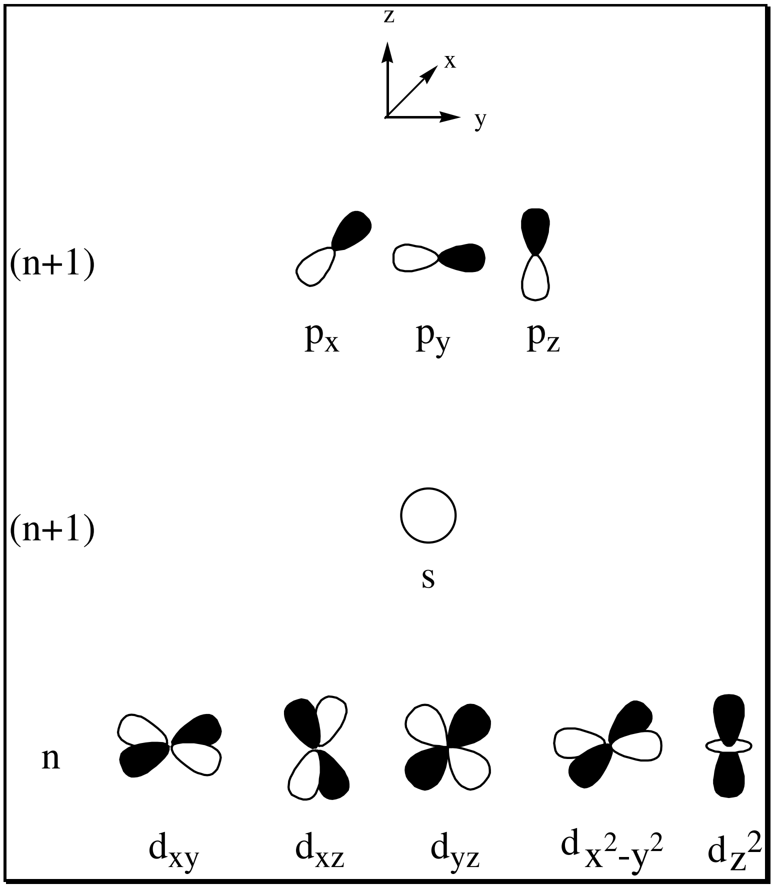
Metal-Ligand and
Metal-Metal Bonding
Core Module 4

RED



Metal-ligand and metal-metal bonding of the transition metal elements
Module 4

Synopsis

Lecture 1:
Recap of trends of the transition metals. Nomenclature (μ, η), coordination number and electron counting.

Lecture 2:
Why complexes form. 18-electron rule. Recap of molecular orbital theory. σ-donor ligands (hydride complexes). Construction and interpretation of octahedral ML_6 molecular orbital energy diagram

Lecture 3:
π–acceptor ligands, synergic bonding, CO, CN^-, N_2,

Lecture 4:
Alkenes and alkynes. Dewar-Duncanson-Chatt model.

Lecture 5:
$M(H_2)$ vs $M(H)_2$, $M_n(O_2)$ complexes, O_2, NO, PR_3.

Lecture 6:
π–donor ligands, metal-ligand multiple bonds, O^{2-}, R_2N^-, RN^{2-}, N^{3-}. Electron counting revisited.

Lecture 7:
ML_6 molecular orbital energy diagrams incorporating π–acceptor and π–donor ligands. Relationship to spectrochemical series, and the trans-effect.

Lecture 8:
Bridging ligands, Metal-Metal bonds, δ-bonding.

Workshop

Learning Objectives: by the end of the course you should be able to

i) use common nomenclature in transition metal chemistry.
ii) count valence electrons and determine metal oxidation state in transition metal complexes.
iii) Understand the physical basis of the 18-electron rule.
iv) appreciate the synergic nature of bonding in metal carbonyl complexes.
v) understand the relationship between CO, the 'classic' π-acceptor and related ligands such as NO, CN, and N_2.
vi) describe the Dewar-Duncanson –Chatt model for metal-alkene and metal-alkyne bonding.
vii) understand the affect of metal binding on the reactivity of a coordinated alkene.
viii) describe the nature of the interaction between η^2-bound diatomic molecules (H_2, O_2) and their relationship to π-acceptor ligands.
ix) describe how H_2 (and O_2) can react with metal complexes to generate metal hydrides and oxides.
x) describe the difference between π-acceptor and π-donor ligands, and why exceptions to the 18-electron rule occur mainly for the latter.
xi) qualitatively describe metal-ligand multiple bonding
xii) understand the origin of the spectrochemical series.
xiii) calculate bond orders in metal-metal bonding species, and understand the strengths and limitations of the bond order concept.
xiv) describe the nature of the quadruple bond in $Re_2Cl_8^{2-}$, particularly the δ component, and triple bond compounds including $Mo_2(NEt_2)_6$.
xv) describe metal-ligand and metal-metal bonding using molecular orbital energy diagrams.

Bibliography:

Shriver and Atkins	"*Inorganic Chemistry*" Ch 8, 9,16.
Cotton, Wilkinson, Murillo and Bochmann	"*Advanced Inorganic Chemistry*"Ch 11, 16
Greenwood and Earnshaw	"*Chemistry of the Elements*" Ch 19, 20-28.
Owen and Brooker	"*A Guide to Modern Inorganic Chemistry*"
Mayer and Nugent	" *Metal-Ligand Multiple Bonds*"

Further reading

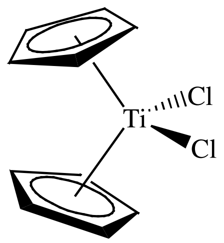
Electron Counting	Huheey, Keiter and Keiter, Inorganic Chemistry, 4th Ed pages 625-630.
Bonding	Murrell, Kettle and Tedder "*The Chemical Bond*" Tetrahedron, 1982, **38**, 1339.
H_2	Angew. Chem. Int. Ed., Engl. 1993, **32**, 789.
O_2	Chem. Rev. 1994, **3** (various articles)

Associated Courses

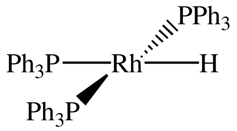
AKDK	Transition metal chemistry	1st year
VC	Structure and bonding	1st year
JEM	Molecular orbitals	1st year
RNP	Group theory	2nd year
KW	Surface Chemistry	2nd year
JML	Transition metal organometallics	2nd year
SBD	Inorganic mechanisms I	2nd year
MCRC	Vibrational spectroscopy	2nd year
MCRC	Photoelectron spectroscopy	2nd year
AKDK	Main group clusters and organometallics	3rd year
RED	Inorganic materials chemistry	3rd year
RED	Inorganic mechanisms II	3rd year
	Catalysis option module	

Why is metal ligand bonding important?

Catalysts – e.g. polymers, pharmaceuticals, bulk chemicals

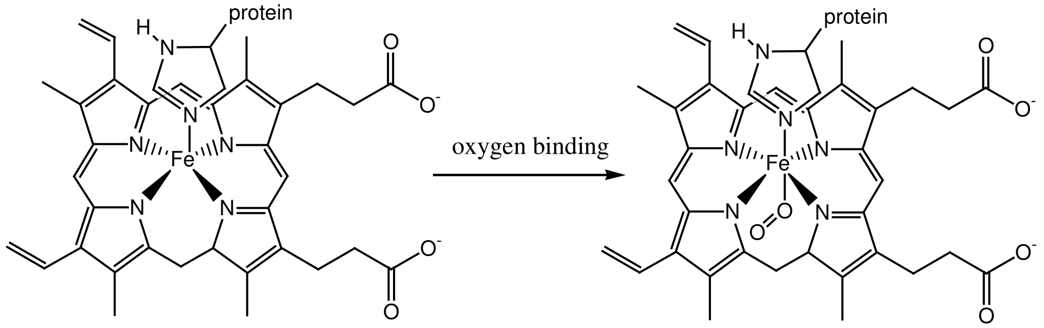


$[(\eta^5\text{- } C_5H_5)_2TiCl_2$

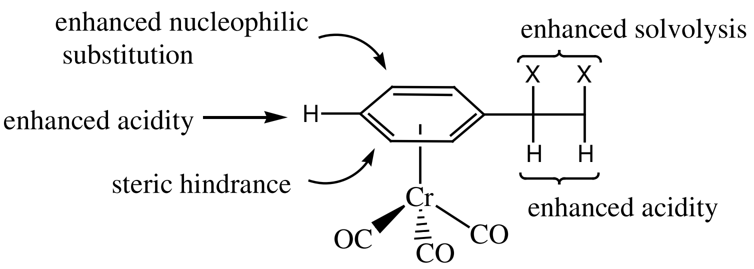


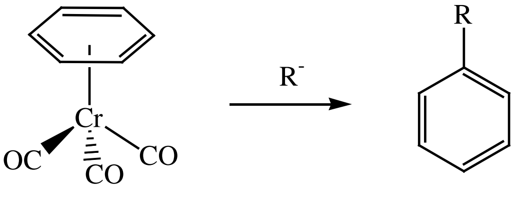
$[Rh(H)(PPh_3)_3]$

Biochemistry – e.g. oxygen transport, photosynthesis, enzymes, medicines, poisons



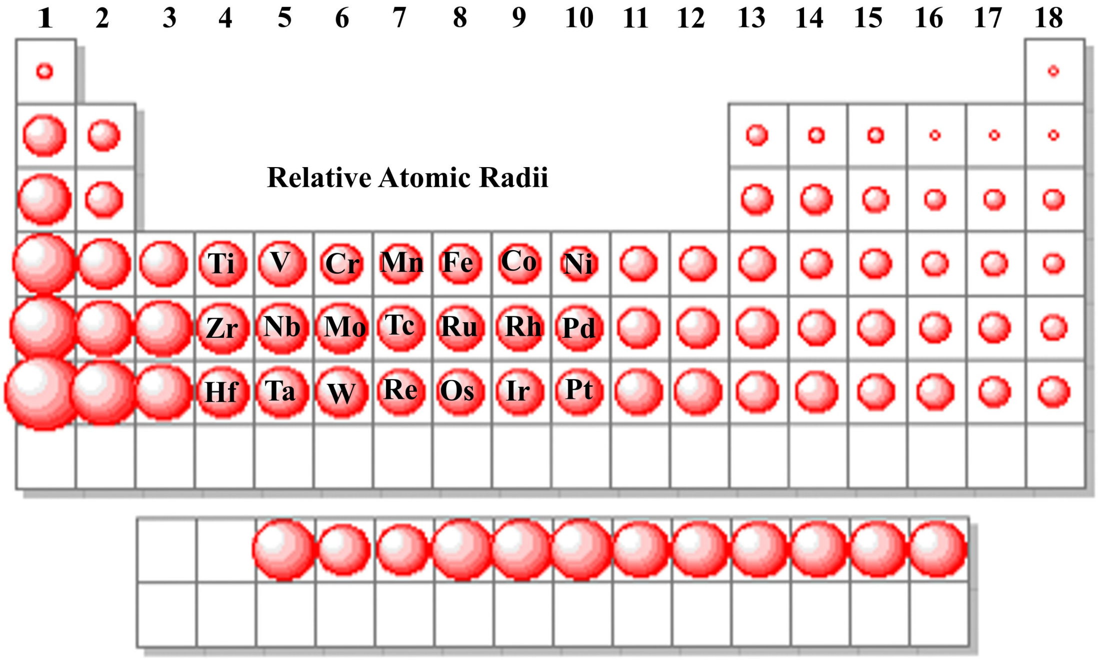
'Organic' chemistry methodology – e.g. $M(CO)_3$ arenes, Pd catalysed C-X (X = C, N, S, O) bond formation, metathesis.





This course is primarily concerned with the transition metals (‘d-block’ metals).

Recap



Important trends:

1. Radius (Covalent/ionic) :- Increases from right to left and down a group.

2. Electropositivity:- electropositive character increases from right to left and down a group.

The trends observed in 1 and 2 are a result of the effective nuclear charge (Z_{eff}) that is a consequence of *shielding* and *penetration*. $s > p > d > f$

The relatively very poor shielding of an electron in an *f*-orbital results in a steady decrease in the radii of the lanthanides (approximately 25%). This is known as the lanthanide contraction. With respect to the transition metals the result is that the radii of the 2nd and 3rd row transition metals are very similar. E.g. Co(III) (0.55), Rh(III) (0.67), Ir(III) (0.68). This has repercussions in metal-ligand bonding and hence chemical properties. In general when descending a group the 1st row transition metal is distinct in terms of its bonding and properties from the 2nd and 3rd row metals.

3. Variety in oxidation state:- earlier metals (group 4 to 7) exhibit the greatest variety in oxidation state. Higher oxidation states more commonly observed for 2nd and 3rd row metals.

e.g. Fe(III), Ru(VIII), Os (VIII).

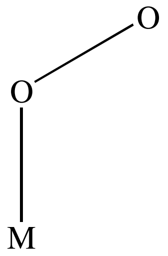
Ionic vs covalent bonding

The 3*d* orbitals in the first row metals are not as diffuse as the 2nd and 3rd row 4*d* and 5*d* orbitals. This leads to a larger ionic component in the bonding of first row metal complexes. However in many cases the bonding in 3*d* metals can be described using covalent theories such as molecular orbital theory.

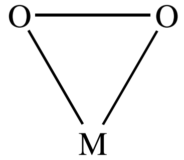
Compare this to the 4*f* orbitals of the lanthanides that are essentially core orbitals and cannot participate significantly in covalent bonding. The bonding in lanthanide complexes can be considered almost totally ionic and they are often considered to be more similar to the alkaline earth metals than the transition metals.

Nomenclature and electron counting

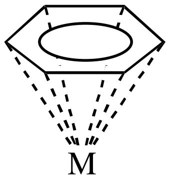
η – hapticity – the number of atoms of a ligand attached to a metal.



η^1-O_2

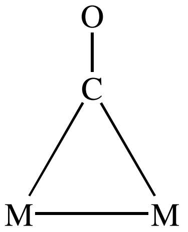


η^2-O_2

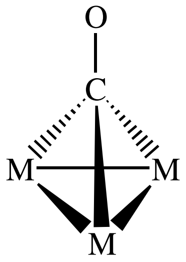


η^6-C_6H_6

μ – The number of metal atoms bridged by a ligand

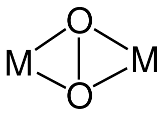


μ_2-CO

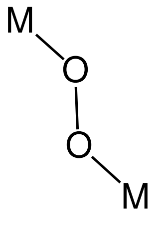


μ_3-CO

e.g.



η^2, μ_2 – O_2



μ_2 – O_2

η^1 taken as default

Metal oxidation state

Oxidation state = Charge on the complex - Sum of the charges of the ligands

Examples of formal charges on some ligands

+1	NO (linear)
0	CO, NR_3, PR_3, N_2, O_2, H_2, C_2H_4, H_2O, RCN, C_6H_6
-1	H, CH_3, F, Cl, Br, I, C_5H_5, CN, NO_2, NR_2, NO (bent)
-2	O, S, CO_3, NR, porphyrin
-3	N, P

e.g. $Ti(CH_3)_4$: $0 – (4 \times –1) = +4$ <u>Ti(IV)</u>

$[CoCl_6]^{3-}$: $-3 – (6 \times –1) = +3$ <u>Co(III)</u>

$[Co(NH_3)_6]^{3+}$: $+3 – (6 \times 0) = +3$ <u>Co(III)</u>

Ignoring NO the charge (n-) can be determined by adding H^+ until a neutral molecule is obtained

$L^{n-} + n\,H^+ \longrightarrow H_nL$

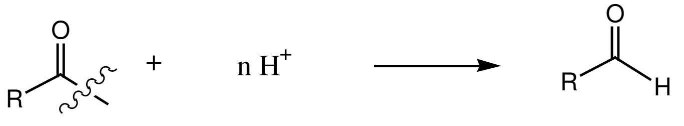
e.g. $Cl^{n-} + n\,H^+ \longrightarrow HCl$ n=1

$CH_3^{n-} + n\,H^+ \longrightarrow HCH_3\ (CH_4)$ n=1

$NR^{n-} + n\,H^+ \longrightarrow H_2NR$ n=2

$CO + n\,H^+ \longrightarrow CO$ n=0

$PPh_3^{n-} + n\,H^+ \longrightarrow PPh_3$ n=0

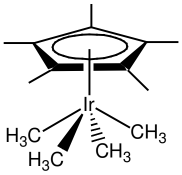


RC(O) RC(O)H n=1

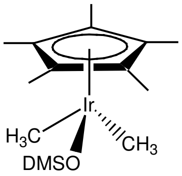
Electroneutrality principle

The electronic structure of substances is such to cause each atom to have essentially zero resultant charge. No atom will have an actual charge greater than ± 1. *i.e. the formal charge is not the actual charge distribution.*

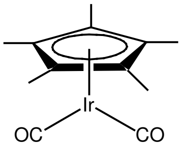
e.g. Photoelectron spectroscopy (PES) is a technique that allows the experimental determination of orbital energies.



Ir(V)



Ir(III)



Ir(I)

PES shows that all three iridium complexes have similar d-orbital energies indicating that the formal oxidation state is not the actual charge on the metal.

d-electron count = group number - oxidation state

Electron Counting

Total Valence Electron Count = d-electron count + electrons donated by the ligands + number of metal-metal bonds

(ignore overall charge on complex)

There are two methods that are commonly used and it is very important to avoid confusion.

$$\text{M-L} \longrightarrow \text{M}^{\cdot} + \text{L}^{\cdot}$$ neutral (or radical) formalism

$$\text{M-L} \longrightarrow \text{M}^{+} + \text{L}^{-}$$ ionic formalism

To avoid confusion we will use the ionic formalism to determine the total number of valence electrons (electron count). However for some ligands O_2, NO and organometallics (carbenes, carbynes) the neutral formalism is more appropriate.

Number of electrons donated by each ligand (using ionic formalism)

2e CO, RCN, NR_3 (amines), PR_3 (phosphines), N_2, ***O_2***, C_2R_4 (alkenes), H_2O, H^-, CH_3^- (or any alkyl or aryl group, R), F^-, Cl^-, Br^-, I^-, CN^-, NR_2^- (bent), $(\eta^1\text{-}C_5H_5)^-$

4e $R_2PCH_2CH_2PR_2$ (bis-phosphines), η^4-dienes, NR_2^-(linear), $(CH_3CO_2)^-$, NR^{2-}(bent), O^{2-} (double bond), S^{2-}

6e $(\eta^5\text{-}C_5H_5)^-$, $\eta^6\text{-}C_6H_6$, NR^{2-} (linear), O^{2-} (triple bond), N^{3-}, P^{3-}

Metal-metal bonds

Single bond counts 1 per metal

Double bond counts 2

Triple bond counts 3

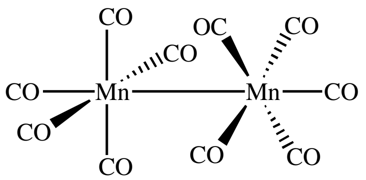
Quadruple bond counts 4

Metal – metal bonding is more common for 2nd and 3rd row metals than for 1st row.

e.g.

$Cr(CO)_6$: 6 + (6 x 2) = 18 $[Co(NH_3)_6]^{3+}$: 6 + (6 x 2) = 18

$[CoCl_6]^{3-}$: 6 + (6 x 2) = 18 $PtBr_2(PPh_3)_2$: 8 + (2 x 2) + (2 x 2) = 16



$Mn_2(CO)_{10}$
per Mn: 7 + (5 x 2) + 1 = 18

c.f. Cl——Cl

7 valence electrons each.
Electron sharing gives a count of 8 per Cl

	Coordination number	metal oxidation state	d-electron count	total valence electrons
$Cr(CO)_6$	**6**	**0**	**6**	**18**
$[Co(NH_3)_6]^{3+}$	**6**	**III**	**6**	**18**
$[CoCl_6]^{3-}$	**6**	**III**	**6**	**18**
$PtBr_2(PPh_3)_2$	**4**	**II**	**8**	**16**
$Rh(CO)(H)(PPh_3)_3$	**5**	**I**	**8**	**18**
$TiCl_4$	**4**	**IV**	**0**	**8**
$Cr(\eta^6\text{-}C_6H_6)_2$	**6**	**0**	**6**	**18**
$Fe(\eta^5\text{-}C_5H_5)_2$	**6**	**II**	**6**	**18**
$[ReOCl_5]^-$	**6**	**VI**	**1**	**15 (17)**

Why complexes form

(Thermodynamic stability of transition metal complexes)

1. The number and strength of metal-ligand bonds.

The greater the number of ligands, and the stronger the bonds, the greater the thermodynamic stability of the resulting complex. i.e. in general the more ligands the better. Larger metals can accommodate more ligands. In general coordination numbers are greater for the earlier transition metals (groups 4 – 7) compared to the later ones. Coordination numbers for lanthanide complexes are generally higher than for transition metals. d^8 square planar complexes are stable because 4 strong bonds are collectively stronger than 6 bonds that would be collectively weaker for this electron configuration.

2. Steric factors.

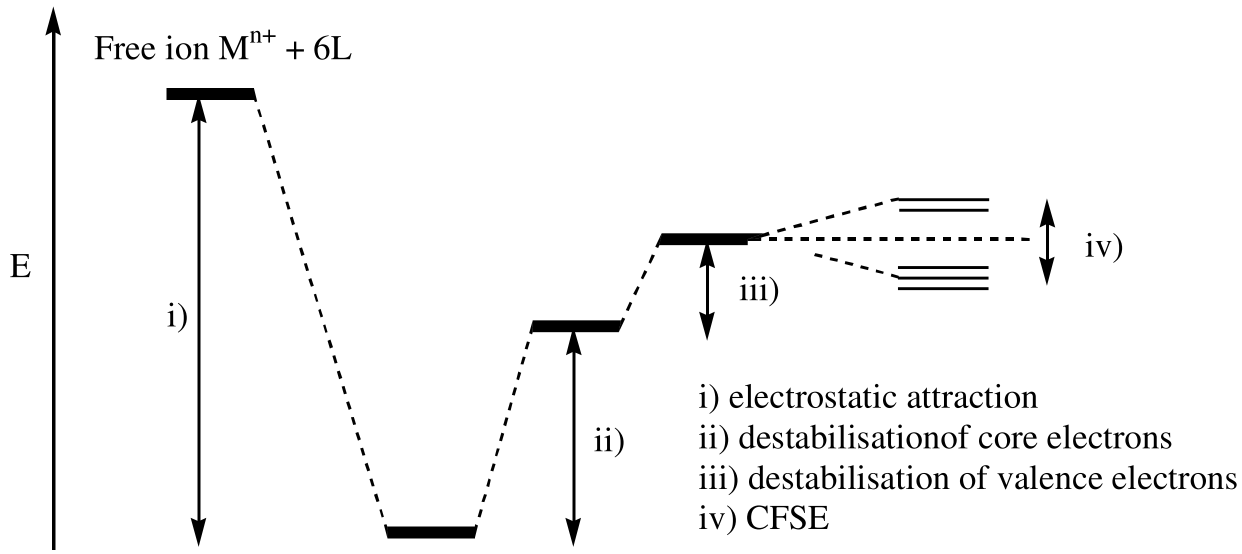
The number of ligands is limited by ligand – ligand repulsion. The size of metals and common ligands leads to transition metals generally accommodating a maximum of six ligands hence the vast number of 6 coordinate transition metal complexes. For similar reasons there are many 9 coordinate lanthanide complexes.

3. The charge on the complex.

Large positive and negative charges cannot easily be supported. Continually removing electrons from a complex will result in increasingly large ionisation energies, and increasing the number of electrons will lead to large electron-electron repulsive forces.

4. The electronic configuration.

Crystal field stabilisation energy, Jahn-Teller distortion.

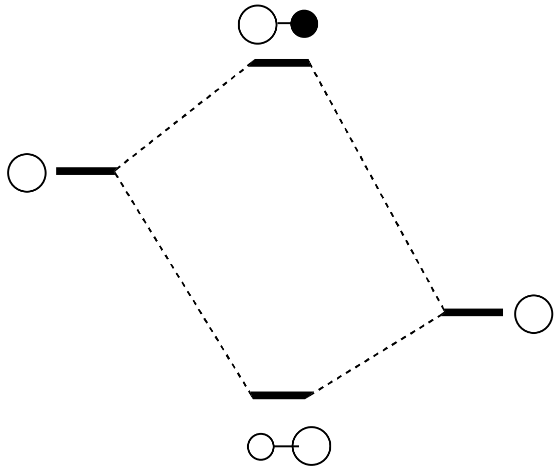


Note that crystal field stabilisation energy (CFSE) contributes only approximately 10% to the overall thermodynamic stability.

Recap of molecular orbital theory

a) Orbitals must be of appropriate symmetry
b) Orbitals must overlap
c) Orbitals should be of similar energy
b) and c) determine the energy of the interaction. The interaction energy is stronger for orbitals that have good overlap and are close in energy.

When the MOs are made up of 2 component orbitals of different energies



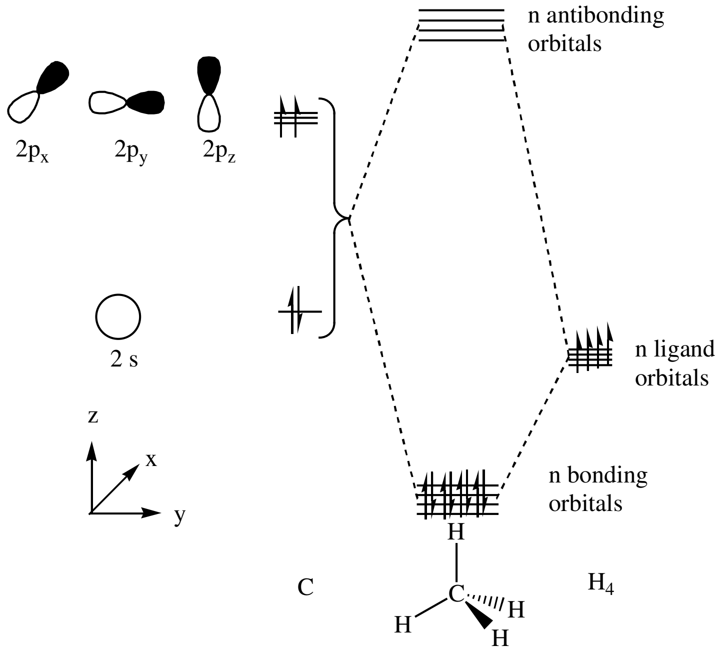
*The **bonding** orbital looks more like the **lower** energy component*

*The **antibonding** orbital looks more like the **higher** energy component*

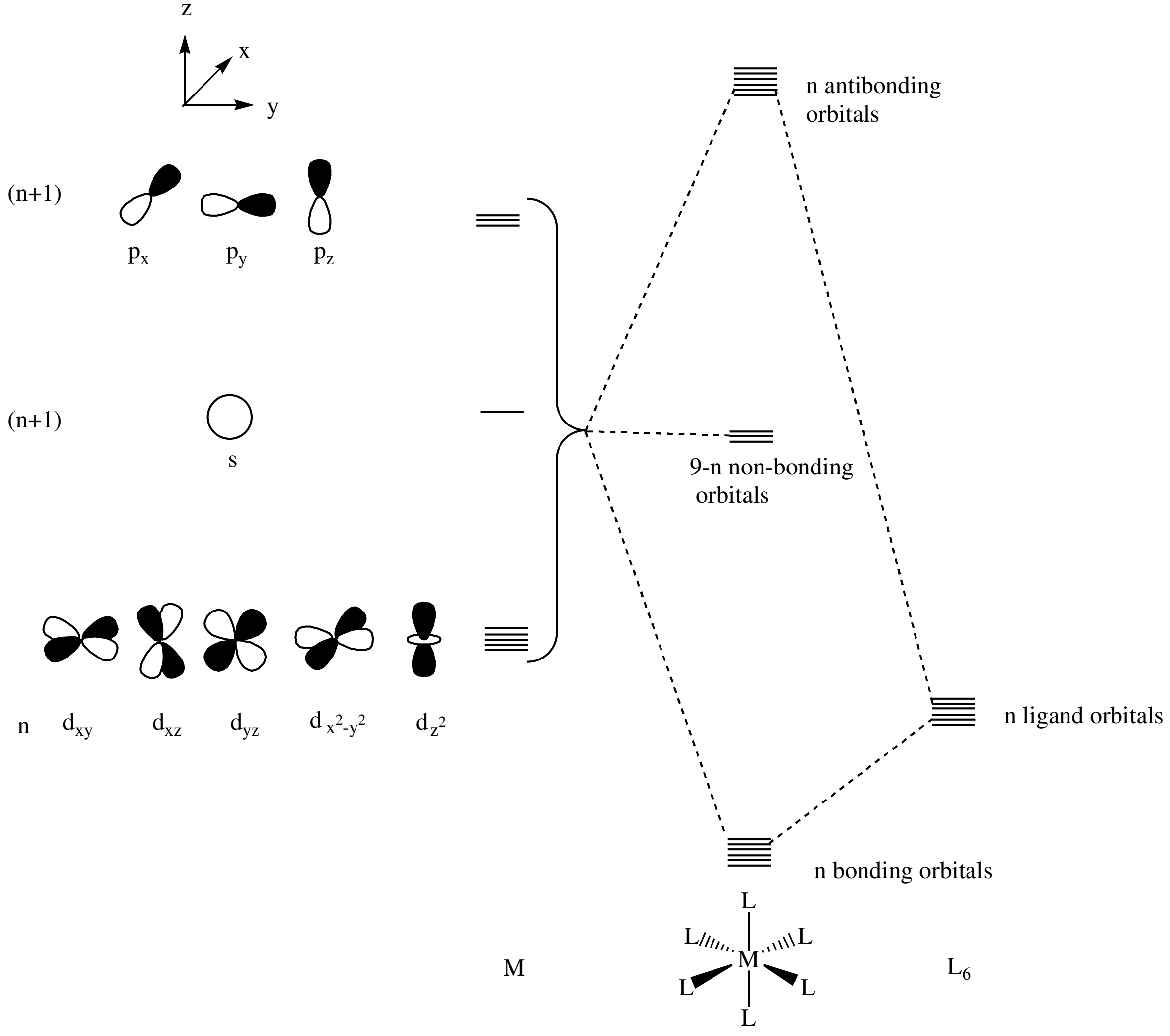
Electronic configuration: Transition metal valence orbitals and the 18 electron rule

Valence shell of transition metals n*d* + (n+1)*s* + (n+1)*p* orbitals (where n = 3-5).
5 + 1 + 3 = 9 orbitals. Two electrons per orbital = **18 electrons**.
(Just a restatement of the Lewis octet rule with extra 10 d-electrons)

For Methane



For a transition metal complex



For many complexes an electronic configuration of 18 valence electrons is the most thermodynamically stable, especially for diamagnetic organometallic complexes, however as noted earlier the electronic configuration is only one factor that contributes to the overall thermodynamic stability of a complex. There are many important exceptions to the 18 electron rule including:

- 1st row coordination complexes where the bonding is predominantly ionic.
- square planar d^8 complexes (16 e^-).
- early metal complexes with π-donor ligands.
- paramagnetic complexes.

Ligand classification

Metal-ligand bonding can be divided into three basic classes

1. σ-donor

e.g. H, CH_3 (or any alkyl or aryl group, R), H_2O, NH_3, NR_2 (bent)

2. σ -donor, π-acceptor (sometimes referred to as 'π-acceptors' or 'π-acids')

e.g. CO, CN, NO, H_2, C_2H_4, N_2, O_2, PR_3, BR_2

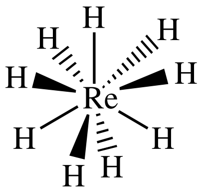
3. σ -donor, π-donor (sometimes referred to as 'π-donors')

e.g. F, Cl, Br, I, O, OR, S, SR, N, NR_2(linear), NR (bent and linear), P, η^3-C_3H_5, η^5-C_5H_5, η^6-C_6H_6

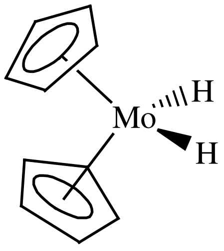
In terms of bond strength the σ-bond is much more important than π-bonding (donor or acceptor)

1. σ-donor

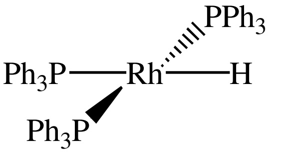
In these compounds the bond between the ligand and metal is a σ- bond. A good example of a σ-donor is hydride (H^-). Some examples of transition metal hydrides are given below. Metal hydrides play a very important role in many catalytic reactions including hydrogenation and hydroformylation.



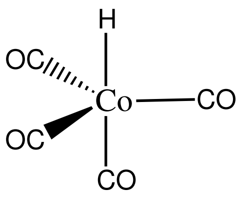
K_2ReH_9



Cp_2MoH_2



$Rh(H)(PPh_3)_3$

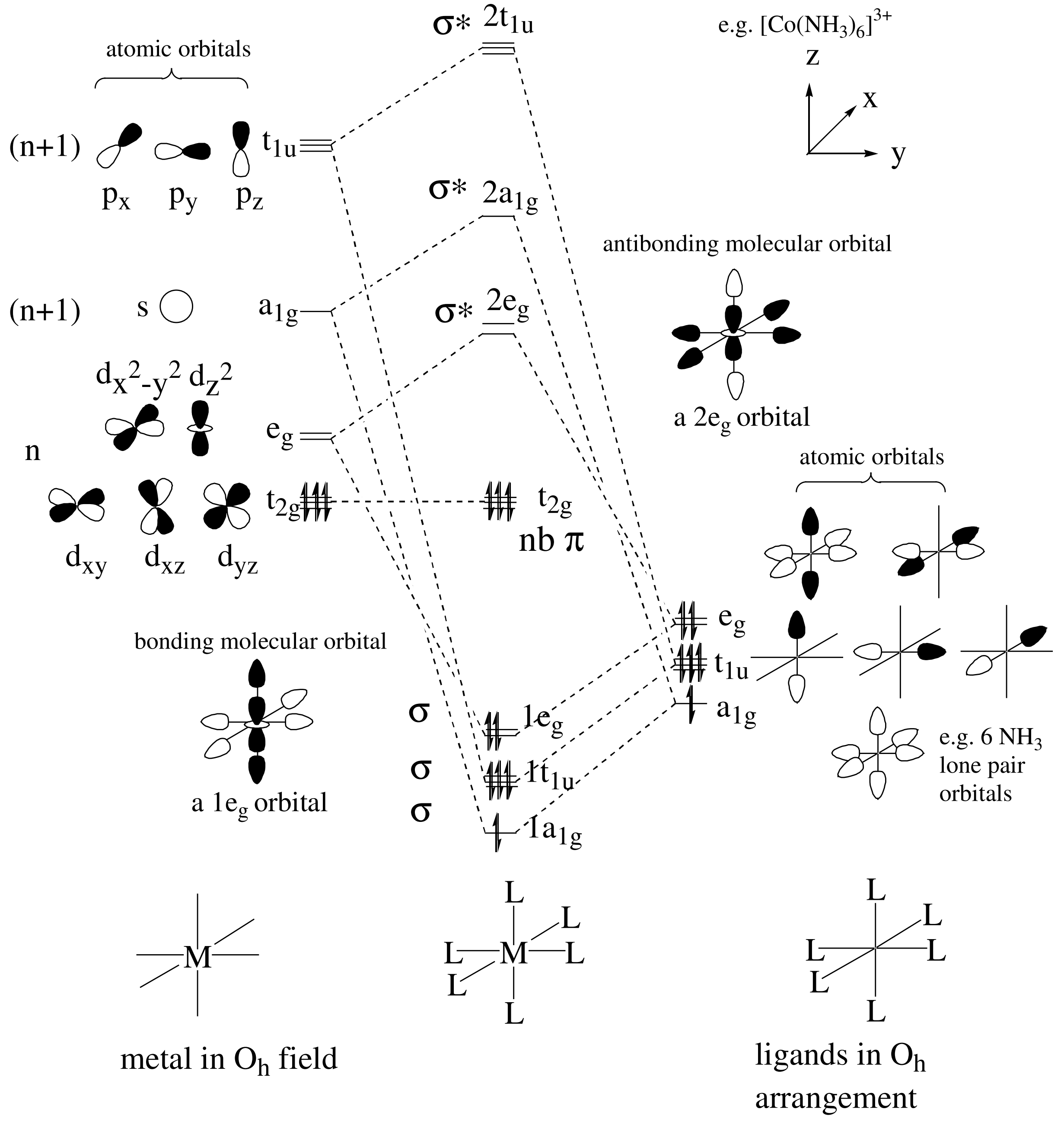


$Co(CO)_4H$

Characterisation of metal hydrides

IR: ν(M-H)~1750 cm^{-1} NMR: Hydride resonance at high field ($\delta < 0$ppm)
Neutron diffraction needed to locate hydrogen nuclei

Molecular orbital diagram of a ML_6 complex (where L is a σ–donor ligand)



Note that there are no linear combinations of ligand orbitals that have t_{2g} symmetry. Therefore the t_{2g} orbitals are non-bonding and completely metal based. The $2e_g$ orbitals are σ* and have ligand character but are approximately 80% metal based (remember the antibonding orbital is mainly of higher energy starting orbital character). When we talk about splitting of metal ‘d-orbitals’ in crystal field theory we are ignoring the ligand character that is present in some of the ‘d-orbitals’, however it is still a good first approximation and the relative energies between d-orbitals are correct. We will see that when we include π-acceptors and π-donors that the t_{2g} orbitals are no longer pure metal orbitals but also contain some ligand character.

Notes on molecular orbital diagrams

1. The total number of molecular orbitals should be the sum of the number of precursor orbitals.

2. Only orbitals of the same symmetry can interact and the resulting molecular orbitals will have the same symmetry as the precursor orbitals

3. Where do the a_{1g}, e_g, t_{1u} linear combinations of atomic orbitals come from?

Using group theory it is possible to determine the symmetry of the orbitals involved.

i) determine the point group of the molecule (in this case O_h).

ii) treat the ligand orbitals (in this case σ) as a single entity and apply each symmetry element of the point group noting how many of the individual orbitals move under each operation. This is the *reducible representation*.

iii) determine which characters sum to the *reducible representation* thus obtaining the *irreducible representation*. (in this case for the octahedral array of σ-H orbitals it will be $a_{1g} + e_g + t_{1u}$).

iv) repeat for the 3 x *p* and 5 x *d* orbitals (the 1 x *s* can be read off directly as having a_{1g} symmetry) or alternatively look at the right hand portion of the group table and read off the orbital symmetries.

v) apply projection operators to determine the linear combinations of orbitals

4. The origin of symmetry labels nx_{yz}

Apart from being characters in group tables the labels can be used to describe the symmetry of orbitals.

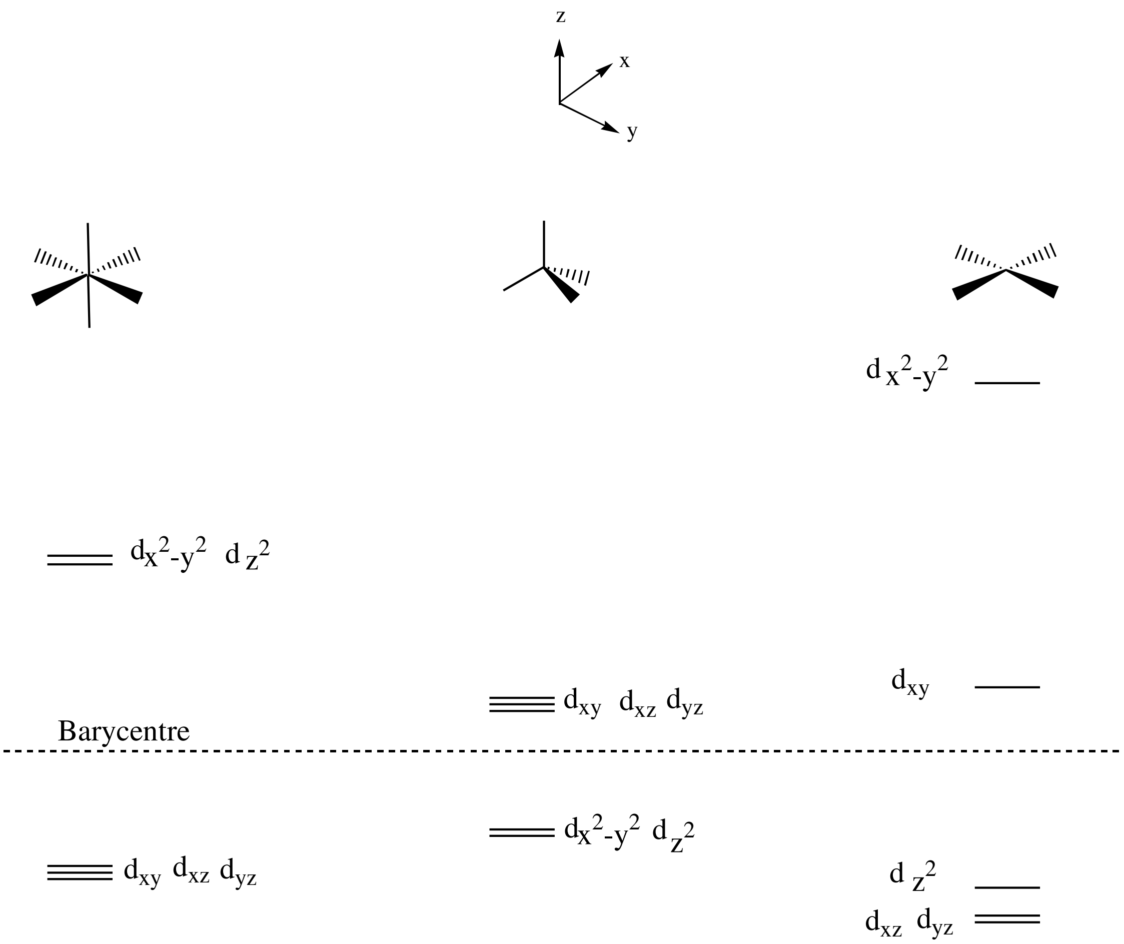
n = orbitals of the same symmetry are numbered successively in order of increasing energy
x = a if singly degenerate and symmetrical to C_{2n} rotation about the principle rotation axis
x = b if singly degenerate and unsymmetrical to C_{2n} rotation about the principle rotation axis
x = e if doubly degenerate
x = t if triply degenerate
y = 1 if symmetrical to reflection through a reference mirror plane
y = 2 if unsymmetrical to reflection through a reference mirror plane
z = 'nothing' if there is no inversion centre
z = g if symmetrical to inversion
z = u if unsymmetrical to inversion

5. What group theory cannot tell us.

i) What the orbitals look like
i) The energy of the orbitals and the magnitude of the precursor orbitals interaction

Recap of crystal field splitting diagrams

By considering the repulsive interactions between electrons it is possible to qualitatively determine the ordering of metal d-orbitals. Crystal field theory is a purely electrostatic approach. Here the d-orbitals are pure. Compare the diagram below and ‘d-orbitals’ of MO diagram above for octahedral complexes.



σ-donor, π-acceptor ('π-acceptors' or 'π-acids')

These include: CO, CN, NO(linear), H_2, C_2H_4, N_2, O_2, PR_3, CR_2

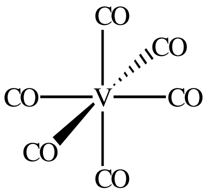
We can view the metal-ligand bonding as a σ-donor interaction (same as for H) with an additional π- interaction that arises from overlap between metal-based orbitals and empty orbitals on the ligand that can *accept* electron density.

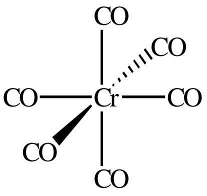
Metal complexes of CO are a good example.

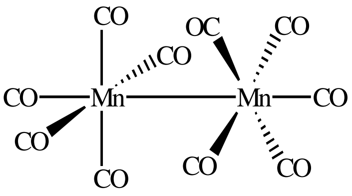
e.g. Some of the binary metal carbonyls

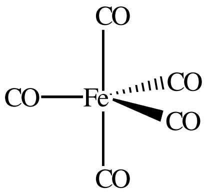
Group5	6	7	8	9	10
$V(CO)_6$	$Cr(CO)_6$	$Mn_2(CO)_{10}$	$Fe(CO)_5$ $Fe_2(CO)_9$	$Co_2(CO)_8$	$Ni(CO)_4$
	$Mo(CO)_6$	$Tc_2(CO)_{10}$	$Ru(CO)_5$ $Ru_2(CO)_9$	$Rh_2(CO)_8$	
	$W(CO)_6$	$Re_2(CO)_{10}$	$Os(CO)_5$ $Os_2(CO)_9$	$Ir_2(CO)_8$	

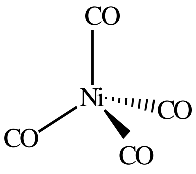
Some structures

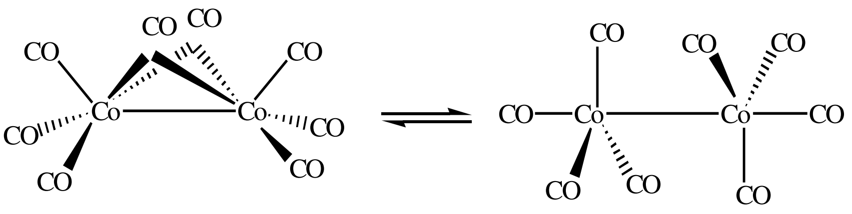






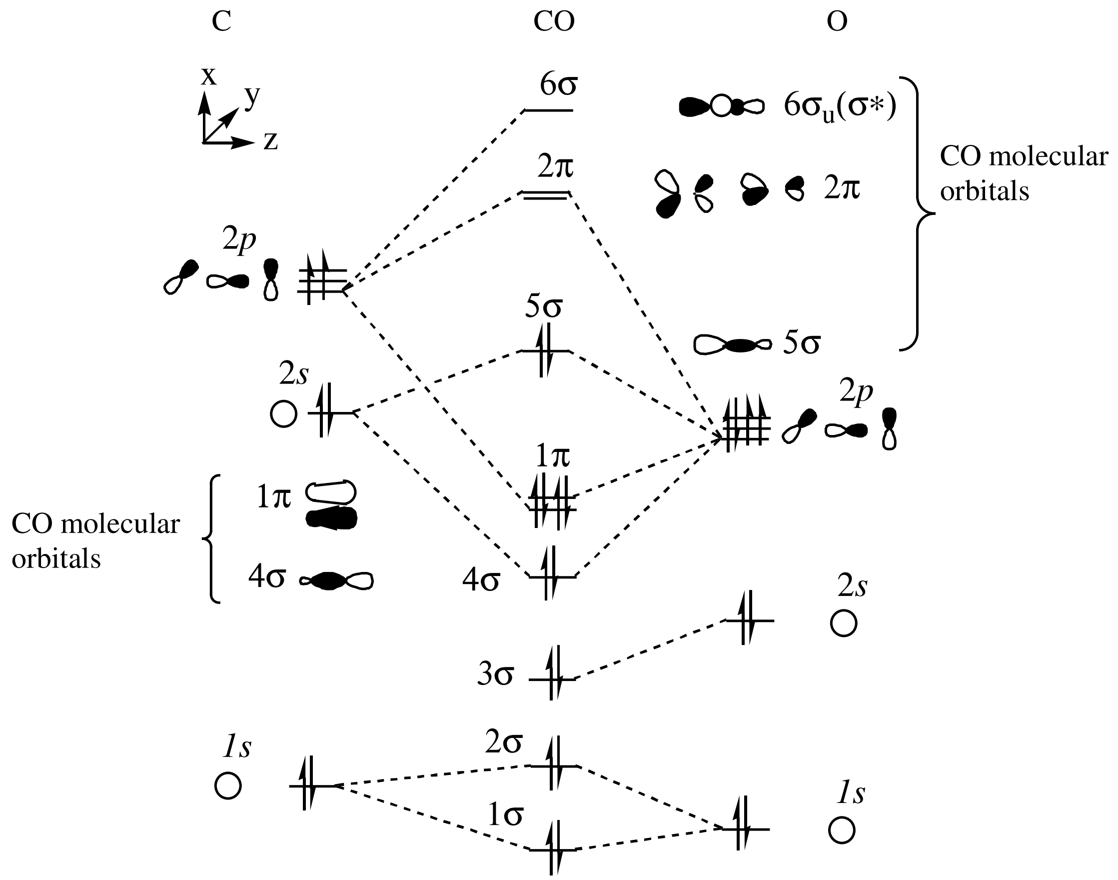






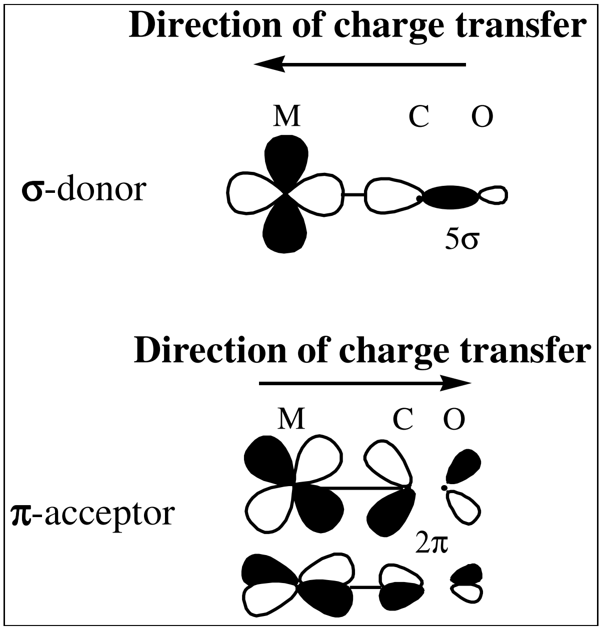
Note: when counting electrons CO always contributes 2 electrons whether terminal or bridging

MO diagram of CO



HOMO 5σ orbital is slightly antibonding and has significant C 2*s* character. This is why CO bonds to a metal as a σ-donor through the C atom and not the O atom (better overlap).

In can be seen that the 2 x 2π LUMO orbitals (antibonding) are empty. It is these orbitals that can interact with metal d-orbitals accepting electron density.



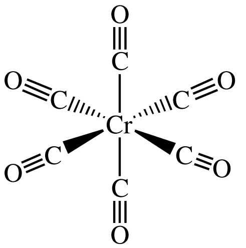
The σ-donor interaction increases the electron density on the metal and decreases the electron density on the CO ligand.
The π-acceptor interaction decreases the electron density on the metal and increases the electron density on the CO ligand.
Both effects 'reinforce' each other. Sometimes referred to as **synergic bonding**.

π -acceptor ligands such as CO can relieve negative charge build-up at a metal centre.
e.g. stabilise complexes with metals in a low formal oxidation state.

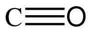
Experimental evidence for bonding model

IR and Raman spectroscopy and single crystal X-ray diffraction.

Characterisation of metal carbonyls

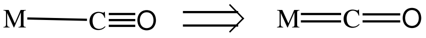


Cr-C = 195.5 pm
C-O = 114.0 pm
ν(C-O) = 1984 cm^{-1}



C-O = 112.8 pm
ν(C-O) = 2143 cm^{-1}

As ν(C-O) decreases C-O bonding decreases and M-C π-bonding increases



Trends in ν(CO)

a) isoelectronic series

	ν(CO) cm^{-1} (T_{1u})
$Mn(CO)_6^+$	2094
$Cr(CO)_6$	1984
$V(CO)_6^-$	1845
$Ti(CO)_6^{2-}$	1750

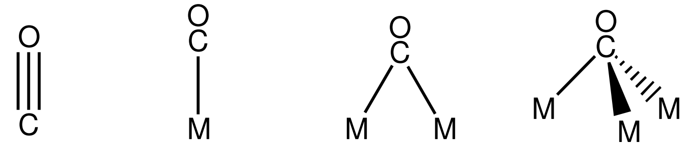
b) as CO ligands are lost

	ν(CO) cm^{-1}
$Mo(CO)_6$	1987
$Mo(CO)_5$	1966
$Mo(CO)_4$	1944,1887
$Mo(CO)_3$	1862

c) as other ligands change

	ν(CO) cm^{-1}
$Ni(CO)(PF_3)_3$	2073
$Ni(CO)(PCl_3)_3$	2059
$Ni(CO)(PMe_3)_3$	1923

d) coordination mode



	Free	Terminal	μ_2-CO	μ_3-CO
ν_{CO} (cm^{-1})	2143	1850-2120	1750-1850	1620-1730

Always think in terms of CO ligands competing for whatever electrons are available on the metal!

Non-classical carbonyls

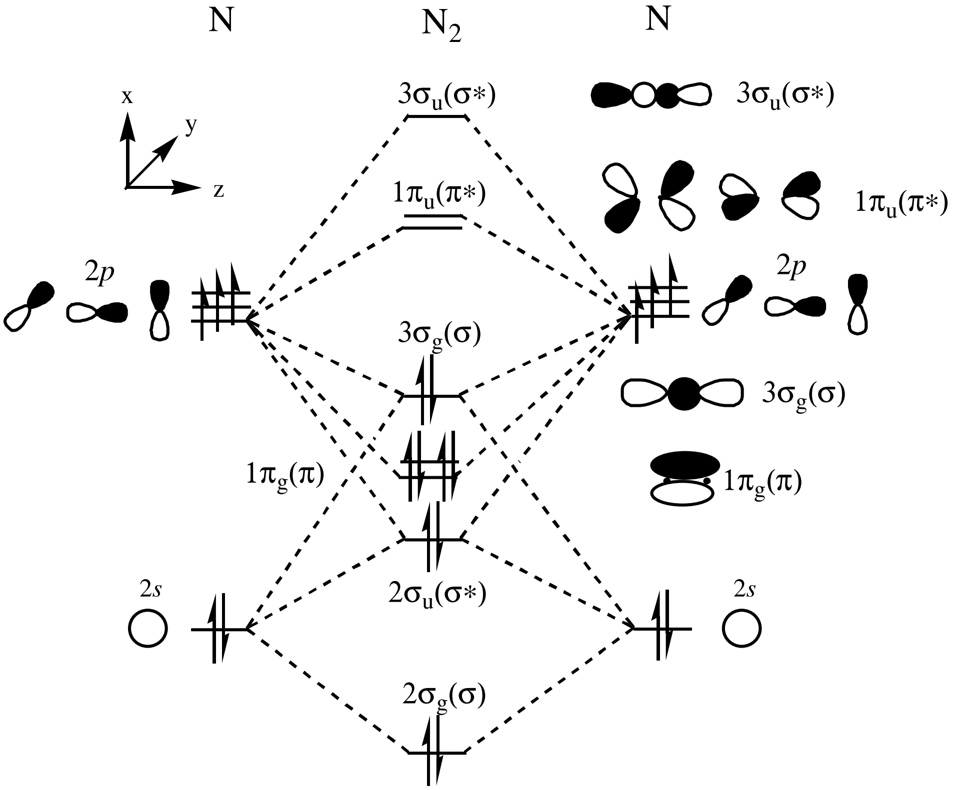
	ν(CO)/cm^{-1}
$Pd(CO)_4^{2+}$	2248
$Pt(CO)_4^{2+}$	2244
$Ag(CO)_2^{+}$	2200
$Au(CO)_2^{+}$	2217
$Hg(CO)_2^{2+}$	2278

In these complexes electron density is not transferred from the metal to the ligand π-accepting orbitals. The major interaction is σ-donation from the CO 5σ (anti-bonding) orbital to the metal. Therefore the CO stretching frequency is > free CO.

Similar π–acceptor ligands

Other ligands that are expected to exhibit very similar bonding to CO are the isoelectronic ligands CN^- and NO^+. (We will see later that NO can also coordinate in an alternative terminal mode).
N_2 is also isoelectronic with CO.

MO diagram of N_2



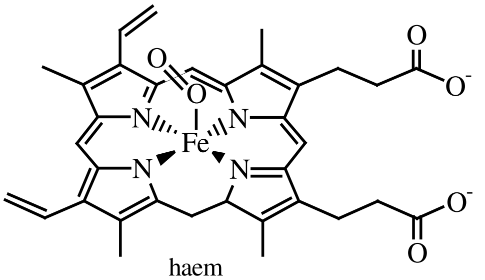
Compare HOMO 5σ (**σ***) of CO and HOMO 3σ_g (**σ**) of N_2.
Coordination of N_2 decreases N-N bond strength.
N_2 can act as a π-acceptor using LUMO 1π_u same as for CO.

Very few metal complexes of N_2 compared to CO.
Another reason is that the energy difference between metal d-orbitals and the $3\sigma_g$ orbital of N_2 is greater than that for metal d-orbitals and the 5σ orbital of CO. (remember the closer in energy the precursor orbitals are, the stronger the bond). Therefore M-N_2 σ–bonds are weaker than M-CO σ–bonds. For similar reasons N_2 is also a poorer π–acceptor ligand than CO.

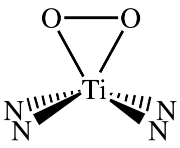
Other π–accepting ligands

Important examples include O_2, H_2, PR_3 and alkenes.

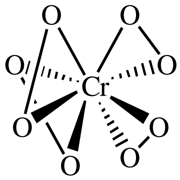
Complexes of dioxygen



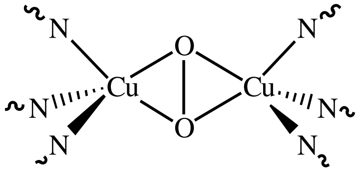
haem



Ti(η^2-O_2)(porphyrin)



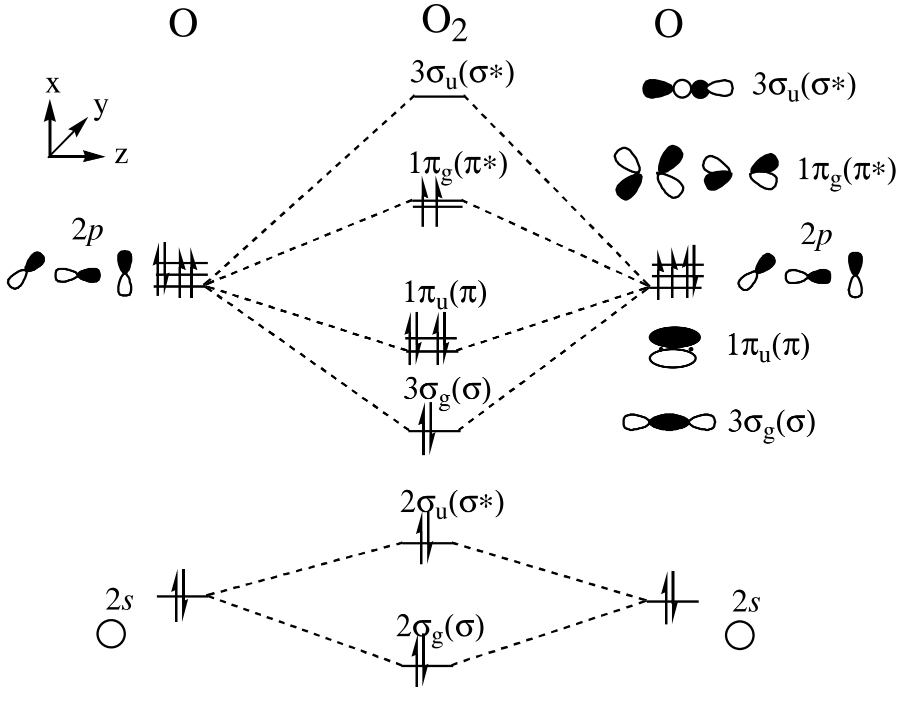
Cr(η^2-O_2)$_4$



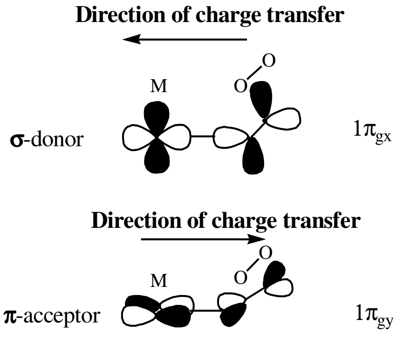
haemocyanin

η^1 vs η^2 bonding in O_2 complexes

MO diagram of O_2

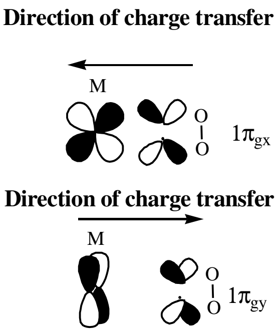


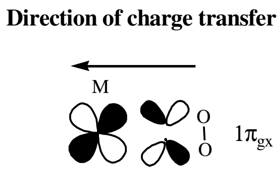
η^1 - bonding



η^2 - bonding (more difficult)

$M + O_2$ or $M^{2+} + O_2^{2-}$ Electron transfer first $1\pi_{gy}$ now full.



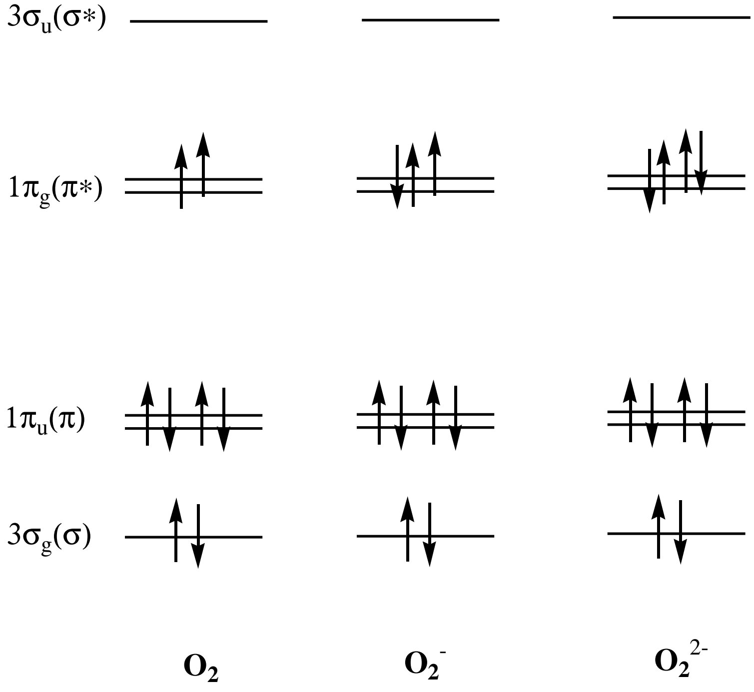


(no back-donation as 'accepting' orbitals are full)

O_2 is very oxidising. Think of as electron transfer followed by binding of O_2^{2-} to M^{2+}. Theory suggests this may be best option.

Characterisation – what is the oxidation state of O_2?

In any given complex, all we know for sure is that the O_2 molecule is bonded to the metal. Neutral dioxygen, superoxide (O_2^-) and peroxide (O_2^{2-}) are all well known forms of the 'O_2' unit, so any given complex could be $\{M\text{-}O_2\}$, $\{M^+\text{-}O_2^-\}$ or $\{M^{2+}\text{-}O_2^{2-}\}$



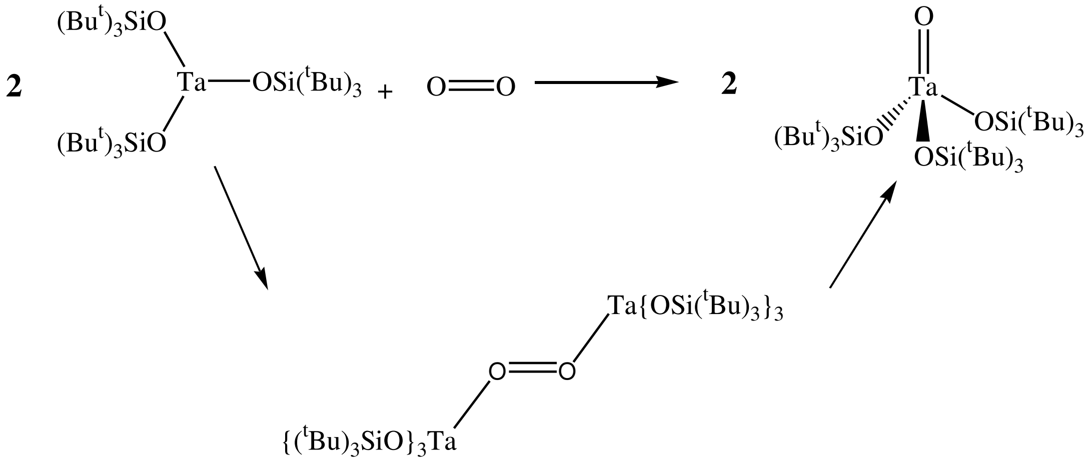
Comparison of MO diagrams of dioxygen, superoxide, and peroxide

Vibrational frequencies and O-O bond lengths

	r(O-O) / pm	ν(O-O) / cm^{-1}
$O_2^+(AsF_6^-)$	**122**	**1858**
O_2	**121**	**1555**
$O_2^-(K^+)$	**133**	**1146**
$O_2^{2-}(Na^+)_2$	**149**	**842**
η^1-O_2	**115-130**	**1130-1195**
η^2-O_2	**130-152**	**800-930**

As the electron density in the π* orbitals increases the O-O distance increases and the vibrational frequency decreases

What happens if the σ* ($3\sigma_u$) orbital becomes occupied?



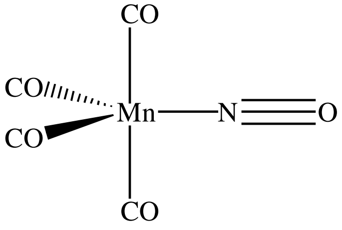
The Ta complex is reducing and has two electrons in a high-energy orbital HOMO. The Ta complexes have orbitals of the correct symmetry and can donate 4 electrons to a molecule of O_2 occupying $1\pi_g$ and $3\sigma_u$ of O_2 causing cleavage of the O_2 bond.

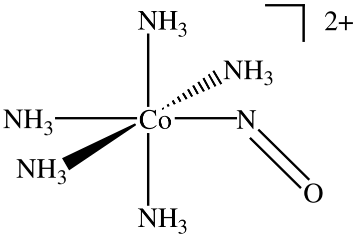
Why is η^1-O_2 bent when CO is linear?

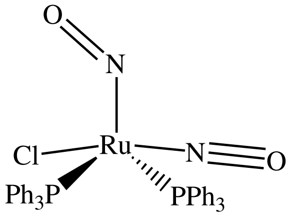
Simply because O_2 has to accommodate an extra pair of electrons in the $1\pi_g$ (π*) orbital. These occupy $1\pi_{gx}$ (to form the σ-bond through one lobe of the $1\pi_{gx}$ orbital) leaving $1\pi_{gy}$ to form a π-acceptor interaction.

NO revisited

NO typically adopts one of two terminal coordination modes (bent and linear)







Characterisation

	M-N-O angle/ °	ν(N-O)/cm^{-1}
Fe(CN)$_5$(NO)$^{2-}$	178	1935
Mn(CN)$_5$(NO)$^{3-}$	174	1700
Co(NH$_3$)$_5$(NO)$^{2+}$	119	1610
CoCl(en)$_2$(NO)$^+$	124	1611

How many electrons does NO donate?

Linear:

i) 1 electron goes *from NO to the metal*, giving NO$^+$ + M$^-$.
ii) NO$^+$ is then isolectronic with CO, and donates 2 electrons *from NO to metal*

2+1 = 3, so NO is a 3-electron donor.

Bent:

i) 1 electron goes *from metal to NO*, giving NO$^-$ + M$^+$.
ii) NO$^-$ is then isolectronic with O$_2$, and donates 2 electrons *from NO to metal*

-1 + 2 = 1, so NO is a 1-electron donor

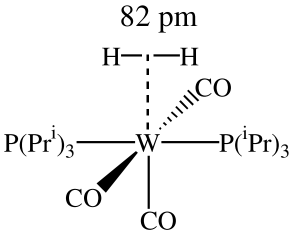
Strategy for determining bent or linear, electron count and oxidation state:

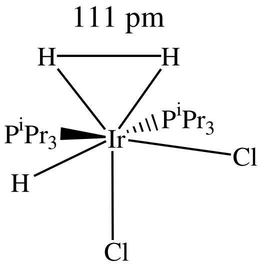
1) Remove NO (neutral) from complex and calculate electron count and oxidation state of remaining fragment.
2) Add 1 or 3 electrons per NO to increase electron count to 18 (or as close as possible without exceeding 18). You now have the total electron count at the metal and the M-NO geometry.
3) Determine the metal oxidation state of the complex including the NO ligand(s) and consider linear NO to be NO$^+$ and bent NO to be NO$^-$.

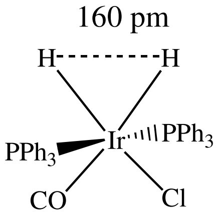
e.g.

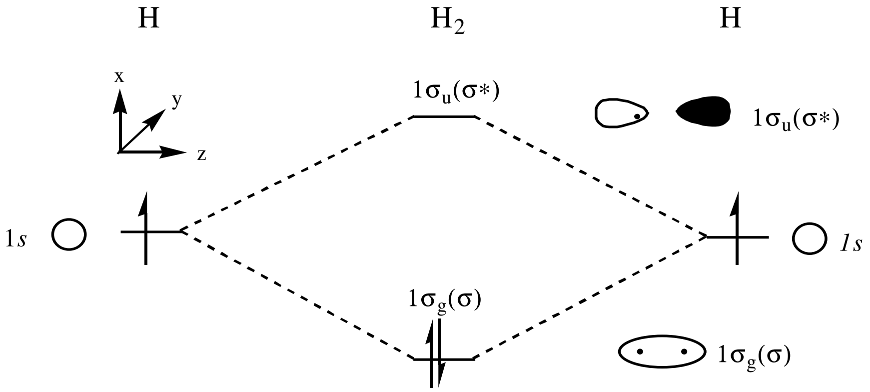
	total valence electrons	metal oxidation state	d-electron count
Mn(CO)$_4$(NO)	**18**	**-I**	**8**
Co(NH$_3$)$_5$(NO)$^{2+}$	**18**	**III**	**6**
RuCl(NO)$_2$(PPh$_3$)$_2$	**17**	**I**	**7**

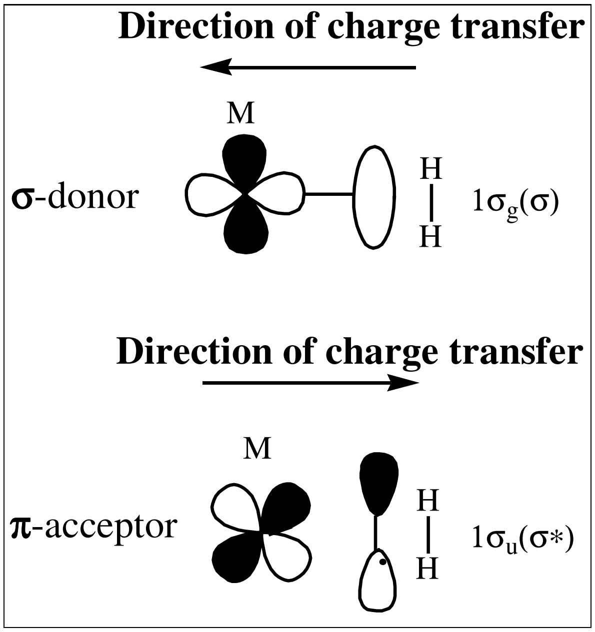
Complexes of dihydrogen (H-H = 74.1 pm in H_2)









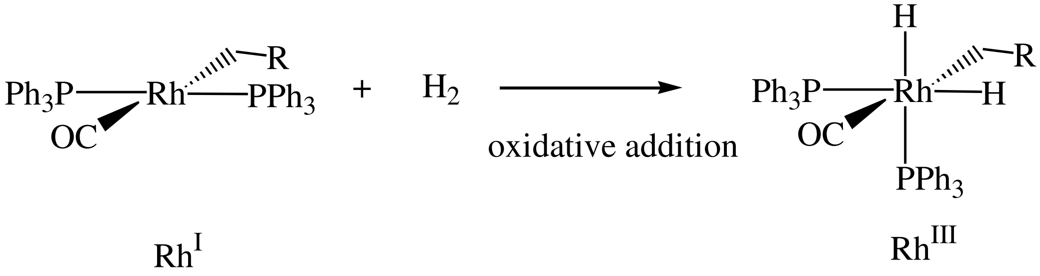


Note: the σ and σ* orbitals of H_2 perform the same roles as the σ and π* orbitals in CO.

The antibonding σ* H_2 orbital is of π-symmetry about an axis perpendicular to the H-H bond and can interact with a metal orbital of π-symmetry.

If sufficient electron density is transferred from the metal to the σ* orbital of H_2 the H-H σ–bond will break and give two M-H (metal-hydride) σ–bonds (oxidative addition).

e.g.



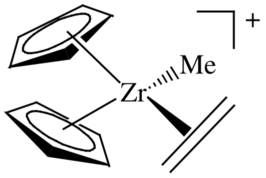
Characterisation – Dihydrogen $M(H_2)$ or dihydride $M(H)_2$ complex ?

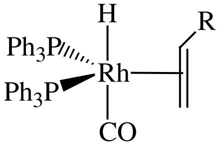
Technique	η^2 H-H	dihydride
Neutron diffraction	H-H~82 pm	H-H~160 pm
NMR	Low field, J_{HD}~30Hz	High field, J_{HD}~5Hz
IR	ν(H-H) ~ 3000 cm^{-1}	ν(M-H)~2150-1750 cm^{-1}
	ν(M-H) v. low	

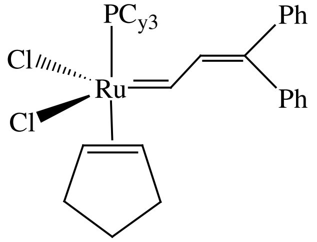
Alkenes

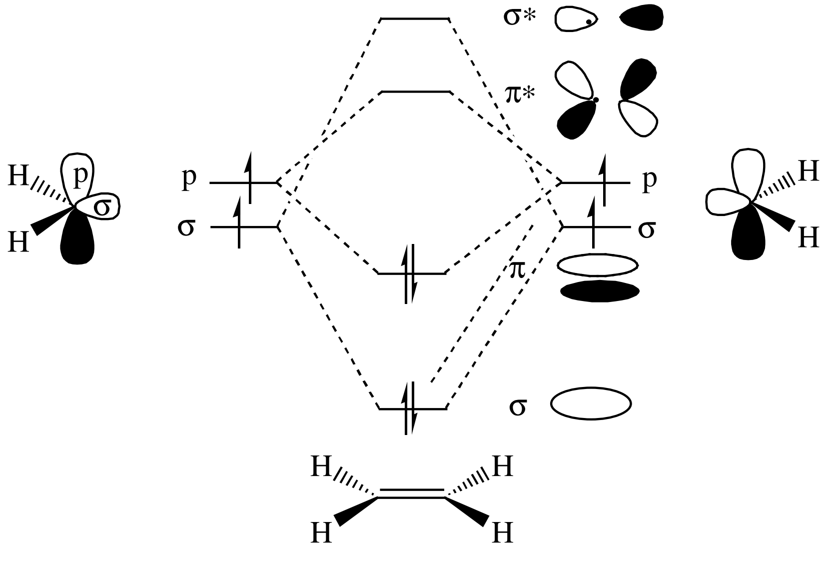
π-acceptor ligands. Alkene complexes form basis of many catalytic reactions e.g. polymerisation, hydrogenation and metathesis.

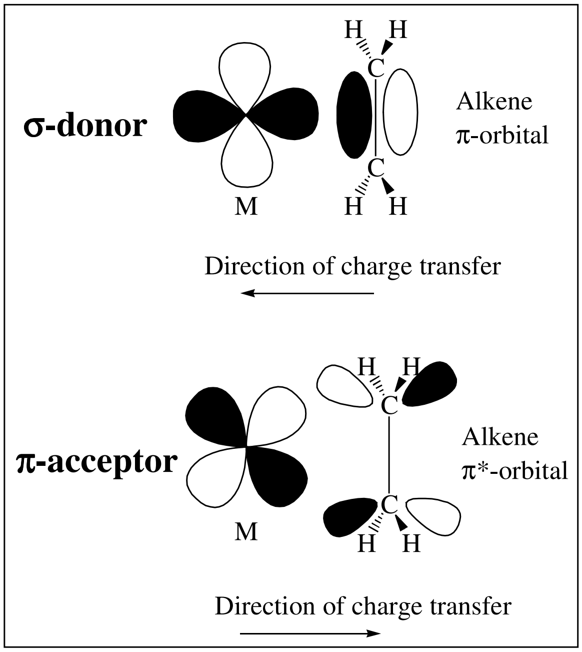
Complexes of alkenes

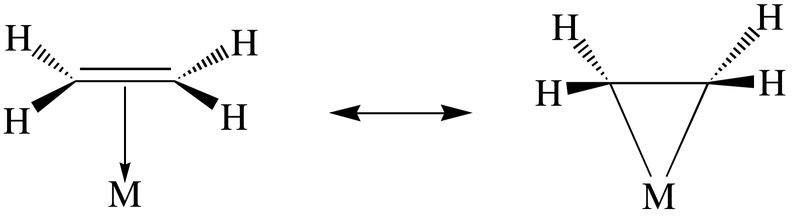




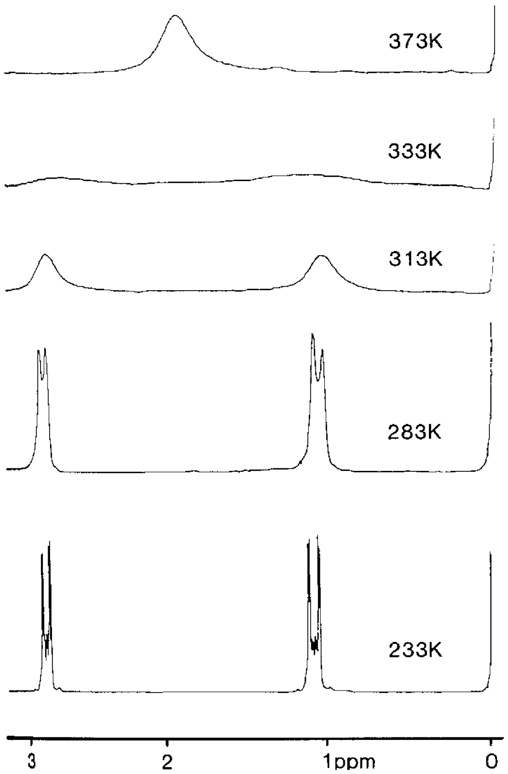


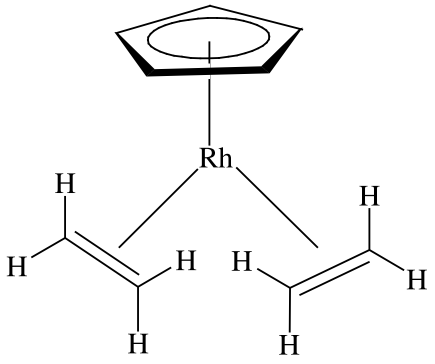


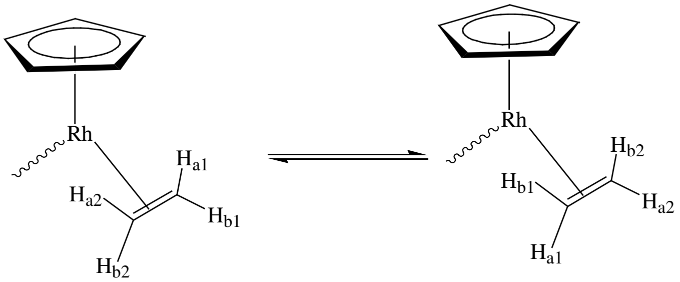




Dynamics in alkene complexes







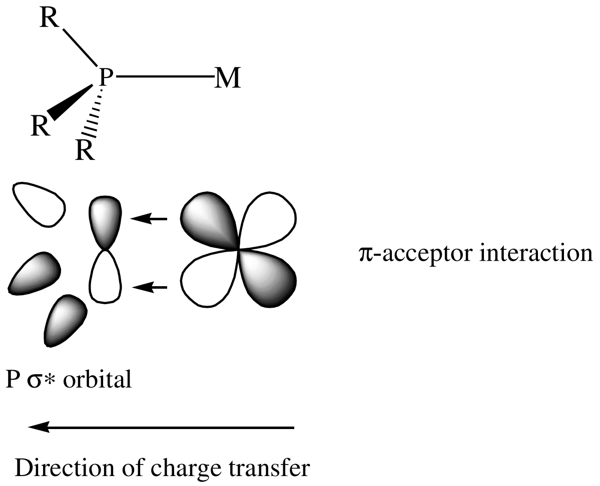
What determines energy barrier to rotation?

1. σ-bonding (dominant) interaction is not affected by rotation (no change in overlap)
2. π-bonding (minor) is broken, but other potential bonding orbitals at 90° to start point help lower activation energy.

PR_3 complexes

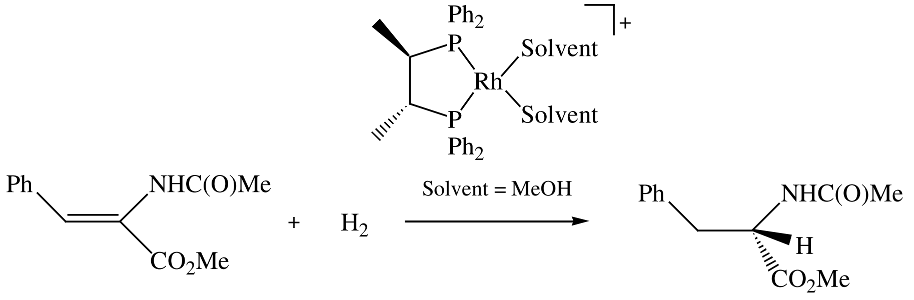
PR_3 can also act as π-acceptor ligands. In this case the orbitals are usually phosphorus σ* orbitals. Complexes of PR_3 ligands are very important catalysts for many reactions.

PR_3 ligands can stabilise low oxidation states by π-acceptor interactions and high oxidation states by strong σ-donation.



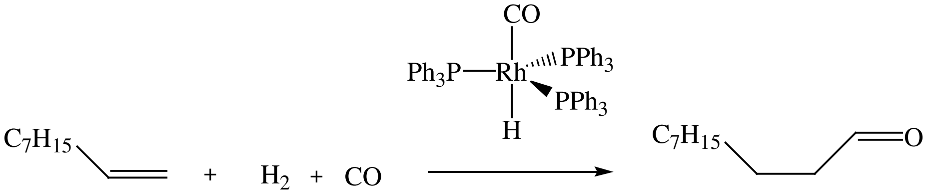
Catalysis examples

Enantioselective synthesis of S-DOPA



S-DOPA precursor

Treatment of Parkinson's Disease



linear aldehyde

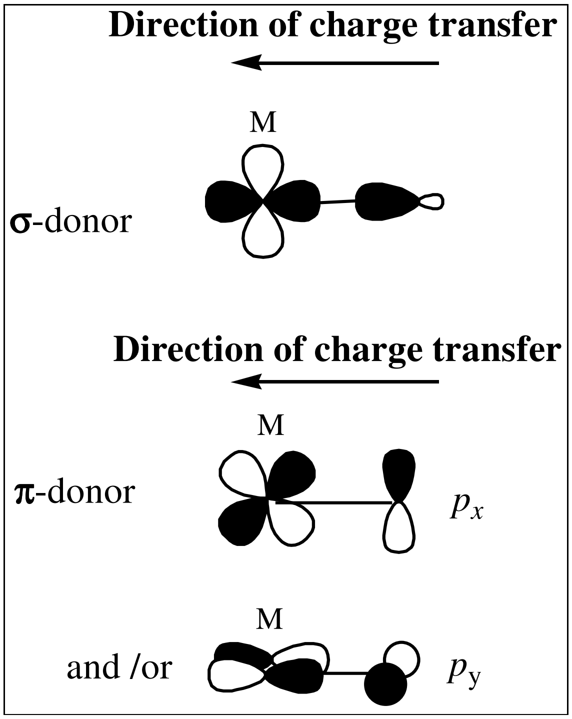
Lots of bulk chemical uses, e.g. Perfumes, agrochemicals

The Rh-L bonding of Rh-CO, Rh-H_2 (Rh-$(H)_2$), Rh-alkene, and Rh-PR_3 all play an integral role in this, and many other, catalytic reactions.

σ-donor, π-donor ('π-donors')

Ligands that fall into this category include: F, Cl, Br, I, O, OR, S, SR, N, NR_2(linear), NR (bent and linear), P.

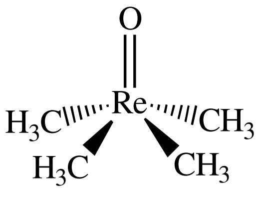
We can view the metal-ligand bonding as a σ-donor interaction (same as for H) with an additional π- interaction that arises from overlap between metal-based orbitals and full orbitals on the ligand that can *donate* electron density.

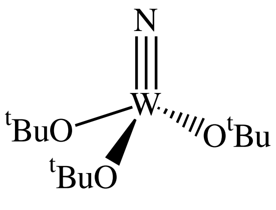


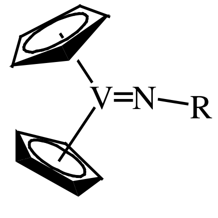
Note: there is no synergic bonding occurring here.

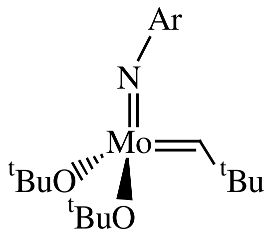
Metal - ligand multiple bonds

e.g.



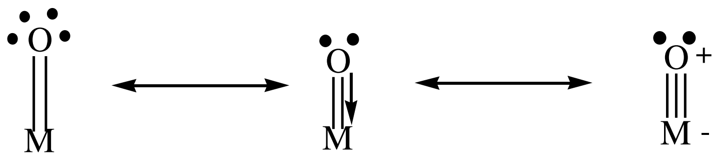






Metal-ligand multiple bonds contain a σ-bond and one or two π-bonds.
Complexes of O and N donor ligands usually have metals in high formal oxidation states with a low d-electron count.
For π-donation to occur there must be an empty metal d-orbital to accept the electrons.

A very important ligand that exhibits multiple bonding is the oxide ligand (O^{2-})



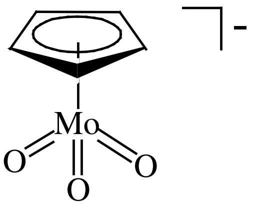
4 electron donor (O^{2-})

6 electron donor

6 electron donor

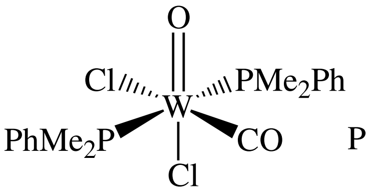
Electrophilic O

Look at M-O bond lengths to determine bonding

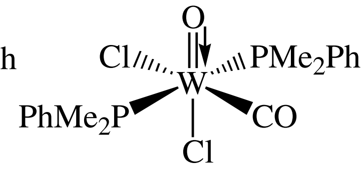


$18\ e^-$

double bond



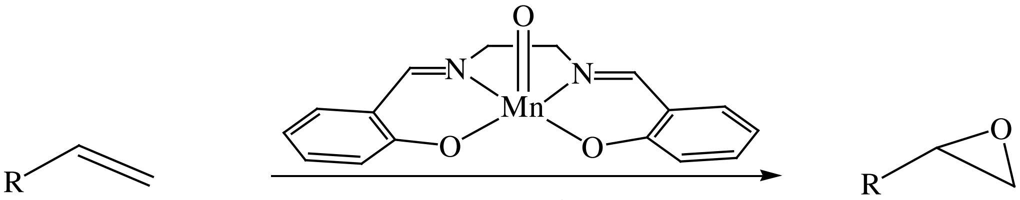
$16\ e^-$



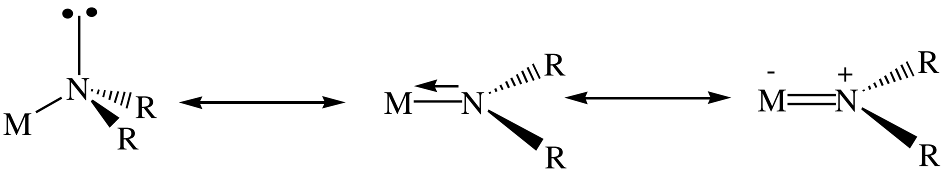
$18\ e^-$

X-ray shows very short W-O distance

Metal oxides are used as source of oxygen for the oxidation of organic compounds e.g. catalytic epoxidation of alkenes.



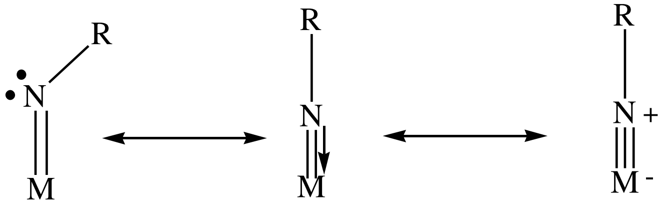
Other common multiple bonds are the amido (NR_2^-), imido (NR^{2-}) and nitrido (N^{3-}) ligands.



2 electron donor

4 electron donor

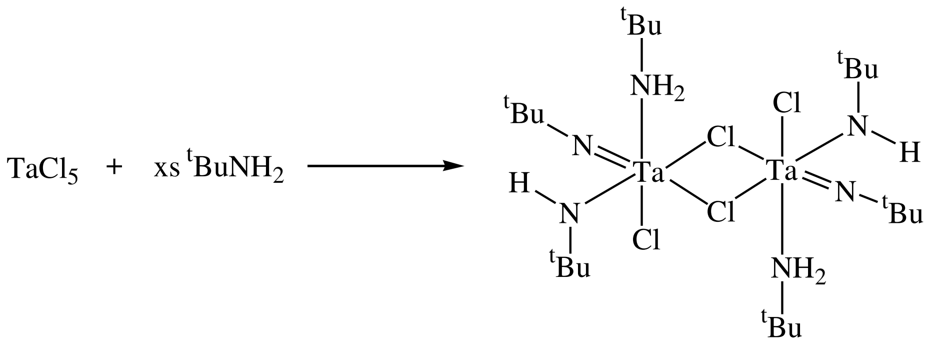
4 electron donor



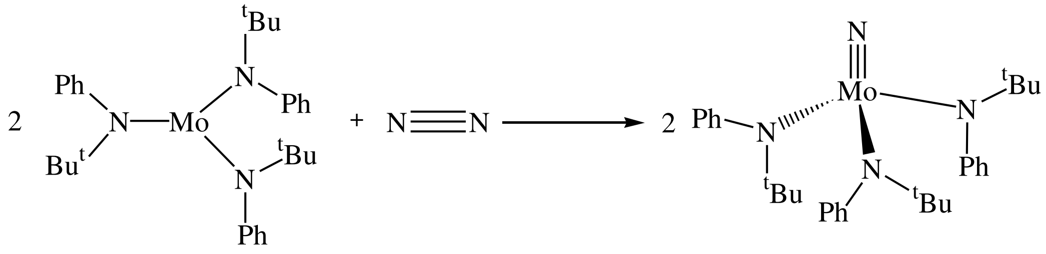
4 electron donor

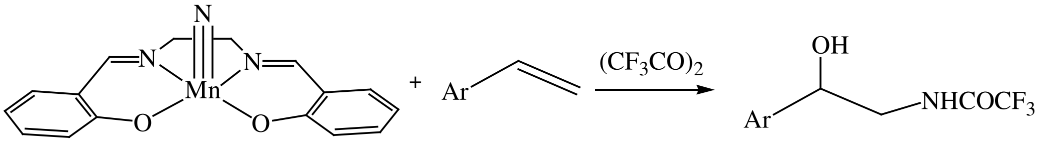
6 electron donor

6 electron donor



Can we use N_2 as a source of nitrogen in organic chemistry?



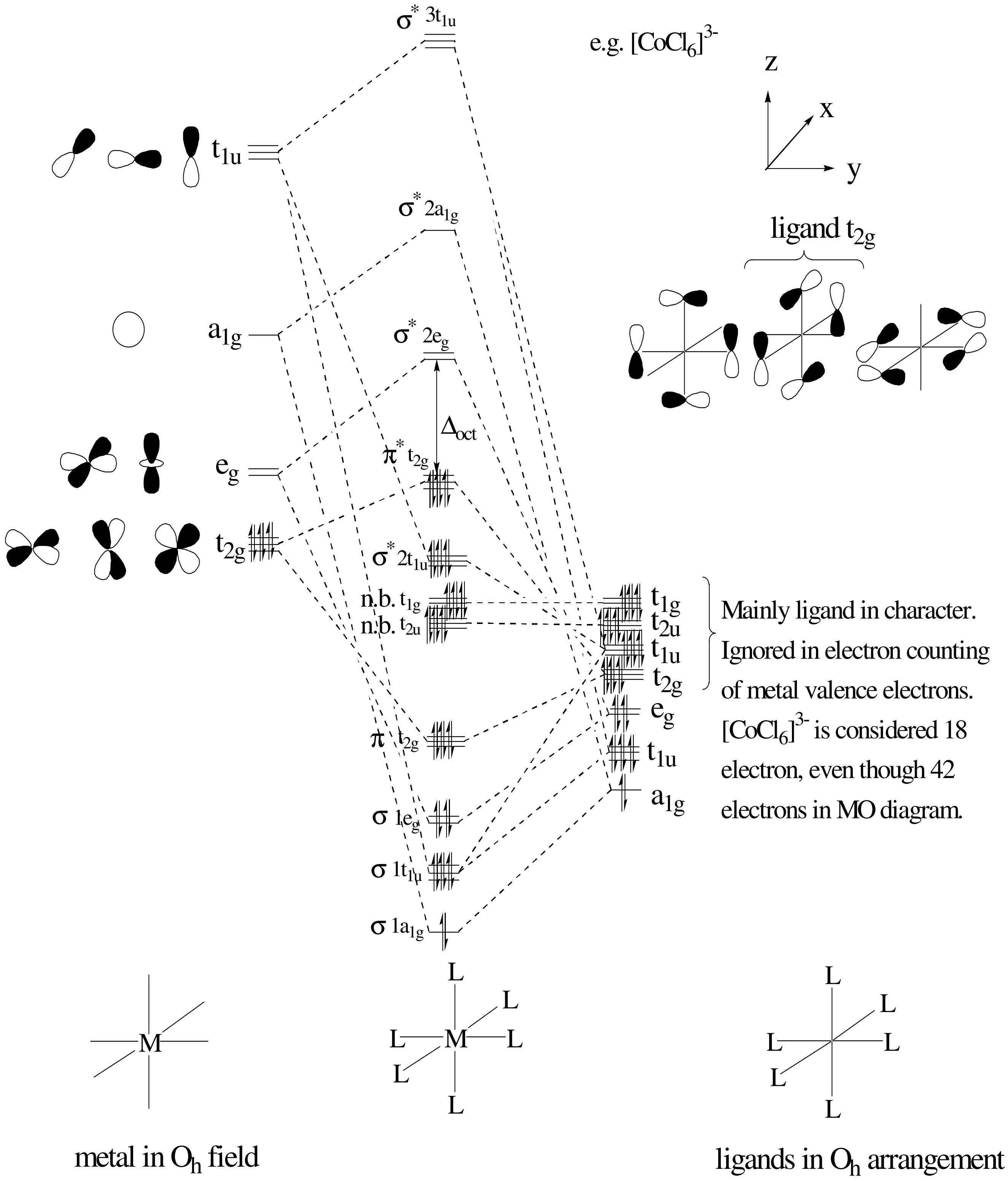


Electron counting of π-donor complexes can be difficult. As a rule of thumb invoke as many multiple bonds as possible to get as close to (but not over) 18.

	total valence electrons	metal oxidation state	d-electron count
$(^tBuO)_3WN$	**12 (18)**	**VI**	**0**
$(\eta\text{-}C_5H_5)_2V(NPh)$	**17**	**IV**	**1**
$ReMe_4(O)$	**13(15)**	**VI**	**1**

What effect do π-acceptors and π-donors have on the chemistry of metal complexes?

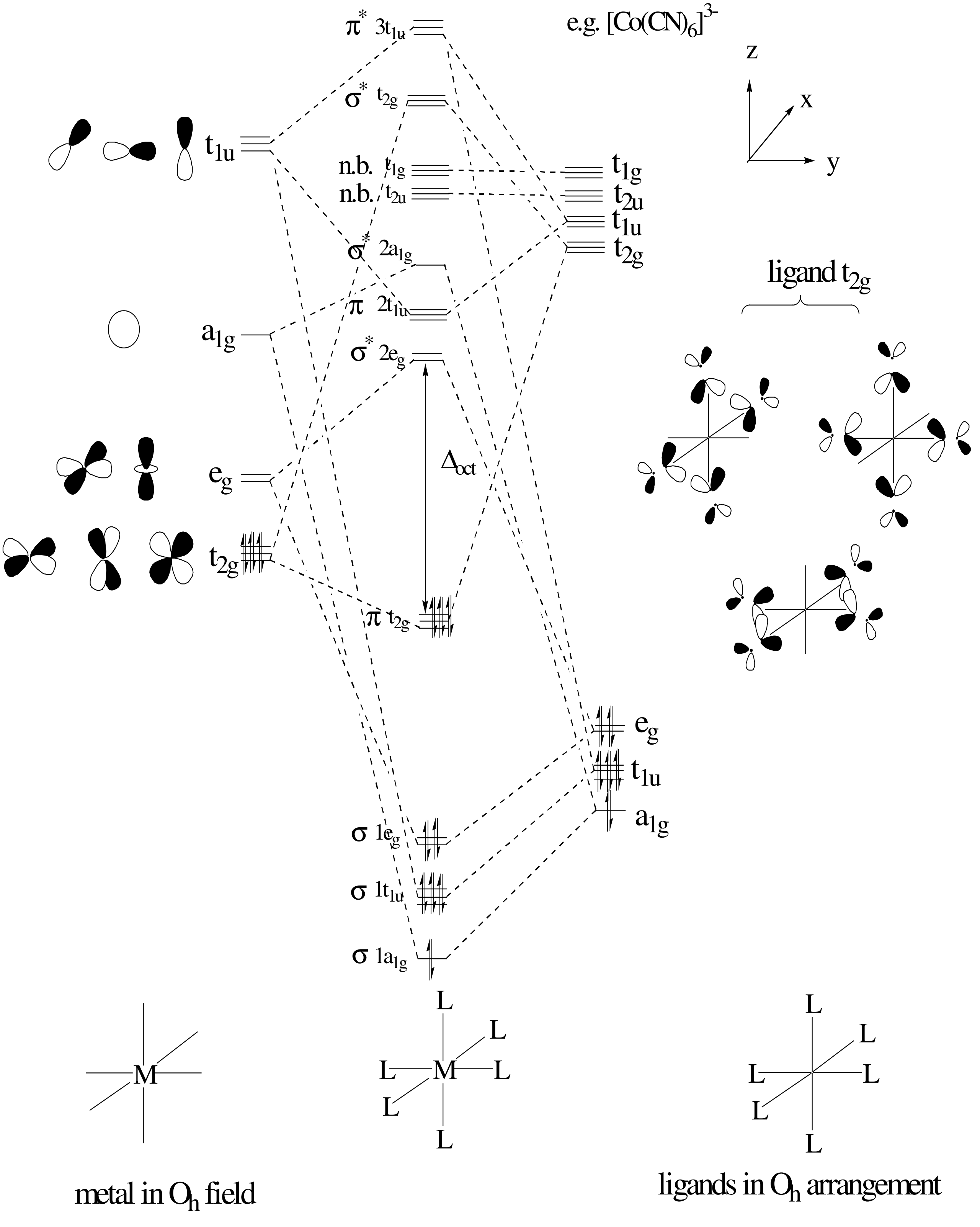
MO diagram of O_h complex with π-donor ligands



Mainly ligand in character. Ignored in electron counting of metal valence electrons. $[CoCl_6]^{3-}$ is considered 18 electron, even though 42 electrons in MO diagram.

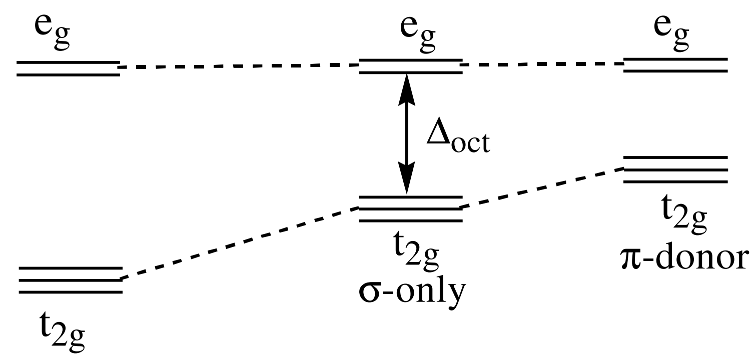
Note the effect on the t_{2g} d-orbitals in comparison to the σ-only case. These t_{2g} orbitals have risen in energy, closer to the e_g level, resulting in a reduction of Δ_{oct} (10 Dq).

MO diagram of O_h complex with π-acceptor ligands



Note the effect on the t_{2g} d-orbitals in comparison to the σ-only case. The t_{2g} has been lowered in energy with respect to the e_g level resulting in an increase in Δ_{oct} (10 Dq).

Summary



Δ_{oct} π-accetor > σ-only > π-donor

π-donors and the 18-electron rule

π-acceptor ligands usually obey the 18-electron rule, those with π-donors do not necessarily do so. For π-donor ligands the metal t_{2g} orbitals are now slightly antibonding (π*) therefore it is less energetically favourable to fill them.
e.g. $CrCl_6^{3-}$ with 15 total valence electrons is stable.

Spectrochemical series

The spectrochemical series is a list of ligands in order of increasing ligand field strength. Electrostatic model cannot account for the order.

$CO > CN^- > PPh_3 > NH_3 > H_2O > OH^- > F^- > Cl^- > S^{2-} > Br^- > I^-$

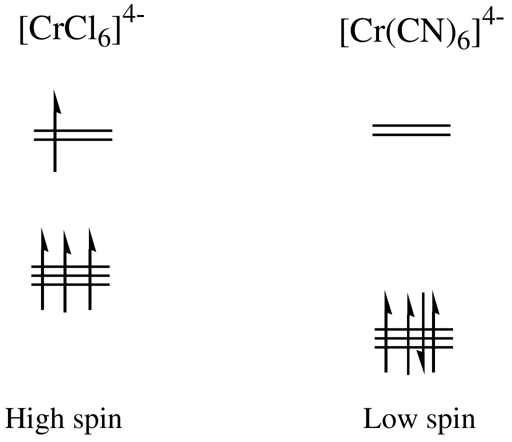
π-acceptor **σ-only** **π-donor**

Increasing Δ_{oct}

←

Δ_{oct} increases with increasing π-acidity of the ligands

e.g. Field strength determine spin state of metal complexes



Trans-effect and Trans-influence

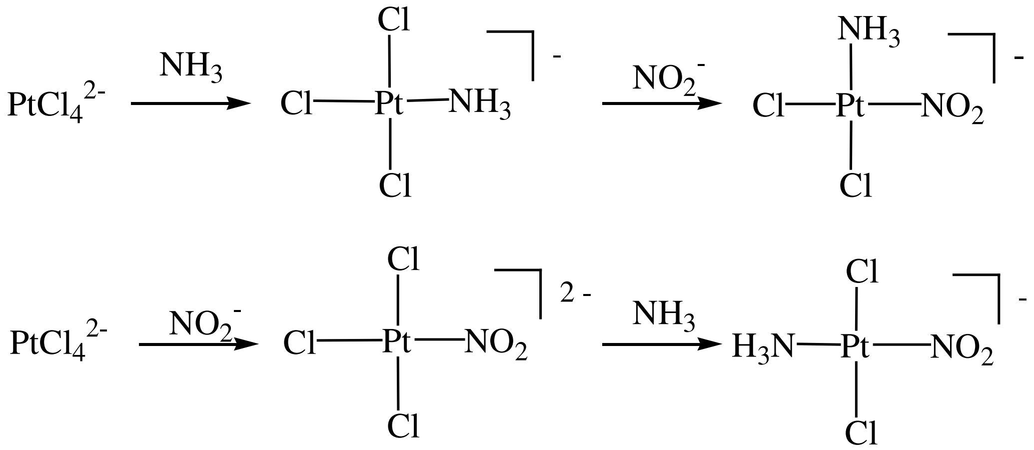
These phenomena will be discussed in more detail later in *Inorganic Mechanisms I.* The trans-effect and trans-influence help to rationalise the stability and substitution chemistry of transition metal complexes, particularly square planar Pd and Pt complexes.

The *trans effect* is a *kinetic* phenomenon and describes the influence of a non-labile group on the rate of substitution of a ligand *trans* to it.

$$\mathrm{CO,\ CN^- > PPh_3 > NO_2^- > I^- > Br^-,\ Cl^- > NH_3,\ OH^-,\ H_2O}$$

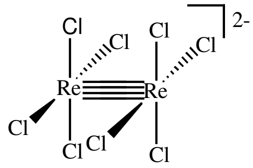
π-acceptor **π-donor** **σ-only**

e.g.

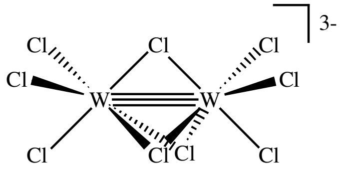


Metal-metal bonding

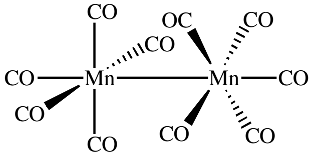
Complexes with metal-metal bonds



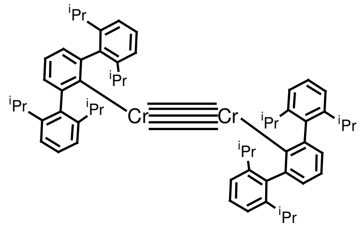
quadruple



triple

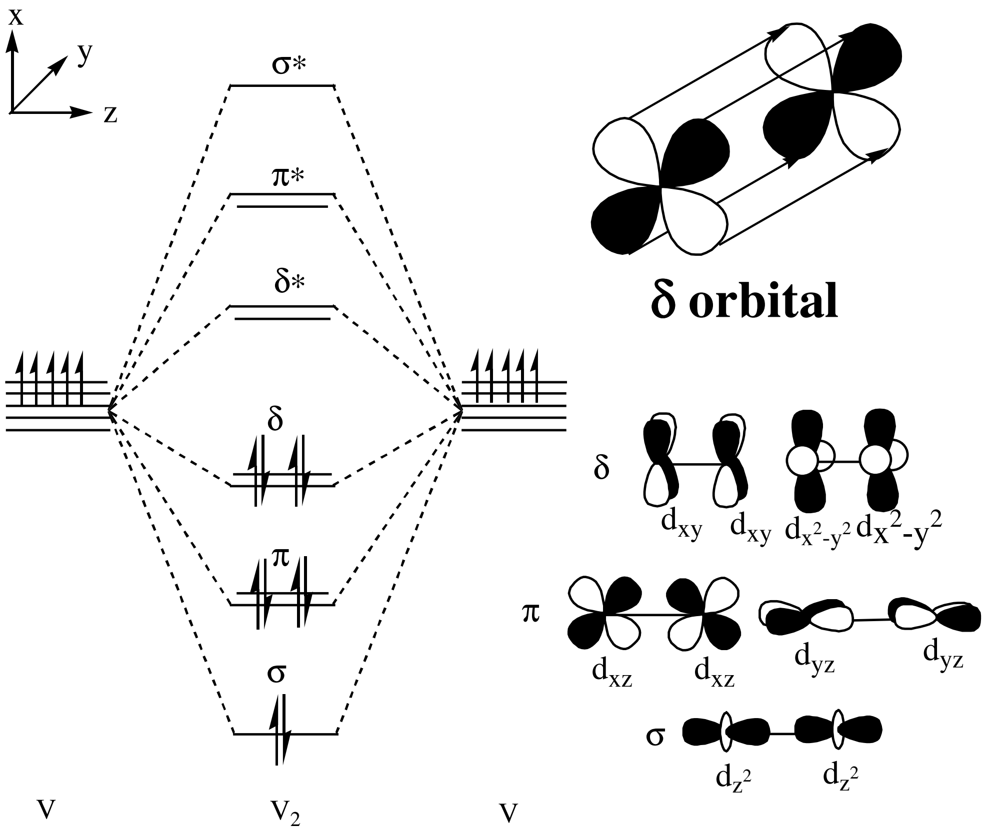


single



quintuple?

Bonding in 'Bare' M_2 dimers (e.g. V_2)

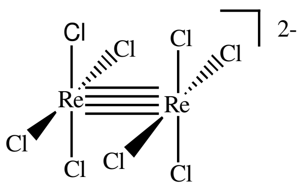


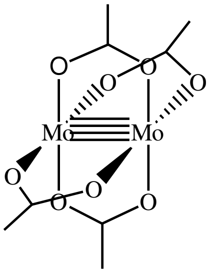
configuration $\sigma^2\pi^4\delta^4$

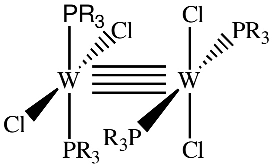
δ-bonds are weaker than π-bonds (and therefore σ-bonds). This is due to the poor overlap between precursor orbitals.

Note: Bond order is usually less that 5 because metal *d*-orbitals are required for the M-L bonds.

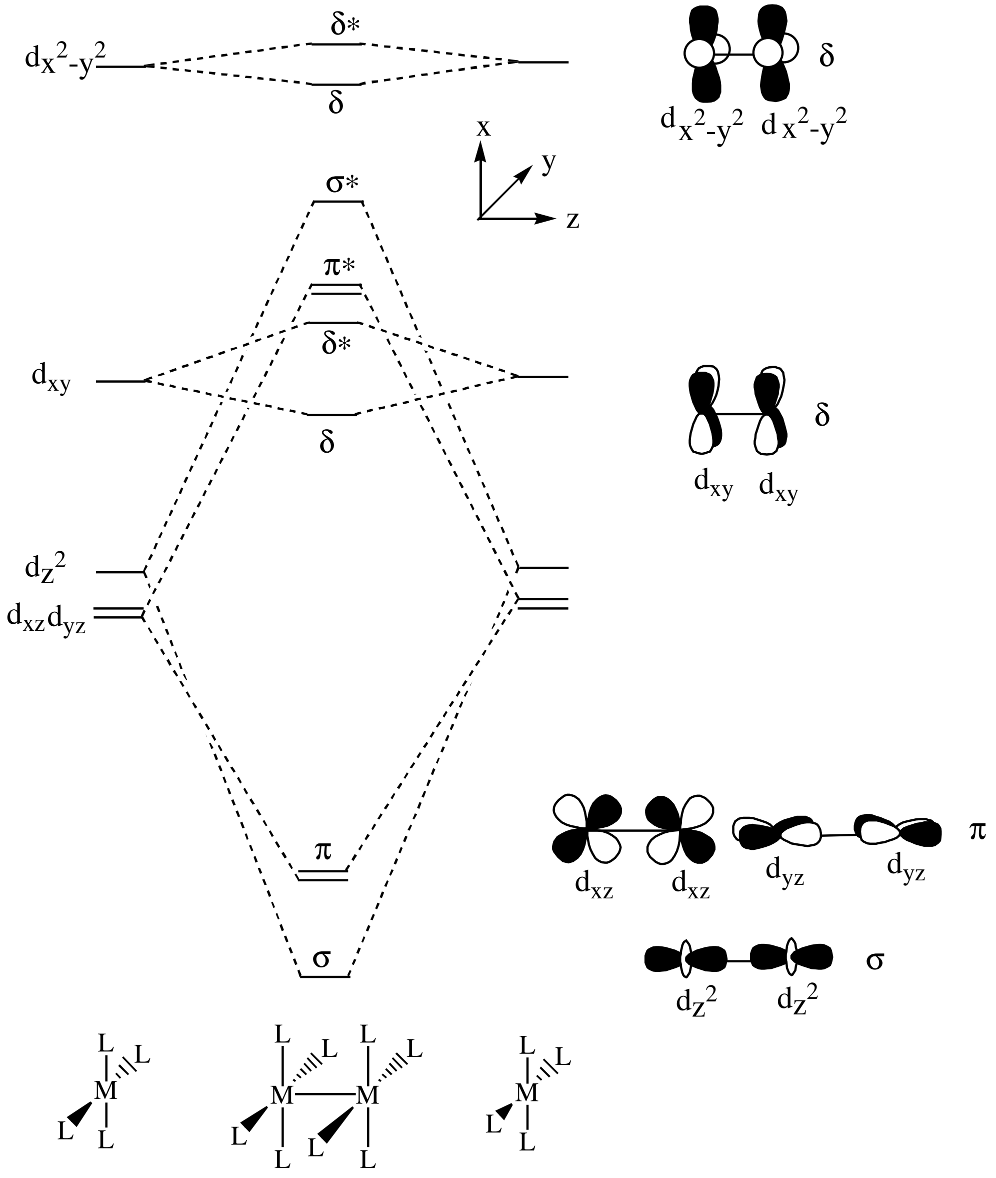
Quadruple bonds





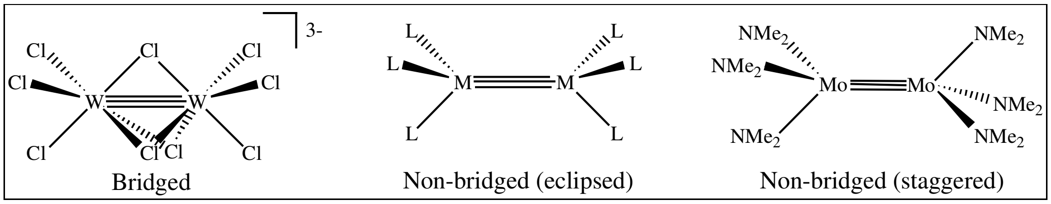


There is a competition between metal-metal and metal-ligand bonding. One orbital can't (usually) do both, so if it's involved in metal-ligand bonding, it's effectively 'factored out' of the metal-metal bond.

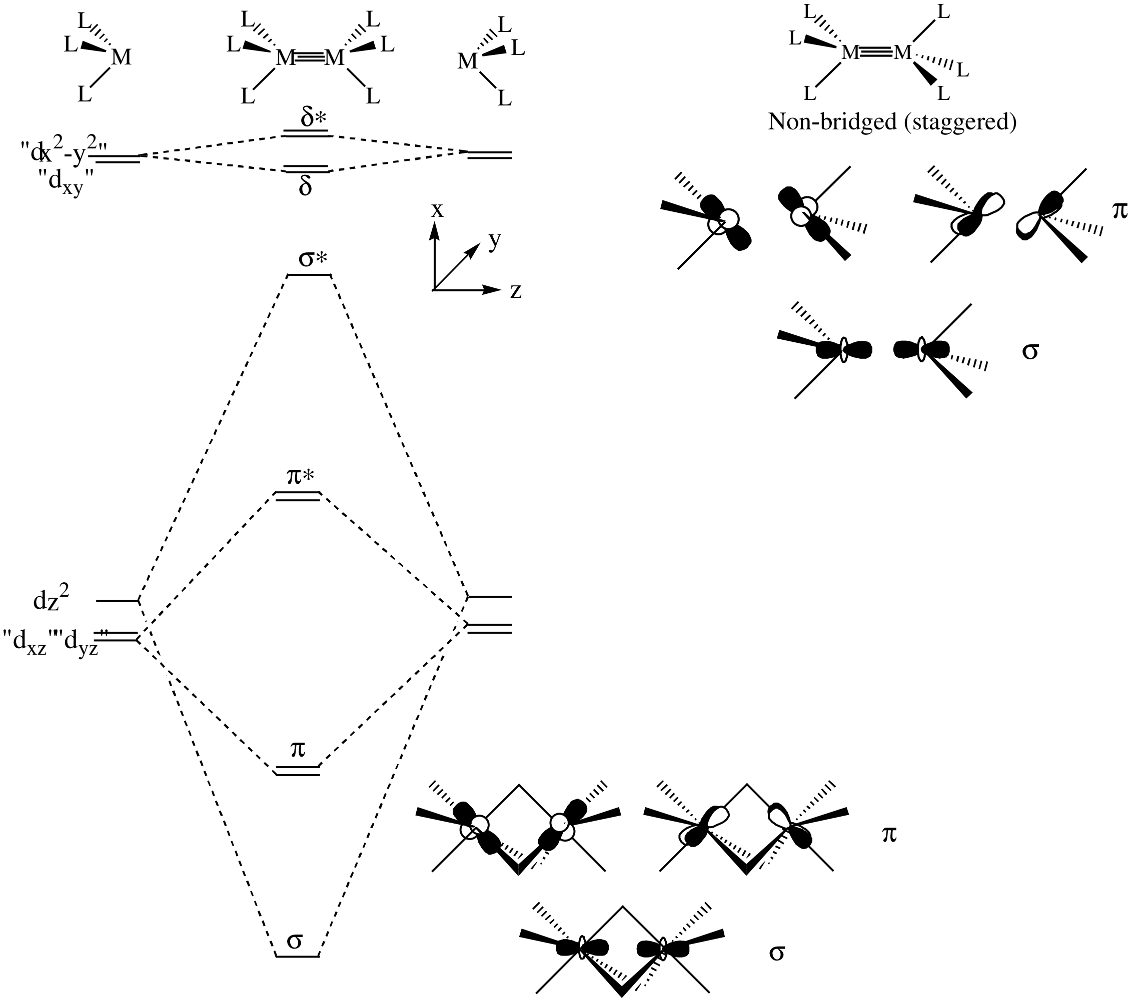


	Configuration	rM-M / pm	Orientation of ML_4 units
$Re_2Cl_8^{2-}$	$\sigma^2\pi^4\delta^2$	222	Eclipsed
$Os_2Cl_8^{2-}$	$\sigma^2\pi^4\delta^2\delta^{*2}$	218	Staggered or eclipsed

Triple bonds



note: *2* d orbitals per metal are now 'factored out'



The d-orbitals other than the d_{z^2} are hybrids (needed for metal-ligand bonding), the predominantly d_{xz} orbital has some $d_{x^2-y^2}$ mixed in, the d_{yz} orbital some d_{xy} and vice versa. Also due to the tilting it should be noted that the π and π* have some δ and δ* character respectively. As can be seen for M_2L_6 the eclipsed conformation gives the best overlap, however most compounds of this type are in fact staggered due to steric reasons (*c.f.* ethane).

	Configuration	rM-M / pm	Magnetism
$Cr_2Cl_9^{3-}$	$\sigma^2(\delta/\pi)^4$	310	Paramagnetic
$Mo_2Cl_9^{3-}$	$\sigma^2(\delta/\pi)^4$	253-288	Variable
$W_2Cl_9^{3-}$	$\sigma^2(\delta/\pi)^4$	242-250	Diamagnetic