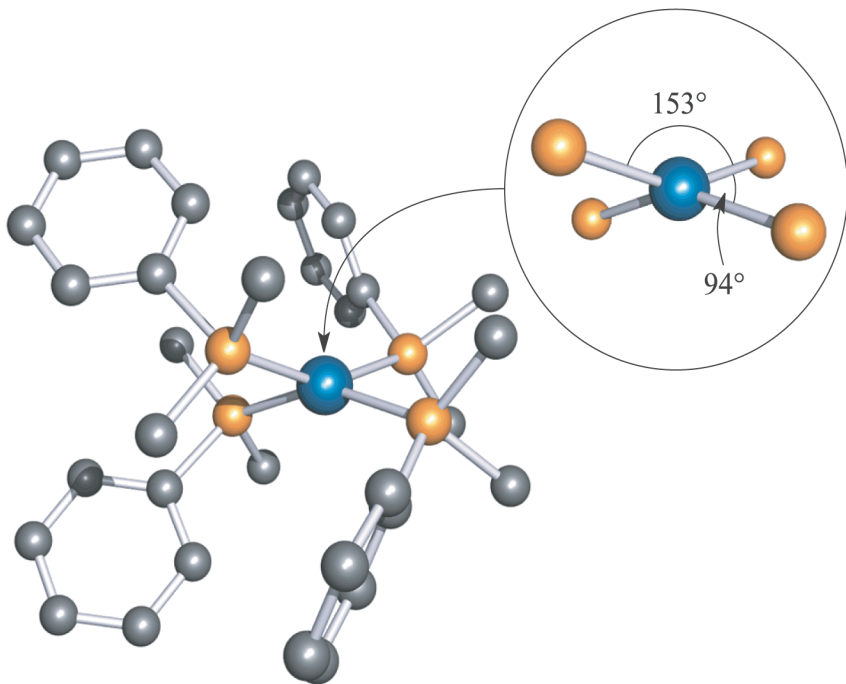
anioni poco coordinanti: NO_3^- , ClO_4^- , CF_3SO_3^- (triflato),
 BF_4^- , PF_6^- , SbF_6^-



Tetrahedral complex, T_d



Square-planar complex, D_{4h}



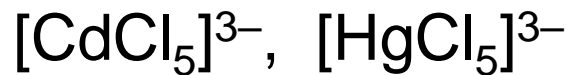
D_{2d}



Distorsione della geometria planare-quadrata causata da leganti voluminosi

Complessi pentacoordinati

Bipiramide trigonale



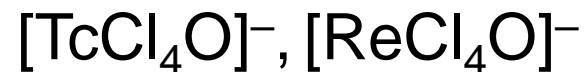
d^{10}

minimizza le repulsioni fra i leganti

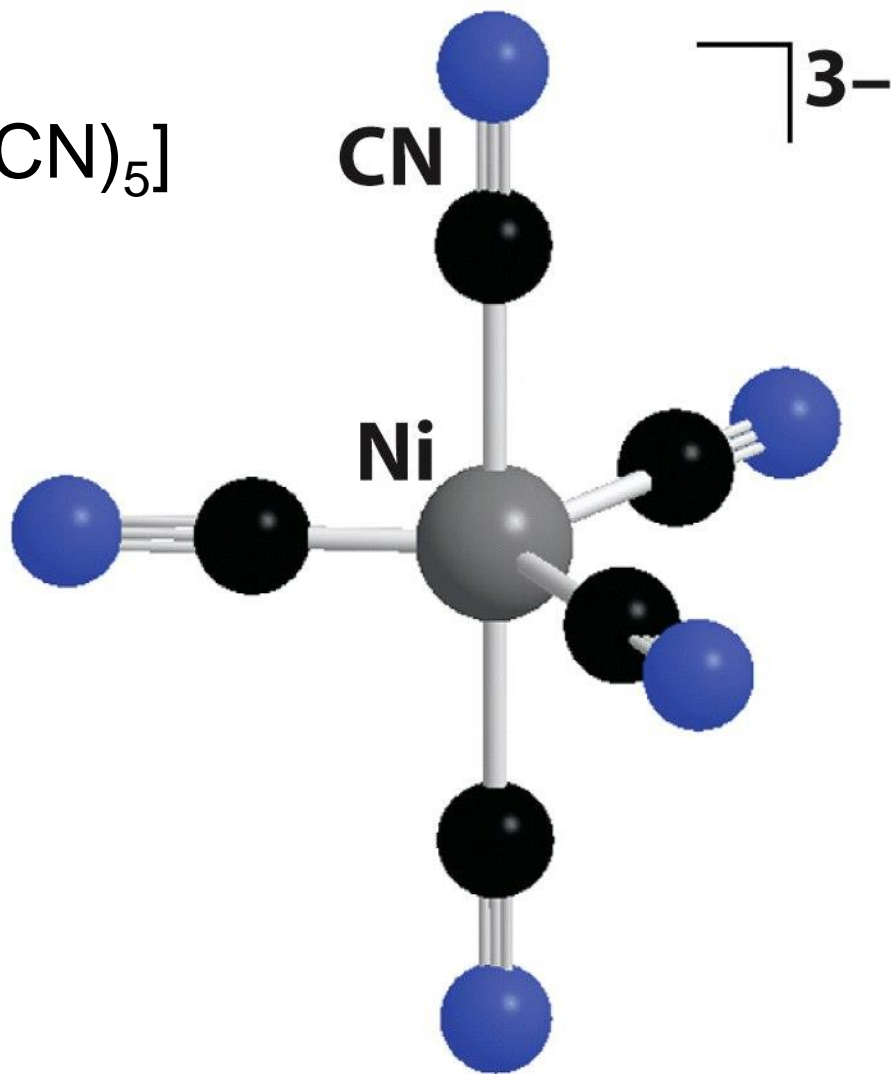
Piramide a base quadrata

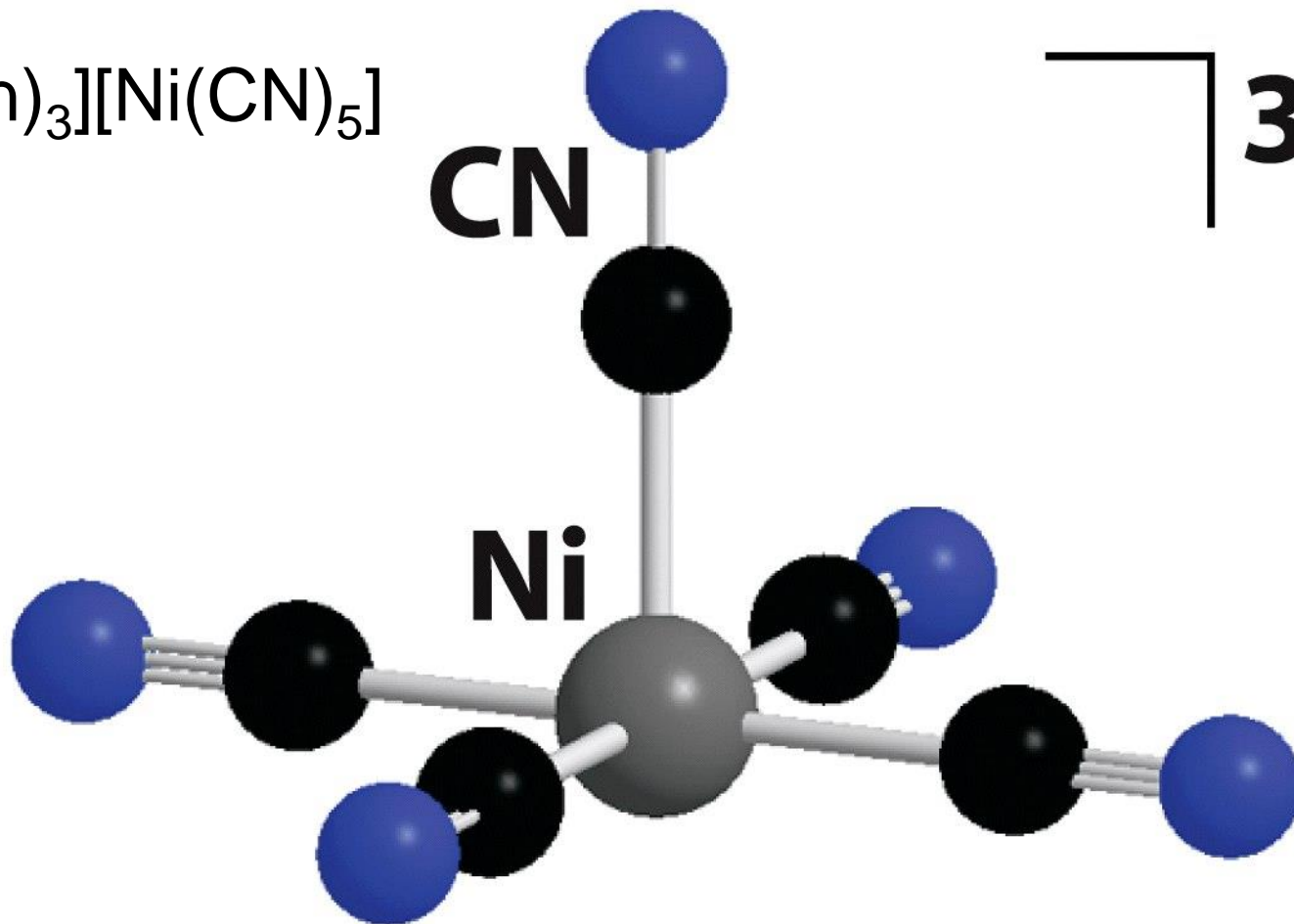


d^1



d^2

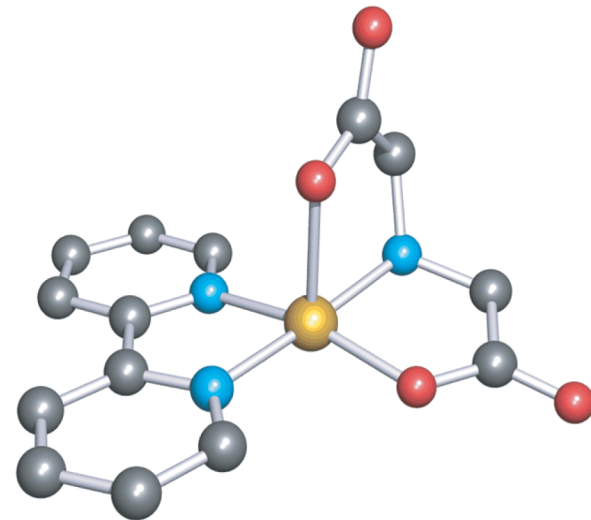
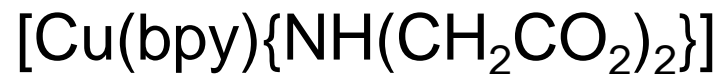
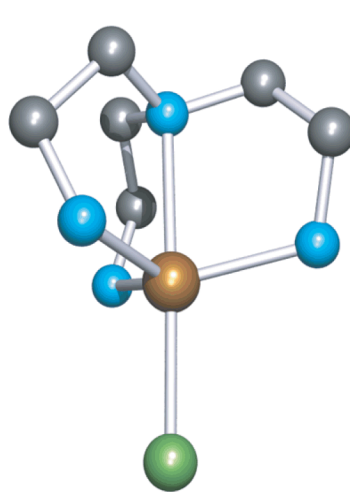




Esempi di complessi pentacoordinati con geometria imposta dai leganti

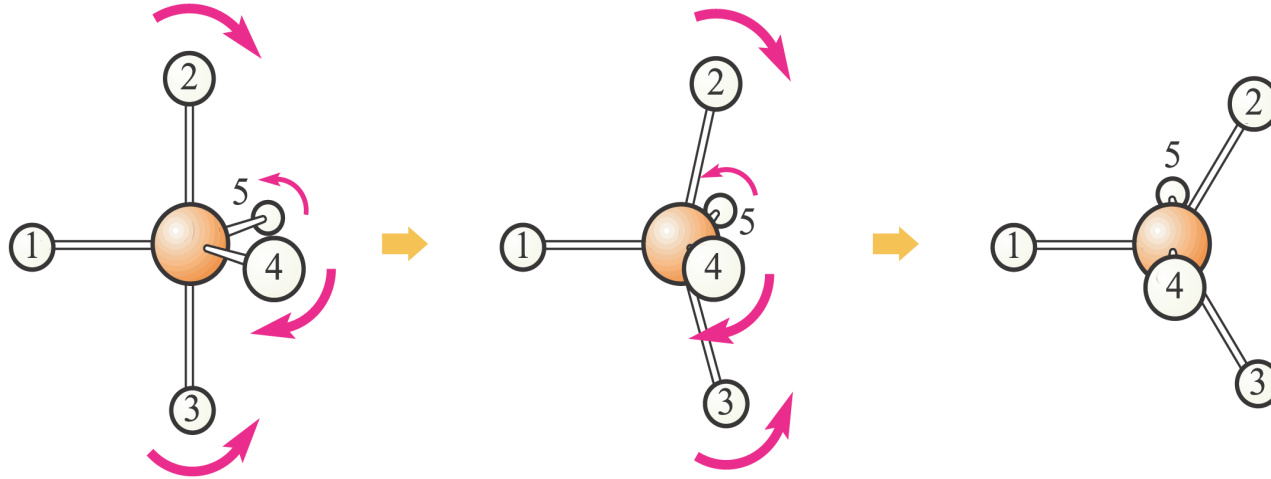


Legante tripodale



Flussionalità

Pseudo-rotazione di Berry

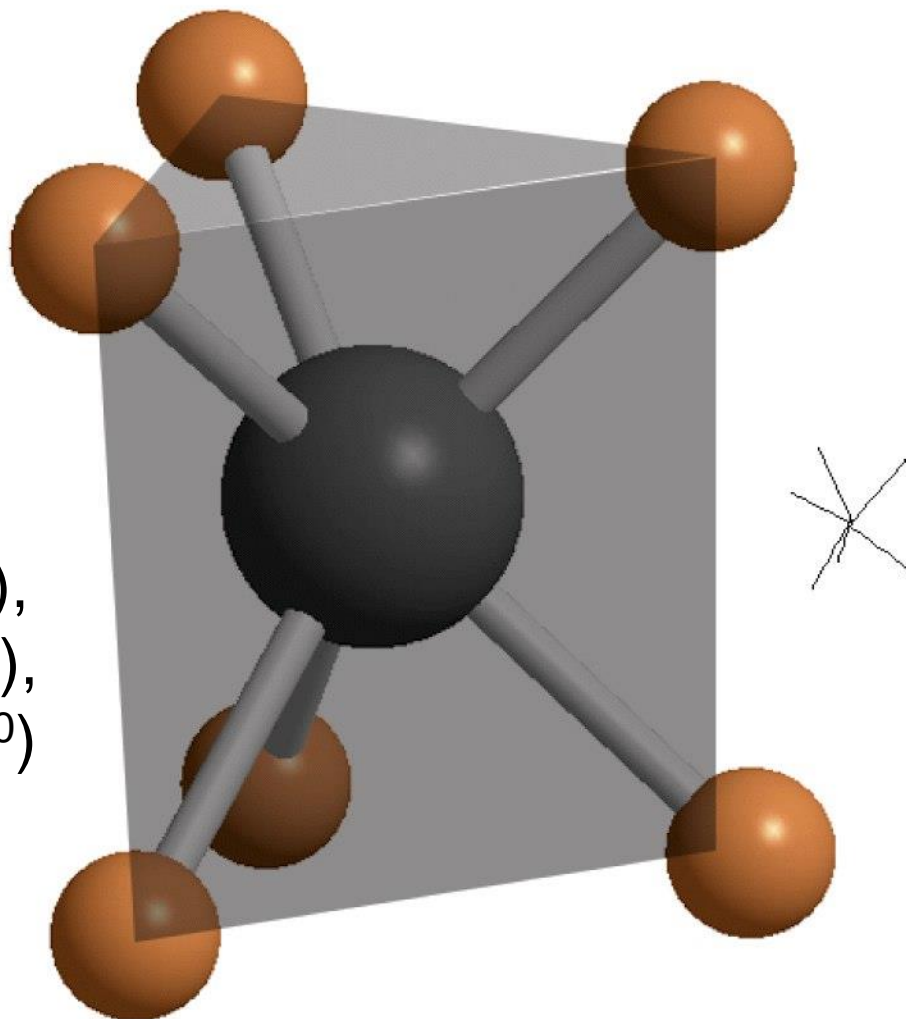


Trigonal bipyramid
(Atoms 2 and 3 are
in axial sites.)

Square-based pyramid

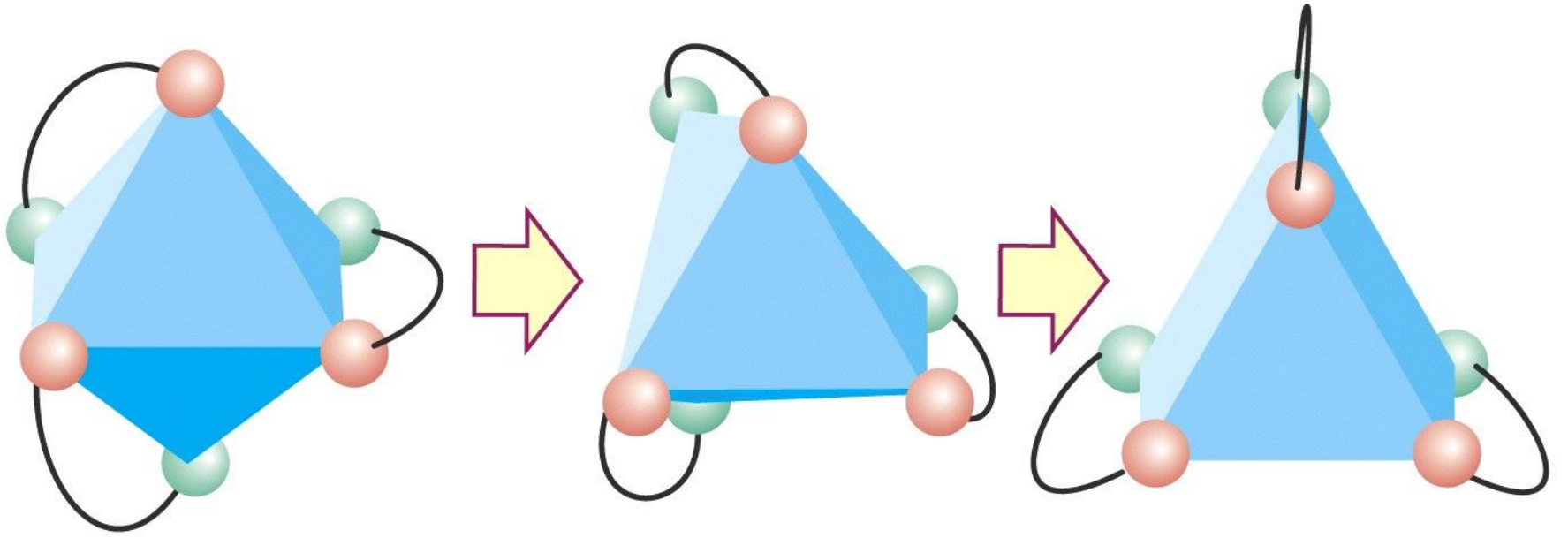
Trigonal bipyramid
(Atoms 4 and 5 are
in axial sites.)

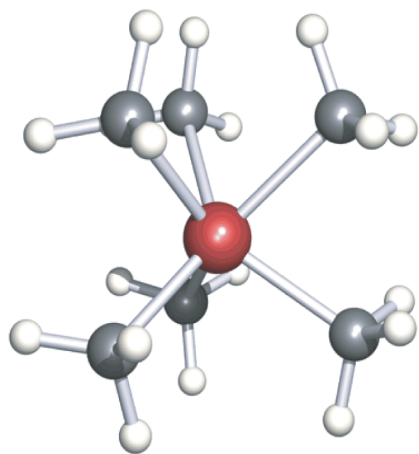
$[\text{Re}(\text{CH}_3)_6]$ (d^1),
 $[\text{Ta}(\text{CH}_3)_6]^-$ (d^0),
 $[\text{Zr}(\text{CH}_3)_6]^{2-}$ (d^0)



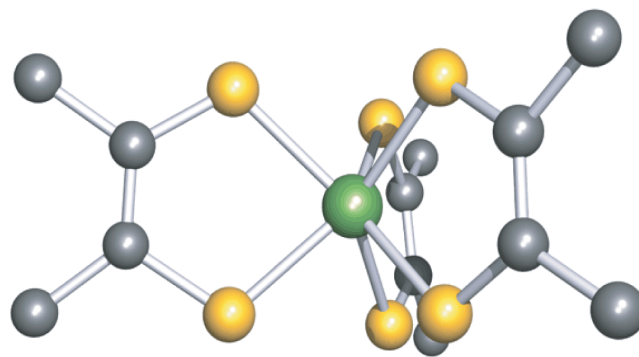
Trigonal prism, D_{3h}

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

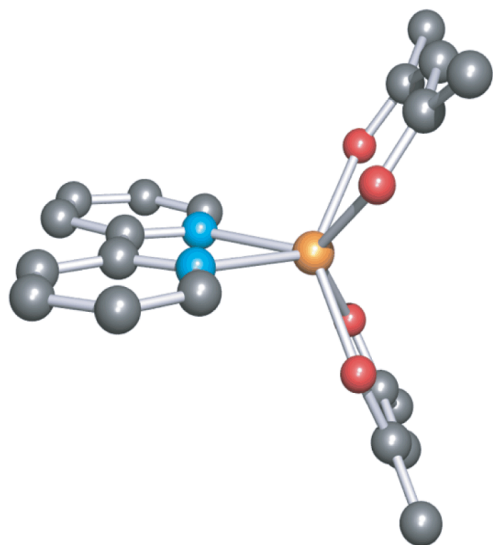




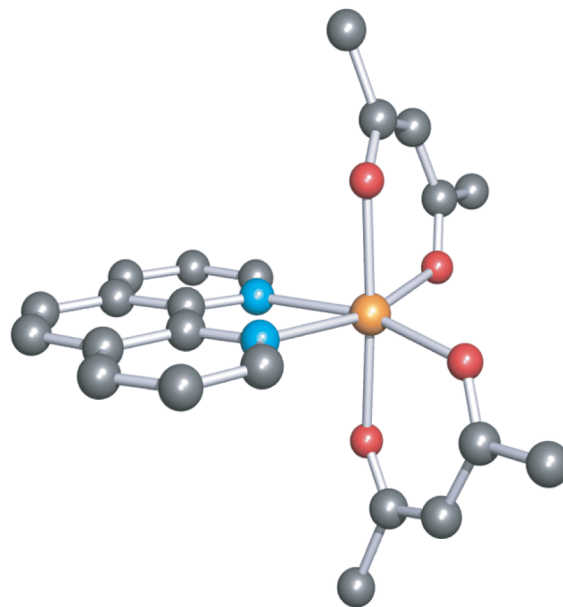
[W(CH₃)₆] (d⁰)



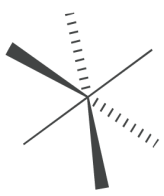
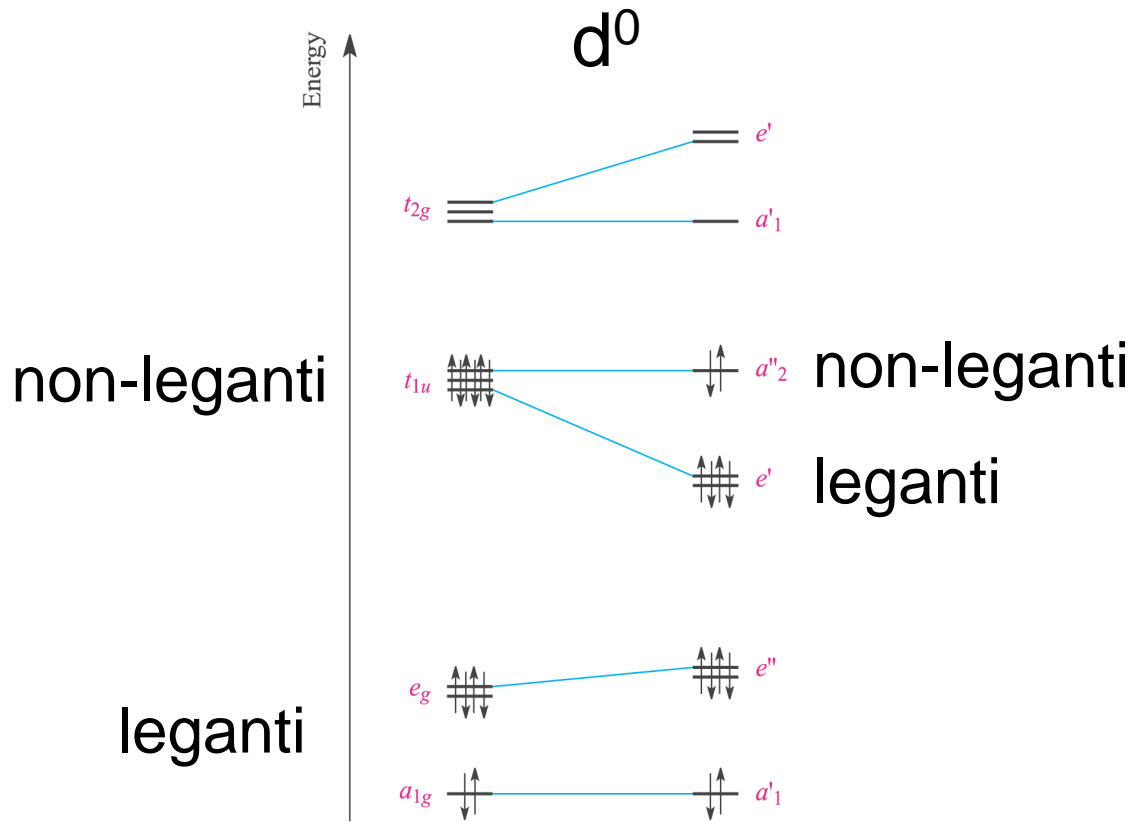
[Re(S₂C₂Ph₂)₃] (d¹)



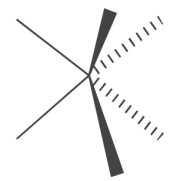
[Mn(acac)₂(bipy)]



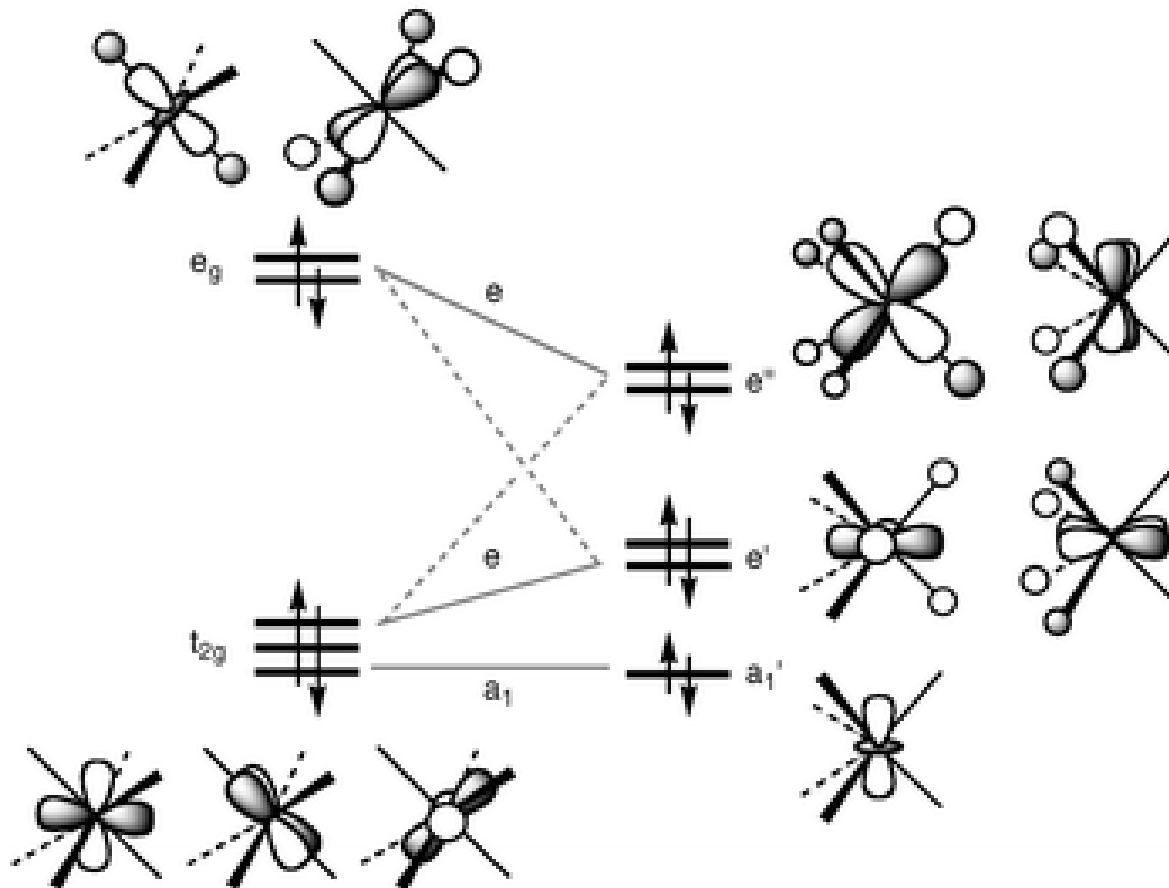
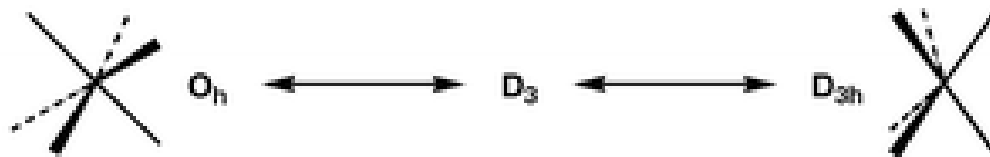
[Mn(acac)₂(phen)]



Octahedral
 O_h

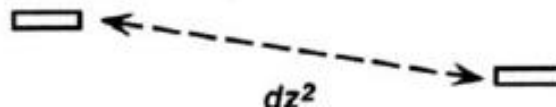
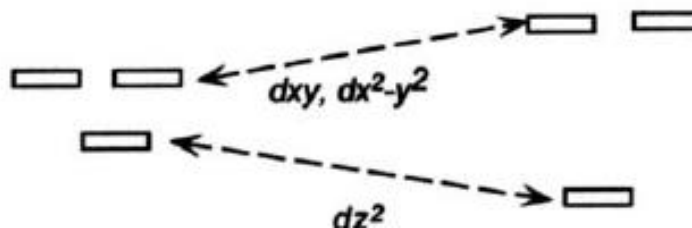
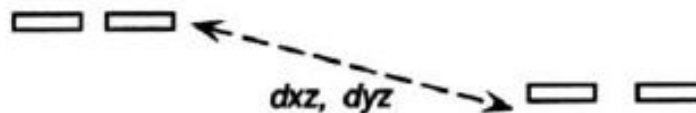
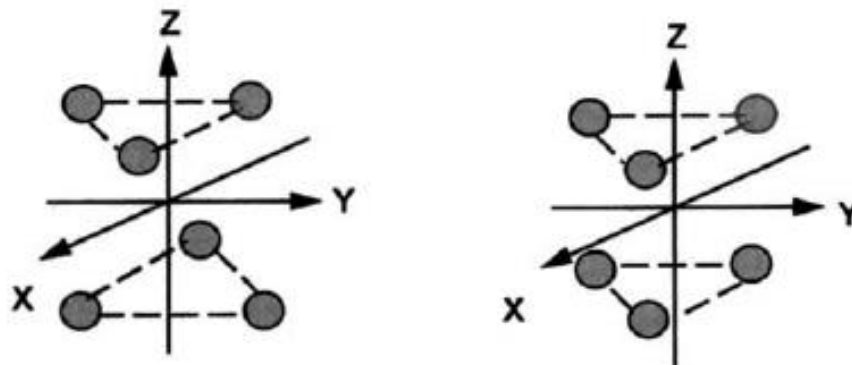


Trigonal prismatic
 D_{3h}

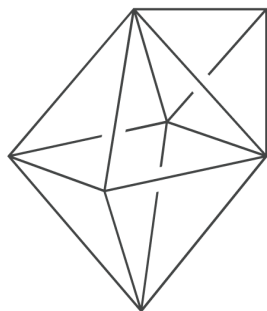


Diversa orientazione degli assi cartesiani

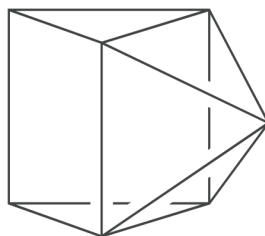
Splitting degli orbitali d in ottaedro e prisma trigonale mantenendo l'orientazione degli assi cartesiani del prisma



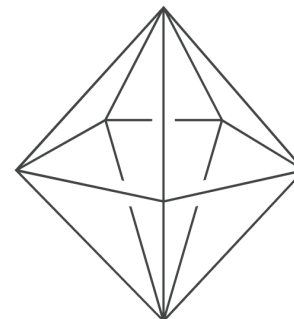
Geometrie per numero di coordinazione 7



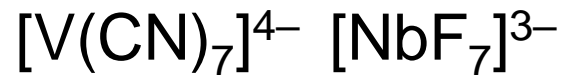
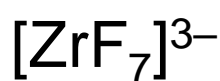
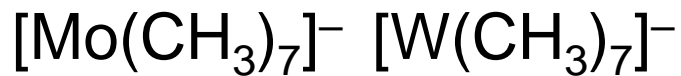
Monocapped
octahedron



Monocapped trigonal
prism

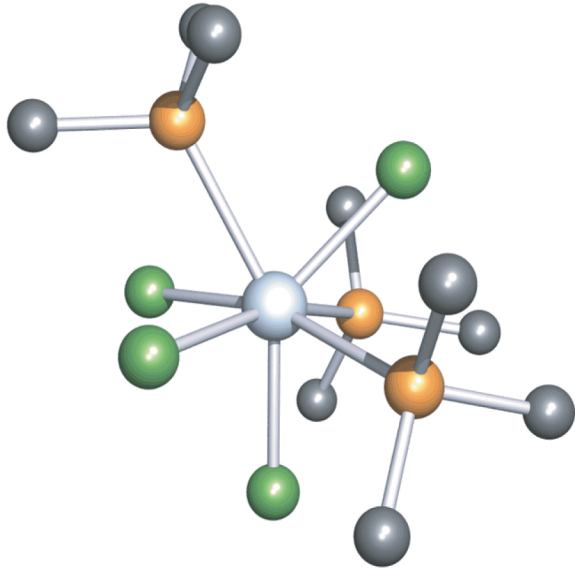


Pentagonal
bipyramid

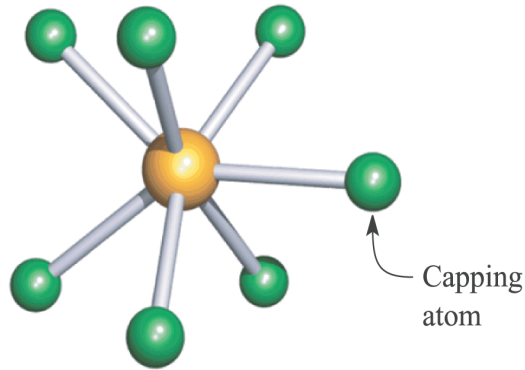


leganti piccoli e/o poco polarizzabili

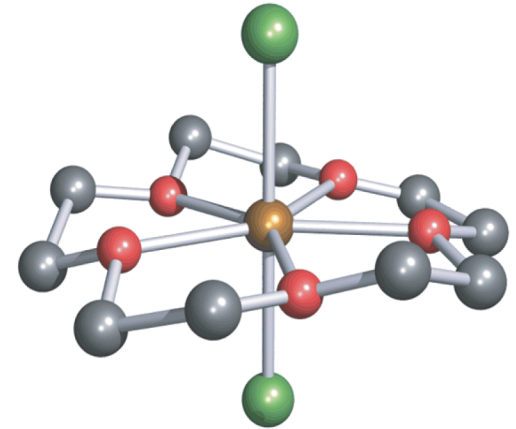
Esempi di complessi eptacoordinati



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



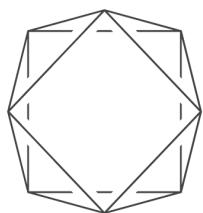
$[\text{ZrF}_7]^{3-}$
prisma trigonale cappato



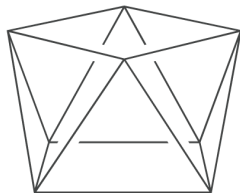
$[\text{ScCl}_2(15\text{-crown-}5)]^+$
bipiramide pentagonale

Cationi = acidi di Lewis deboli

Geometrie per numero di coordinazione 8

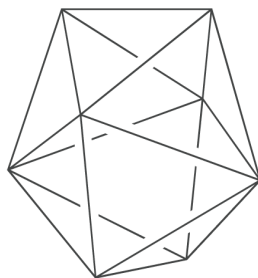
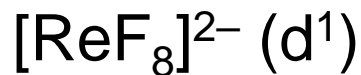
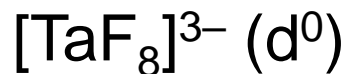


or



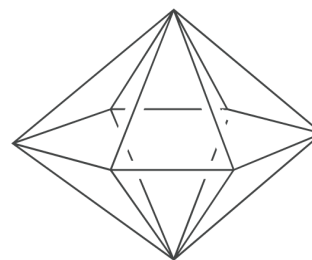
Square antiprism

D_{4d}

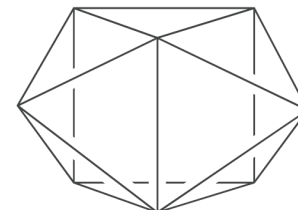


Dodecahedron

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

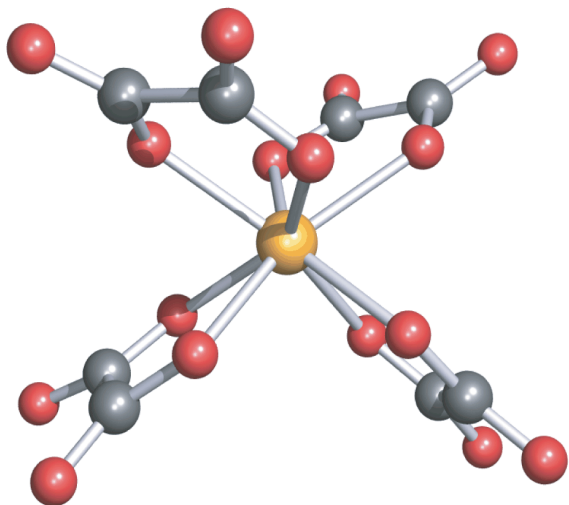


Hexagonal bipyramid

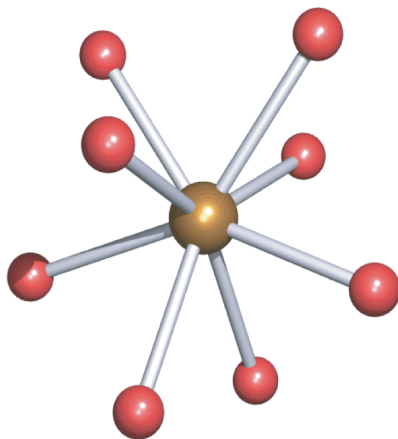


Bicapped trigonal prism

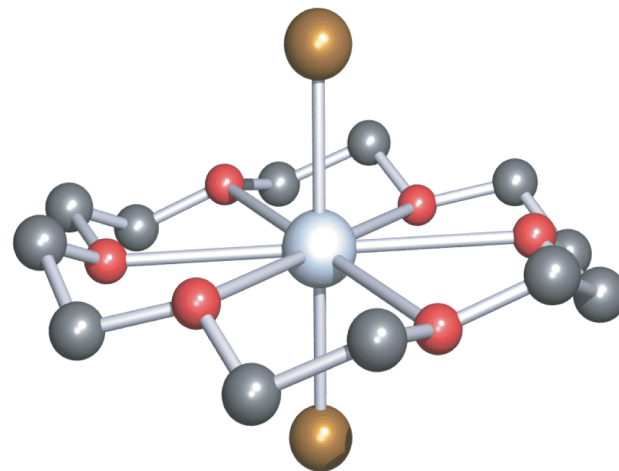
Esempi di complessi ottacoordinati



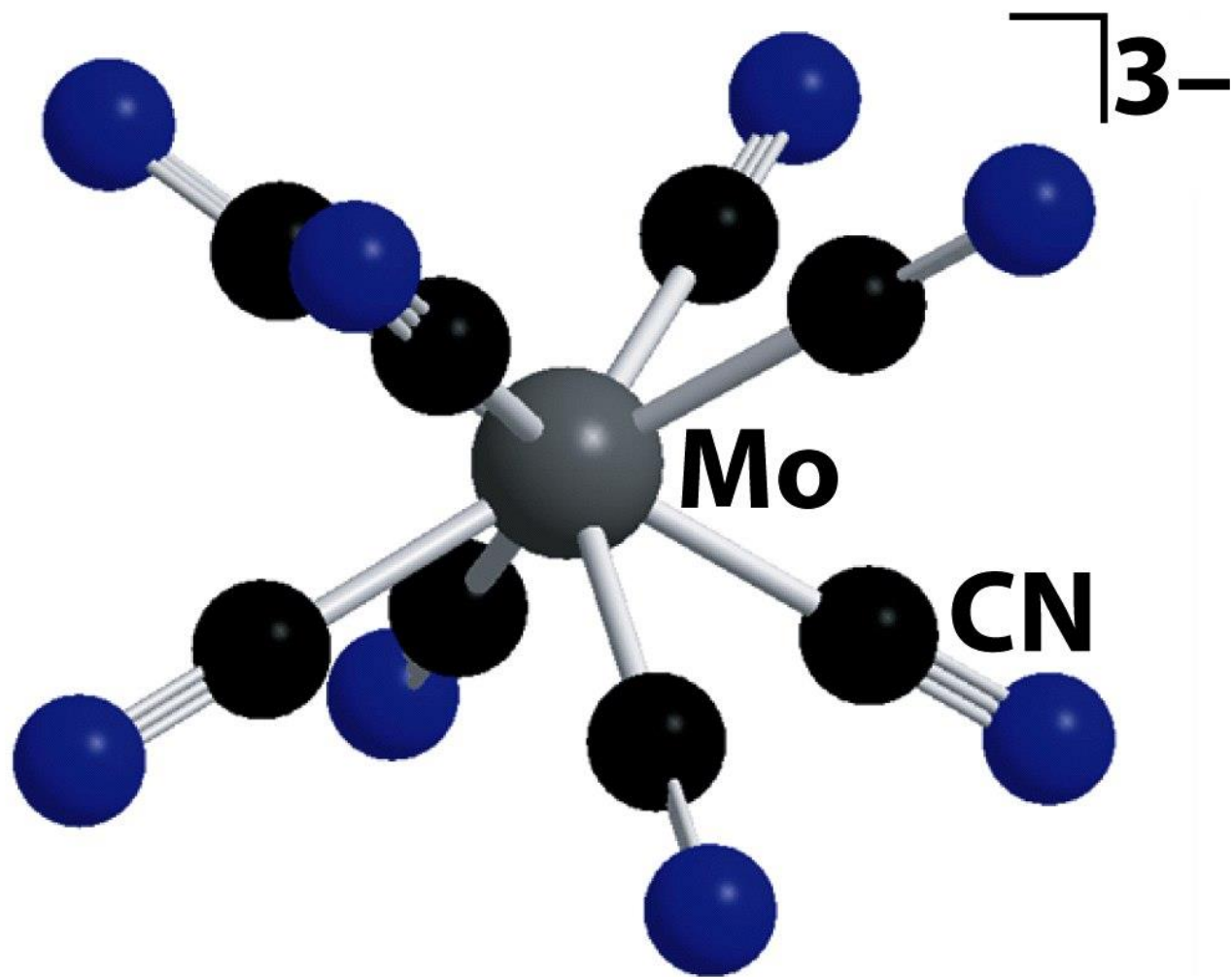
$[\text{Nb}(\text{ox})_4]^{4-}$
antiprisma quadrato

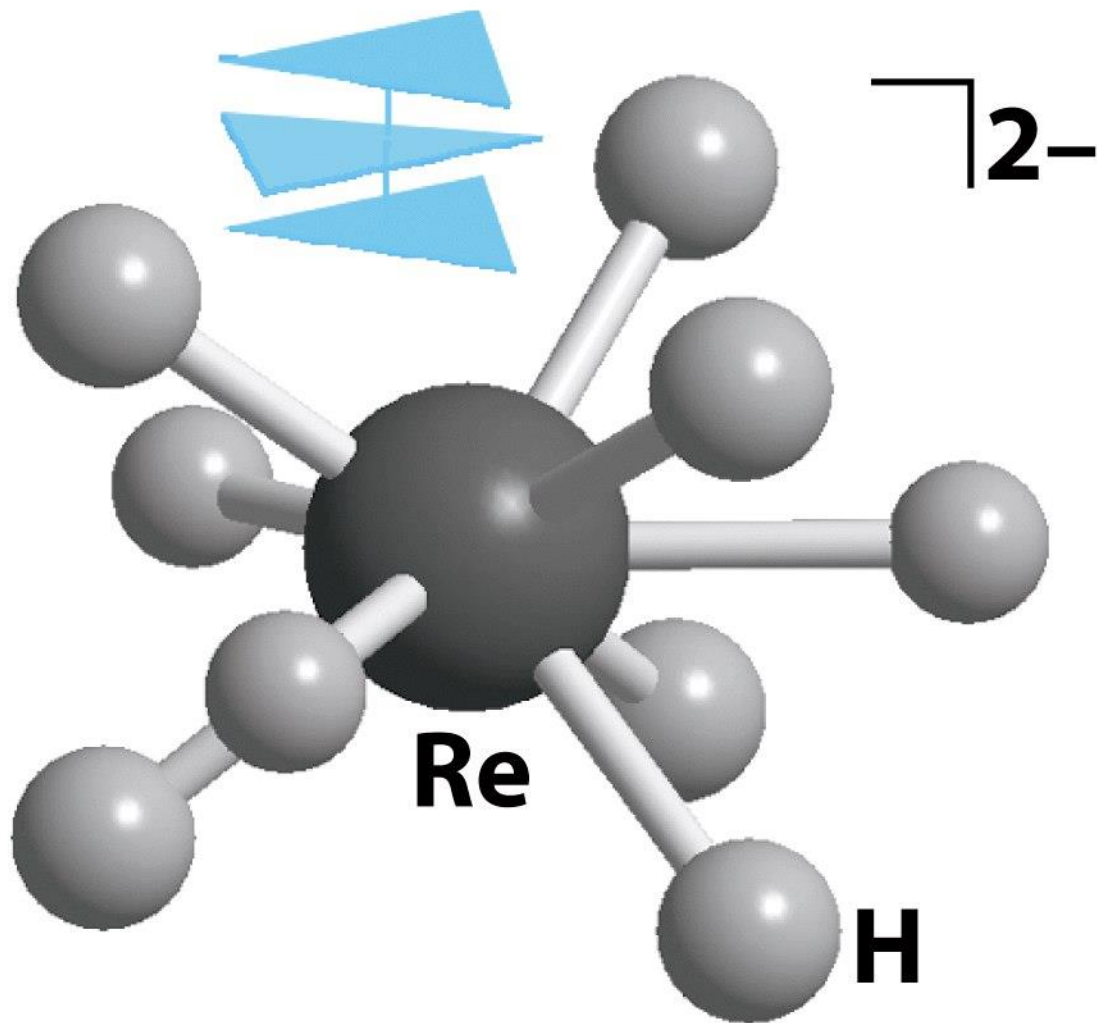


$[\text{Y}(\text{OH}_2)_8]^{3+}$
dodecaedro



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

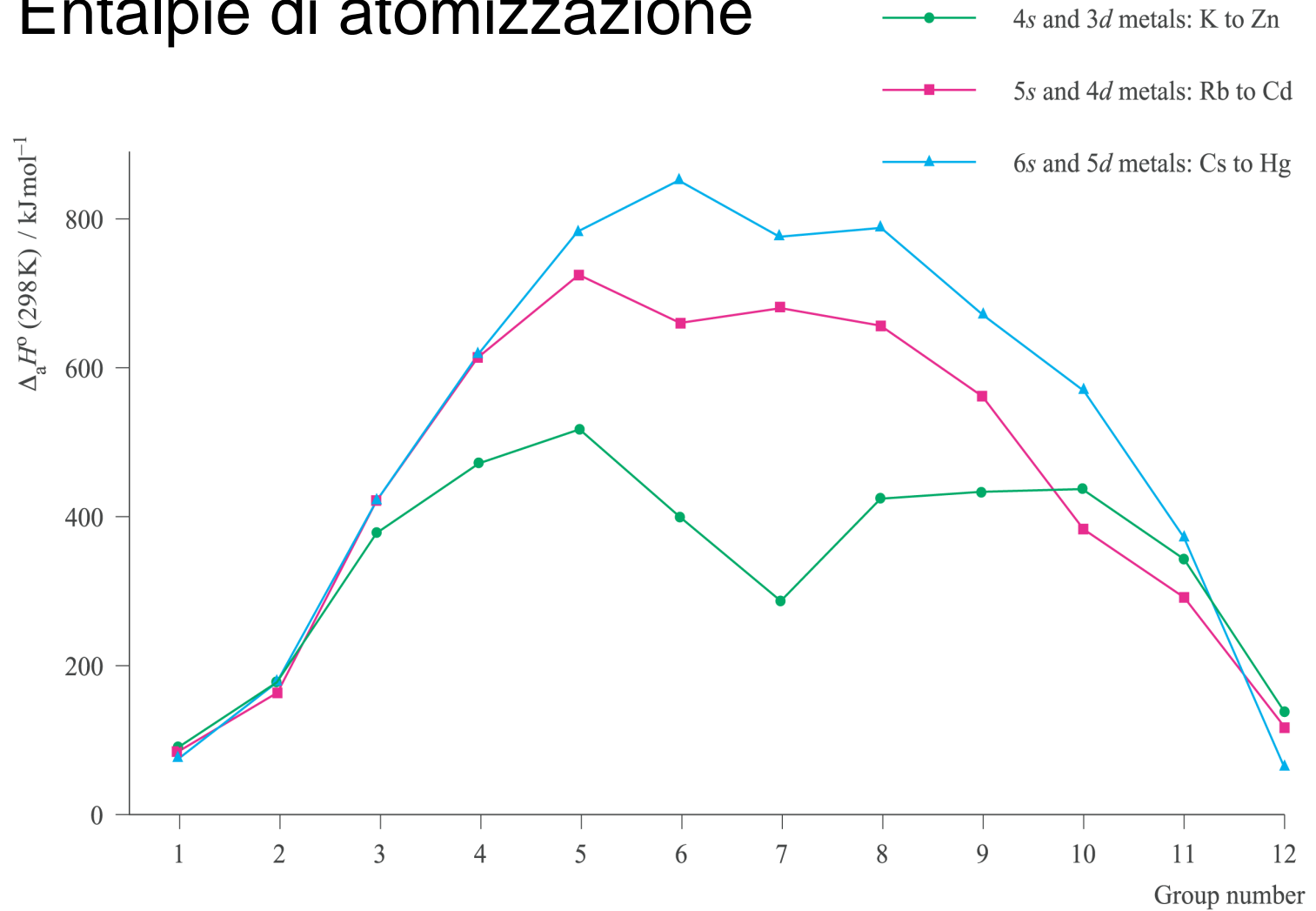


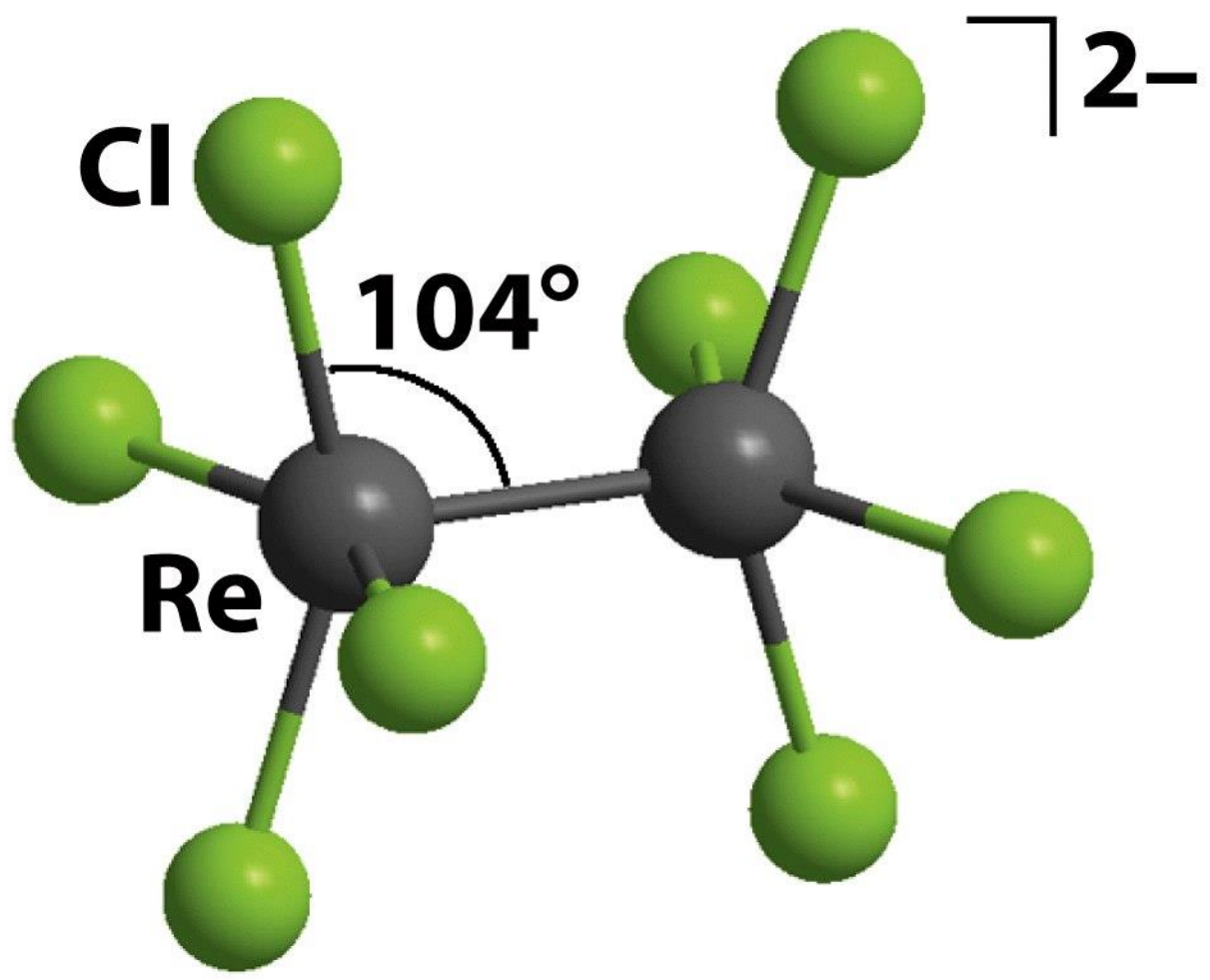


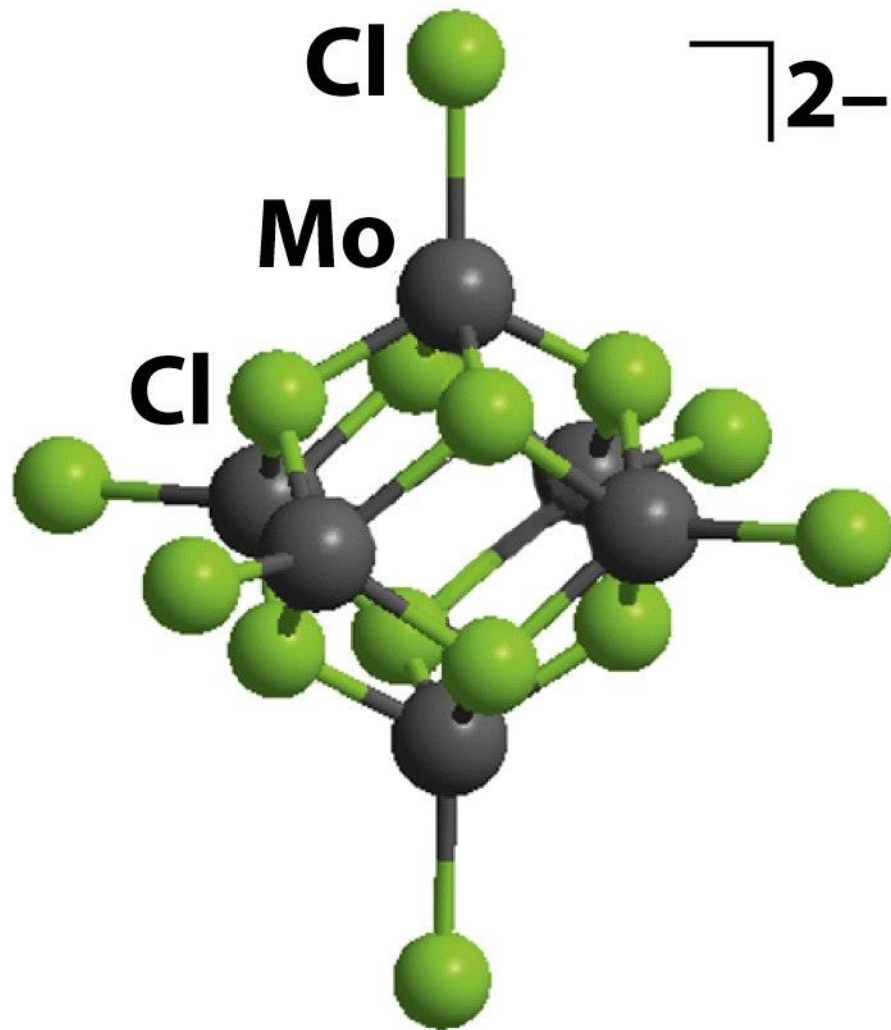
Prisma trigonale tricappato

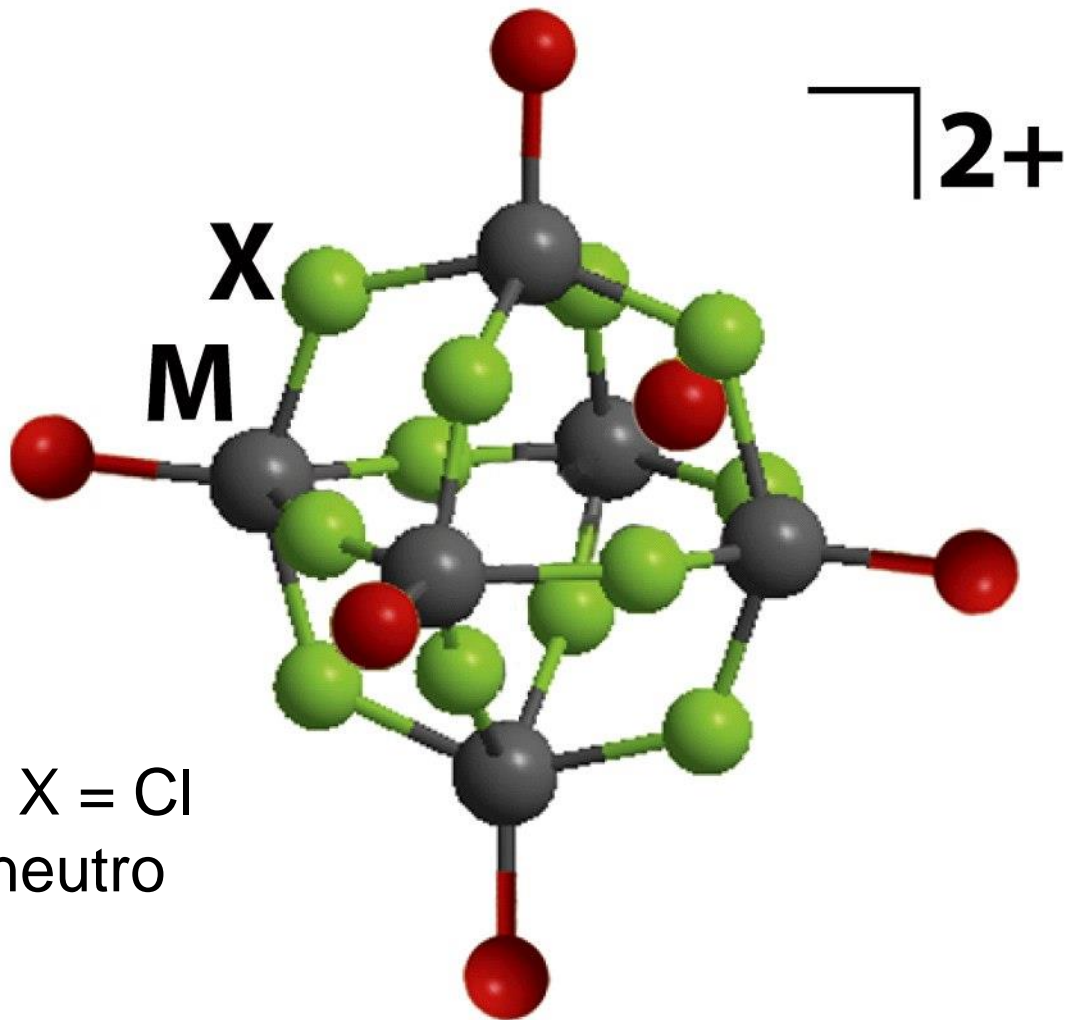
Organometallic clusters											E_nH_n clusters						He
Li	Be	Metal clusters with π -donor ligands					Metal clusters with π -acceptor ligands					B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Naked clusters						
Suboxide clusters																	

Entalpie di atomizzazione



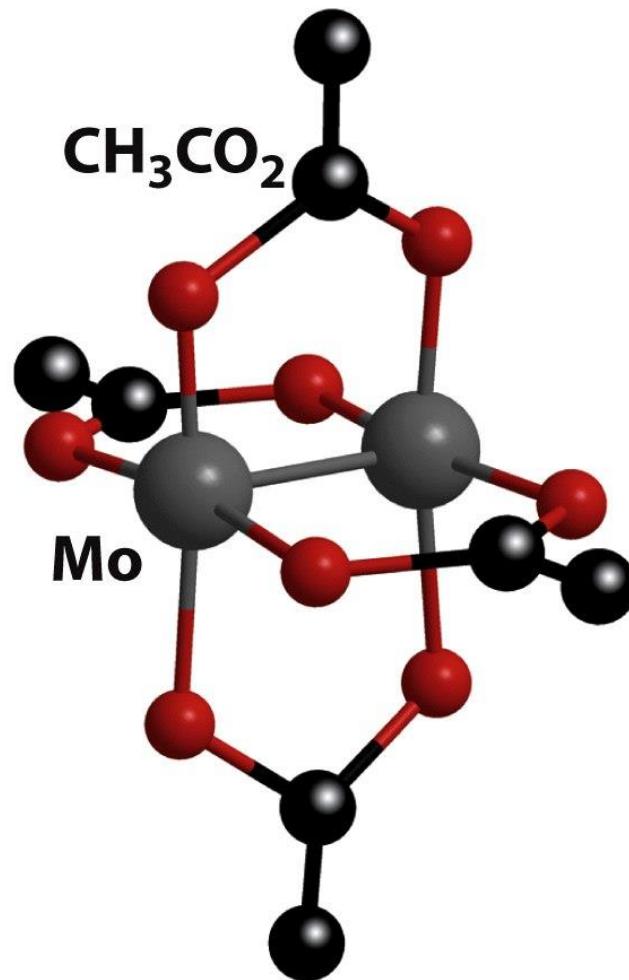






e.g. M = Nb, X = Cl
L = legante neutro

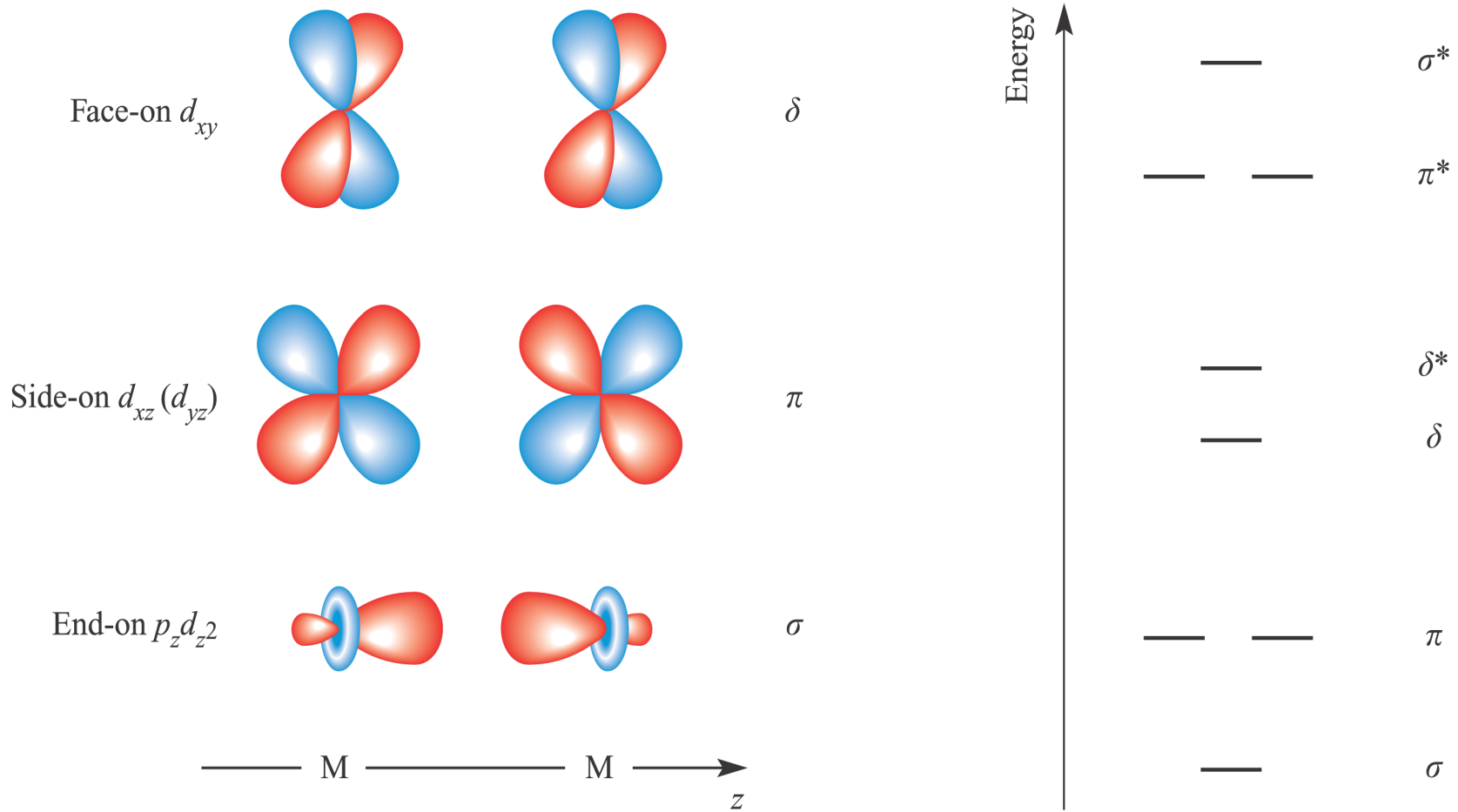


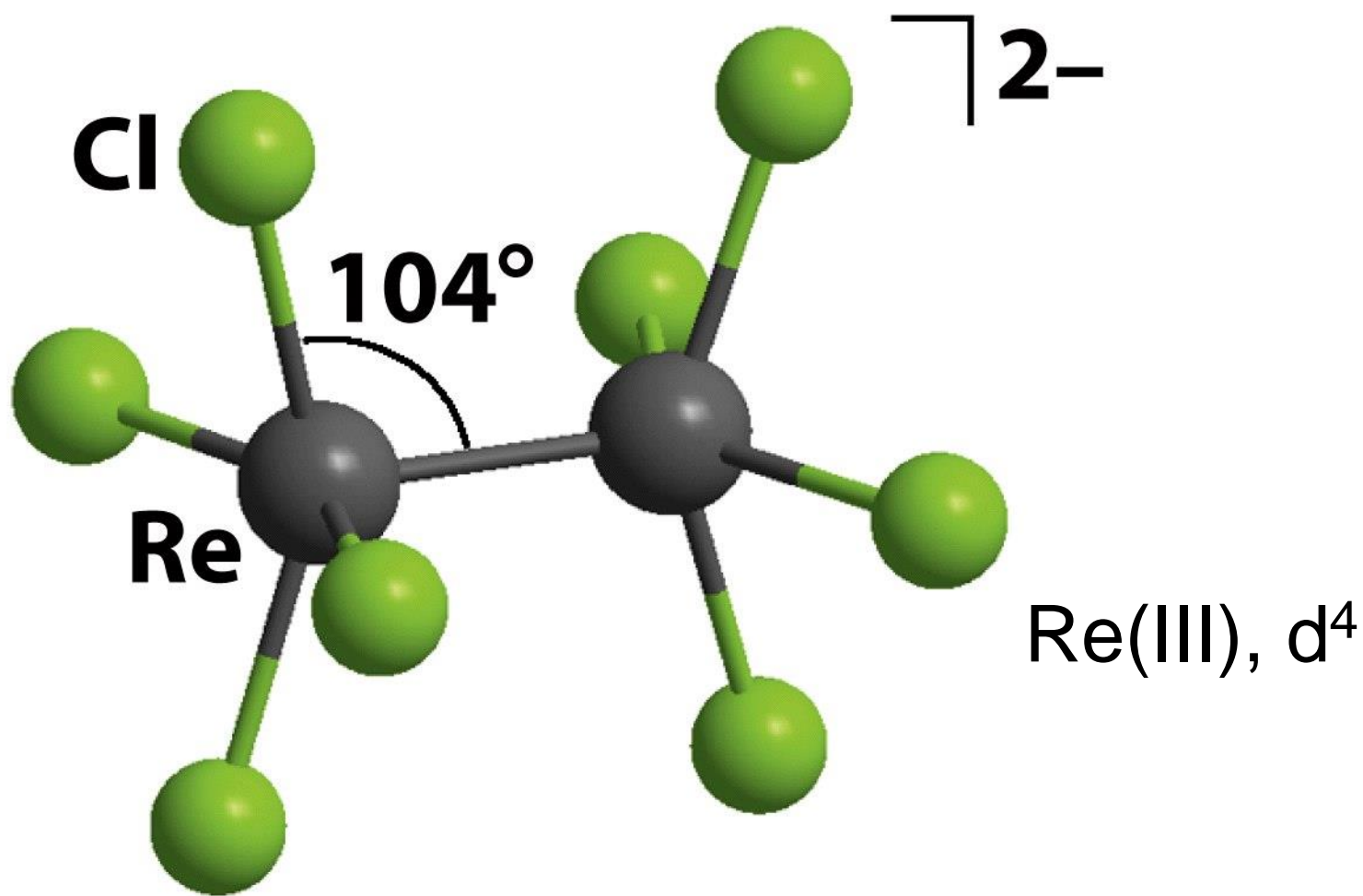


Mo(II), d⁴



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





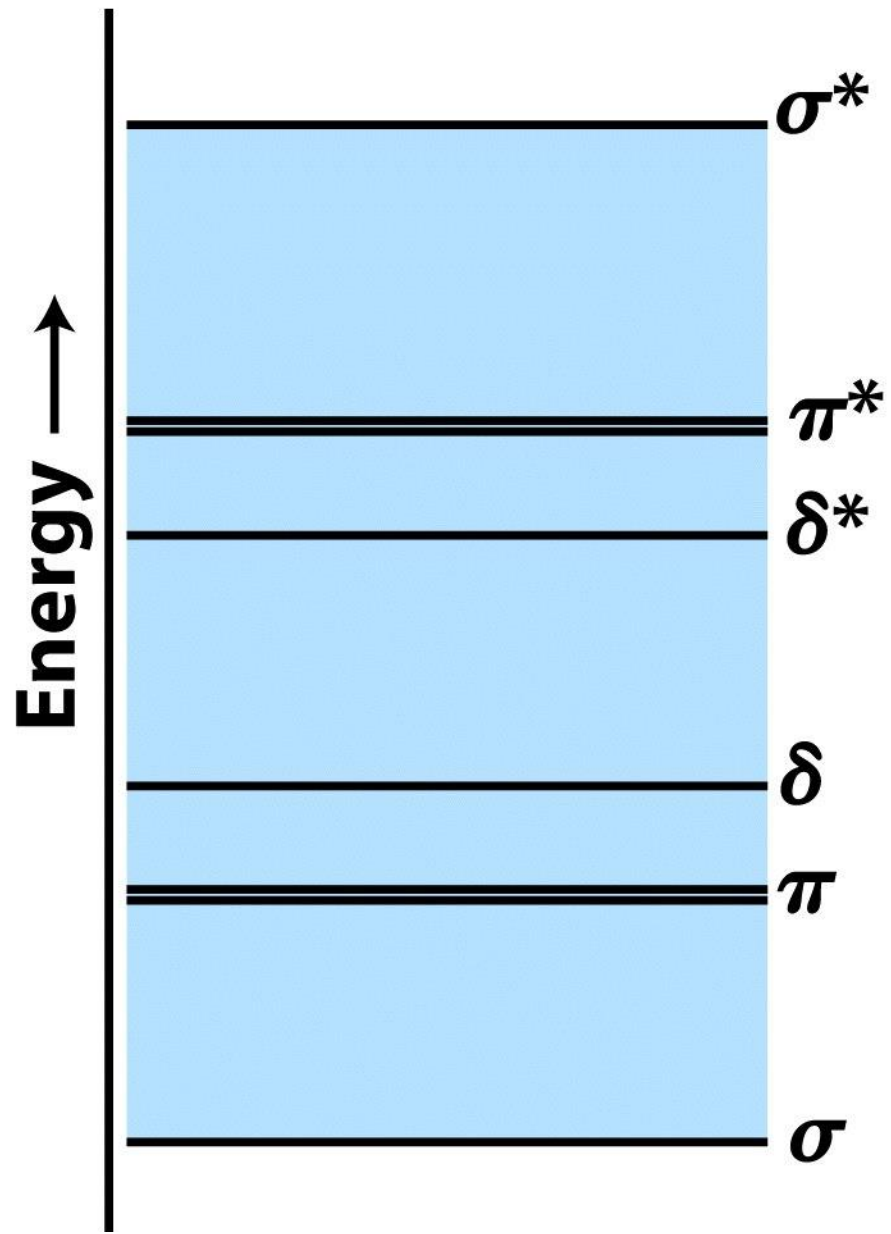


Table 18.9 Examples of metal–metal bonded tetragonal prismatic complexes[†]

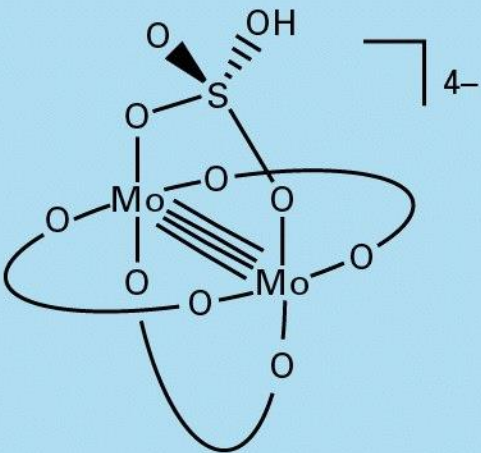
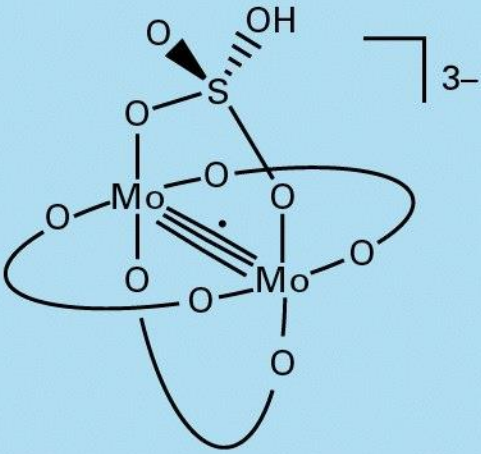
Complex	Configuration	Bond order	M—M bond length/pm
	$\sigma^2\pi^4\delta^2$	4	211
	$\sigma^2\pi^4\delta^1$	3.5	217

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

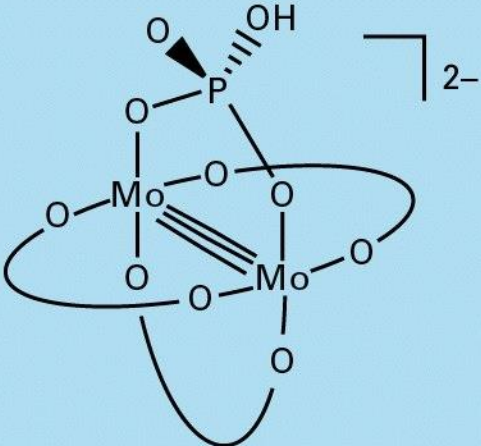
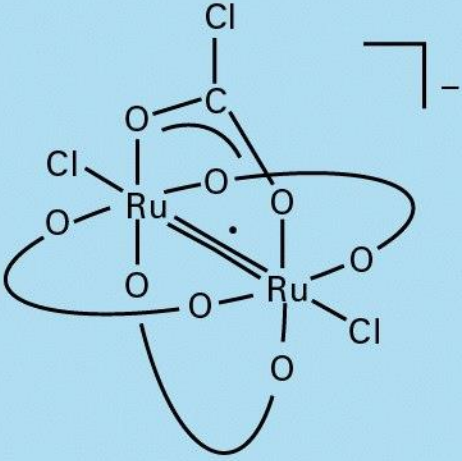
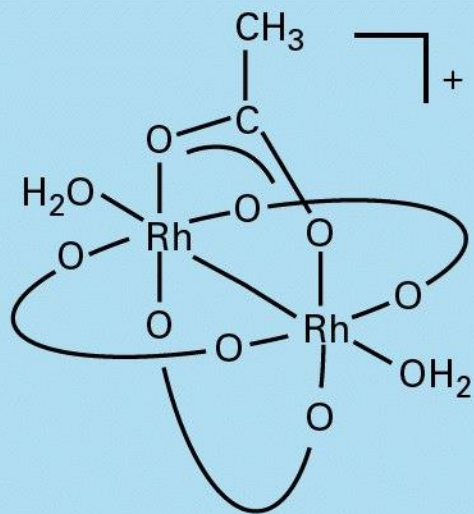
Complex	Configuration	Bond order	M—M bond length/pm
	$\sigma^2\pi^4$	3	222
	$\sigma^2\pi^4\delta^2\delta^*1\pi^*2$	2.5	227

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

239

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

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