

# Molecular Orbitals in Inorganic Chemistry

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Rm 110F (MSRH)



# Feedback!

- 🍌 best parts of the course
- 🍌 worst parts of the course
- 🍌 what extra resources??
- 🍌 what could I revise in L8?

WHZ9KBWC3

socratic quiz!



# Lecture 7 Outline

- **revision: ligands**
- **MO theory for a single  $\pi$ -donor ligand**
- **the spectrochemical series and crystal field theory**
- **MO theory for a single  $\pi^*$ -acceptor ligand**
- **Summary of  $\Delta_{\text{oct}}$  for different ligand types**



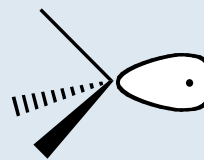
# Revision: Ligands

## 3 key types of ligand

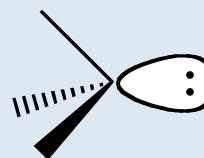
### $\sigma$ -donor ligands

- ◆ ligands with electrons in  $\sigma$ -type orbitals

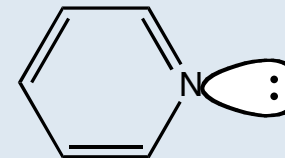
#### $\sigma$ -donor ligands



$\text{CH}_3, \text{CR}_3, \text{SiH}_3, \text{SiR}_3, \text{SiX}_3$



$\text{NH}_3, \text{NR}_3, \text{PH}_3, \text{PR}_3$



Py

Fig. 2

reminder



# Revision: Ligands

## 3 key types of ligand

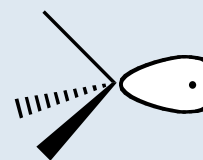
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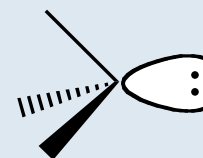
### $\pi$ -donor ligands

- ◆ ligands which have additional filled  $\pi$  orbitals

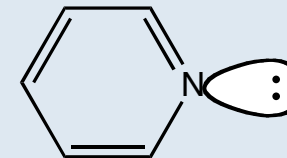
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Py

Fig. 2

#### $\pi$ -donor ligands

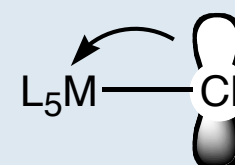
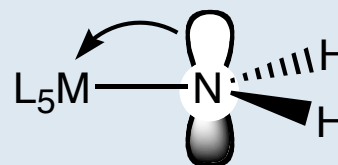


Fig. 2



# Revision: Ligands

## 3 key types of ligand

### $\sigma$ -donor ligands

- ◆ ligands with an available lone pair

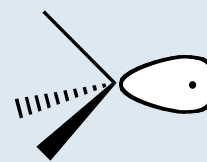
### $\pi$ -donor ligands

- ◆ ligands which have additional filled  $\pi$  orbitals

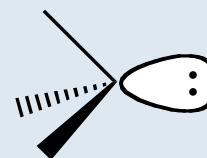
### $\pi$ -acceptor ligands

- ◆ ligands which have additional empty  $\pi$  orbitals

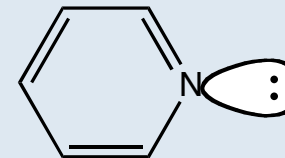
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$\text{CH}_3, \text{CR}_3, \text{SiH}_3, \text{SiR}_3, \text{SiX}_3$



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Py

Fig. 2

#### $\pi$ -acceptor ligands

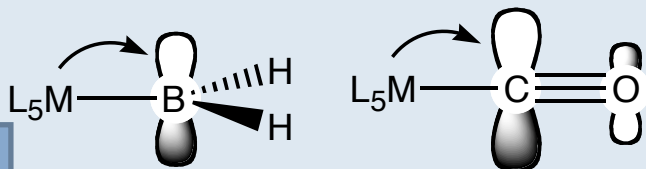


Fig. 2

#### $\pi$ -donor ligands

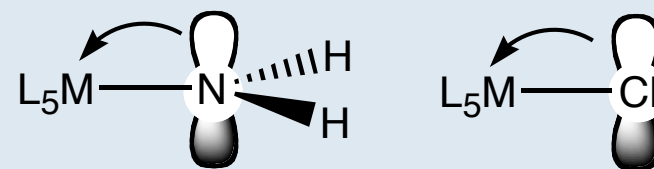


Fig. 2



# Metal-Ligand Interactions

## Dewar-Chatt-Duncanson bonding

♦ alkenes, alkynes  $\Rightarrow$  double or triple bond

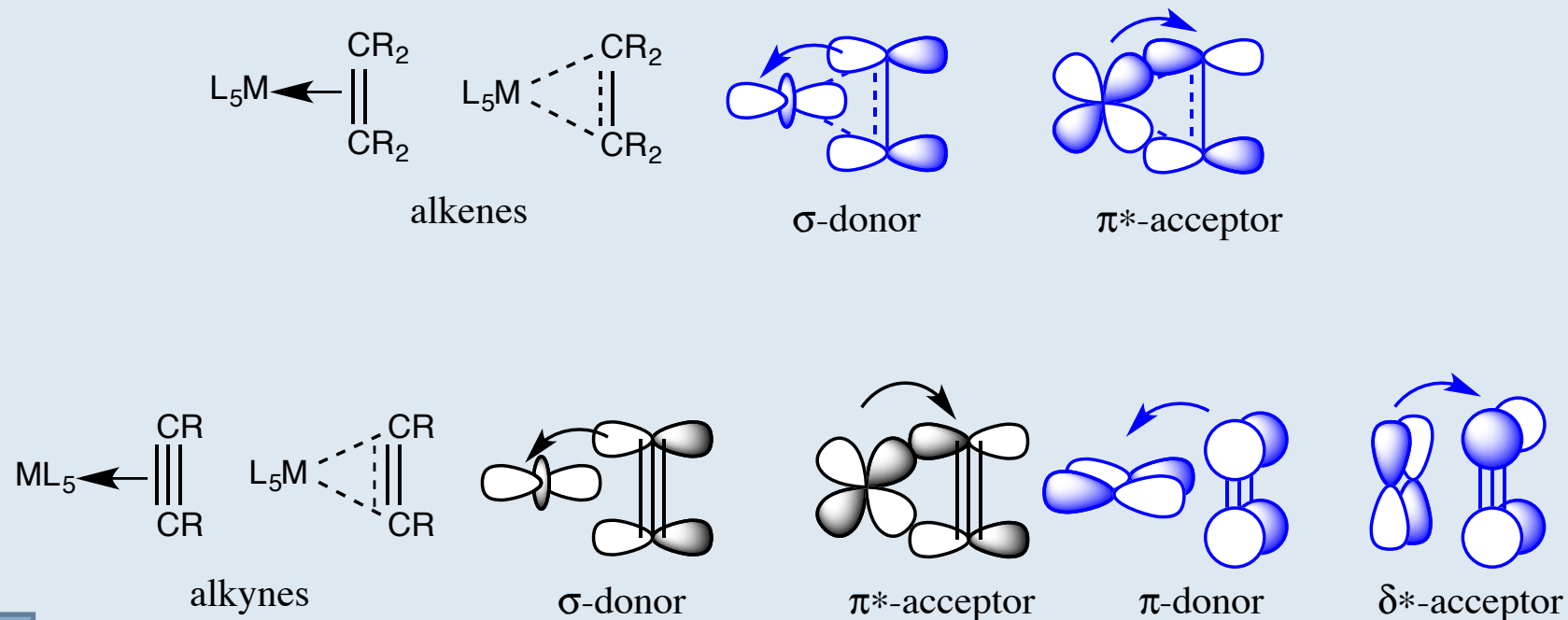
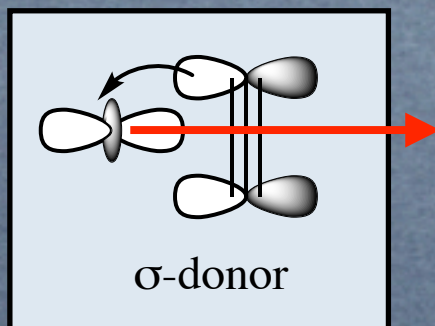


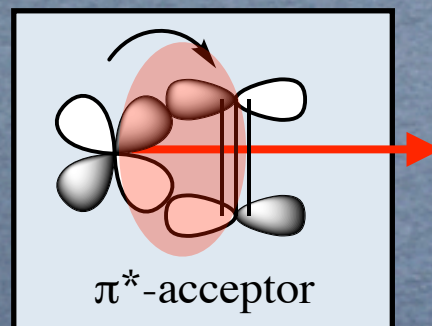
Fig. 3



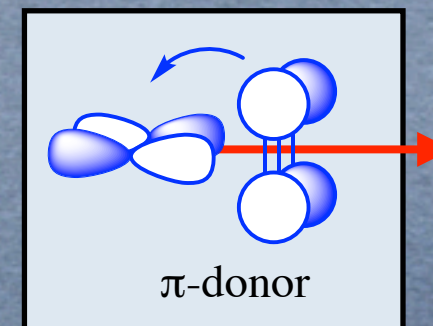
# $\pi$ - and $\delta$ - symmetry



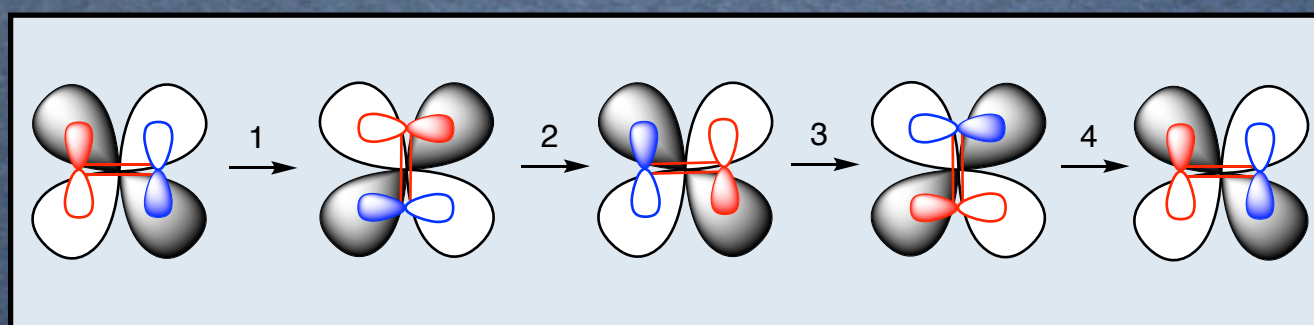
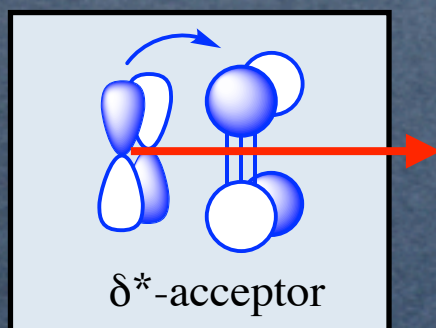
rotate about "bond"  
no phase change  $\Rightarrow \sigma$



rotate about "bond"  
2 phase changes  $\Rightarrow \pi$



rotate about "bond"  
2 phase changes  $\Rightarrow \pi$

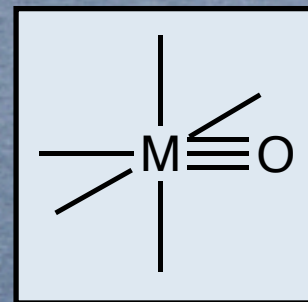


rotate about "bond"  
4 phase changes  $\Rightarrow \delta$



# In-Class Activity

- Draw a diagram showing (just) metal dAOs and the important  $O^{2-}$  FOs interacting
- hint: consider the pAOs on the oxygen atom
- what kind of ligand is  $O^{2-}$ ?



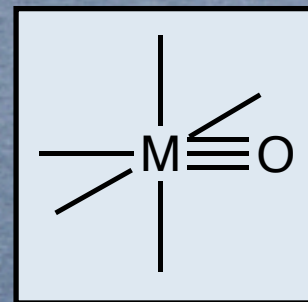
WHZ9KBWC3

socrative quiz!



# In-Class Activity

- Draw a diagram showing (just) metal dAOs and the important  $O^{2-}$  FOs interacting
- hint: consider the pAOs on the oxygen atom





# Method: $\pi$ -Ligands

## consider 6 ligands

- ◆ 1 is  $\pi$ -donor  $\Rightarrow L'$
- ◆ 5 are  $\sigma$ -donor ligands  $\Rightarrow L$

## ALL ligands contribute to $\sigma$ -framework

## $L'$ contributes additional $\pi$ -orbitals

part of  
 $\sigma$ -framework

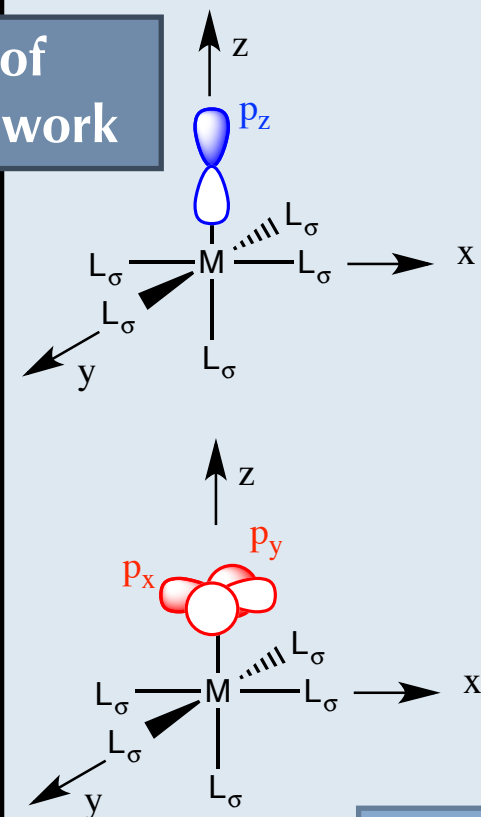


Fig. 4

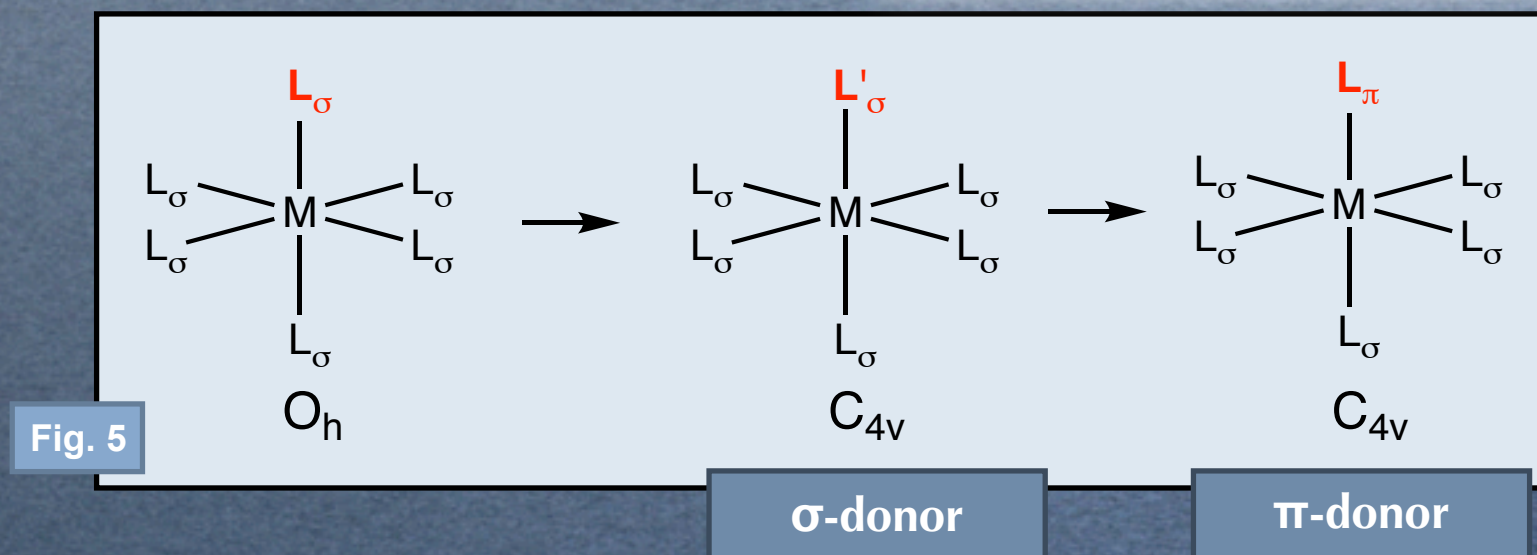
$\pi$ -donor  
fragment orbitals



# Method: $\pi$ -Ligands

first: work out reduced symmetry

descent in symmetry  $O_h \rightarrow C_{4v}$



covered in L6!

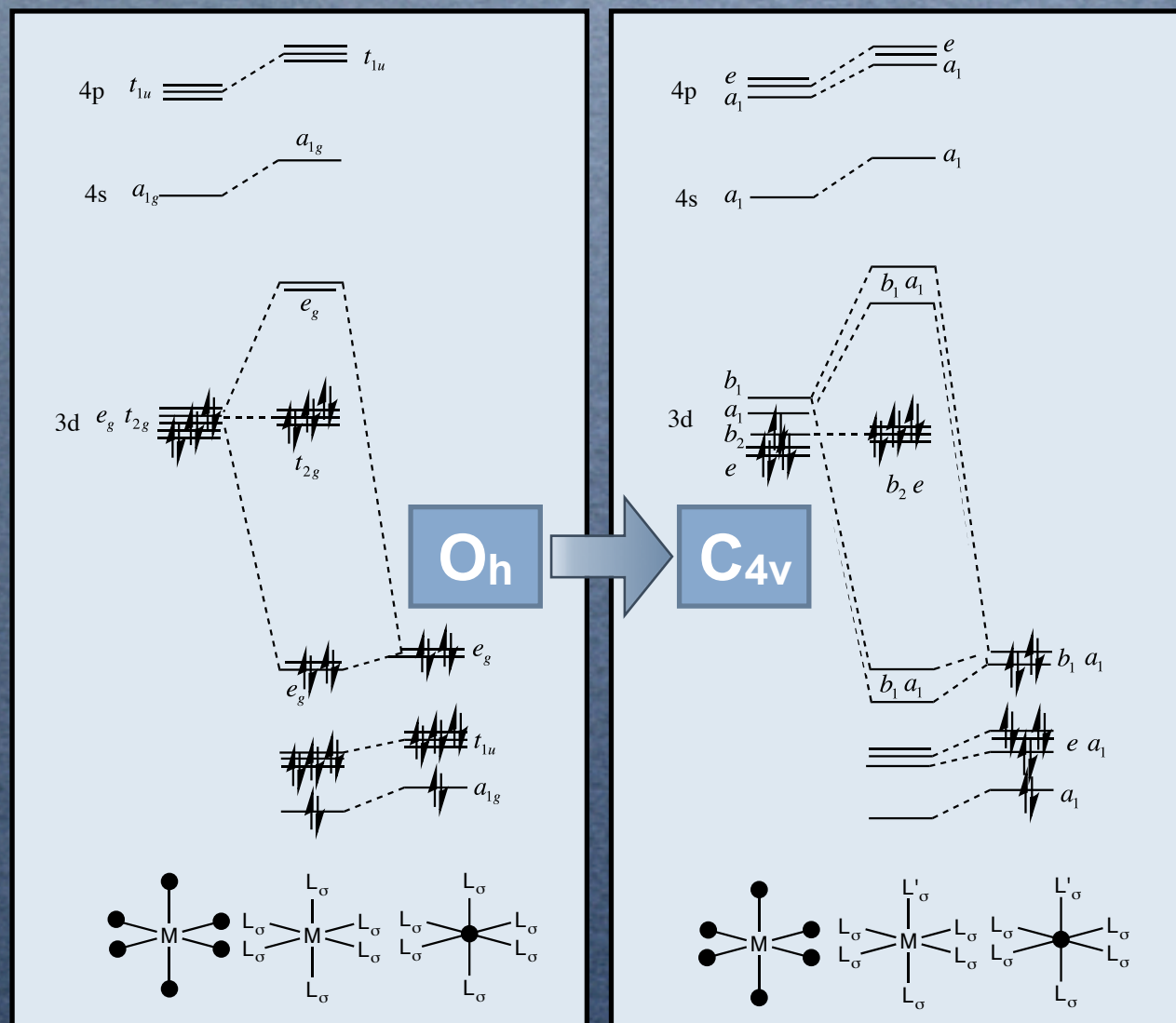


# Method: from last lecture

- start with the octahedral TM diagram
- for  $\sigma$ -framework
- work out the reduced symmetry labels
  - for the metal
  - for the ligands

we did this last lecture!

## Energy Diagrams





# Reduce Symmetry

## $C_{4v}$ diagram for $\sigma$ -ligands

colour the  $L'$   
orbitals in your  
notes BLUE

the remaining  
orbitals are the L  
ligands orbitals

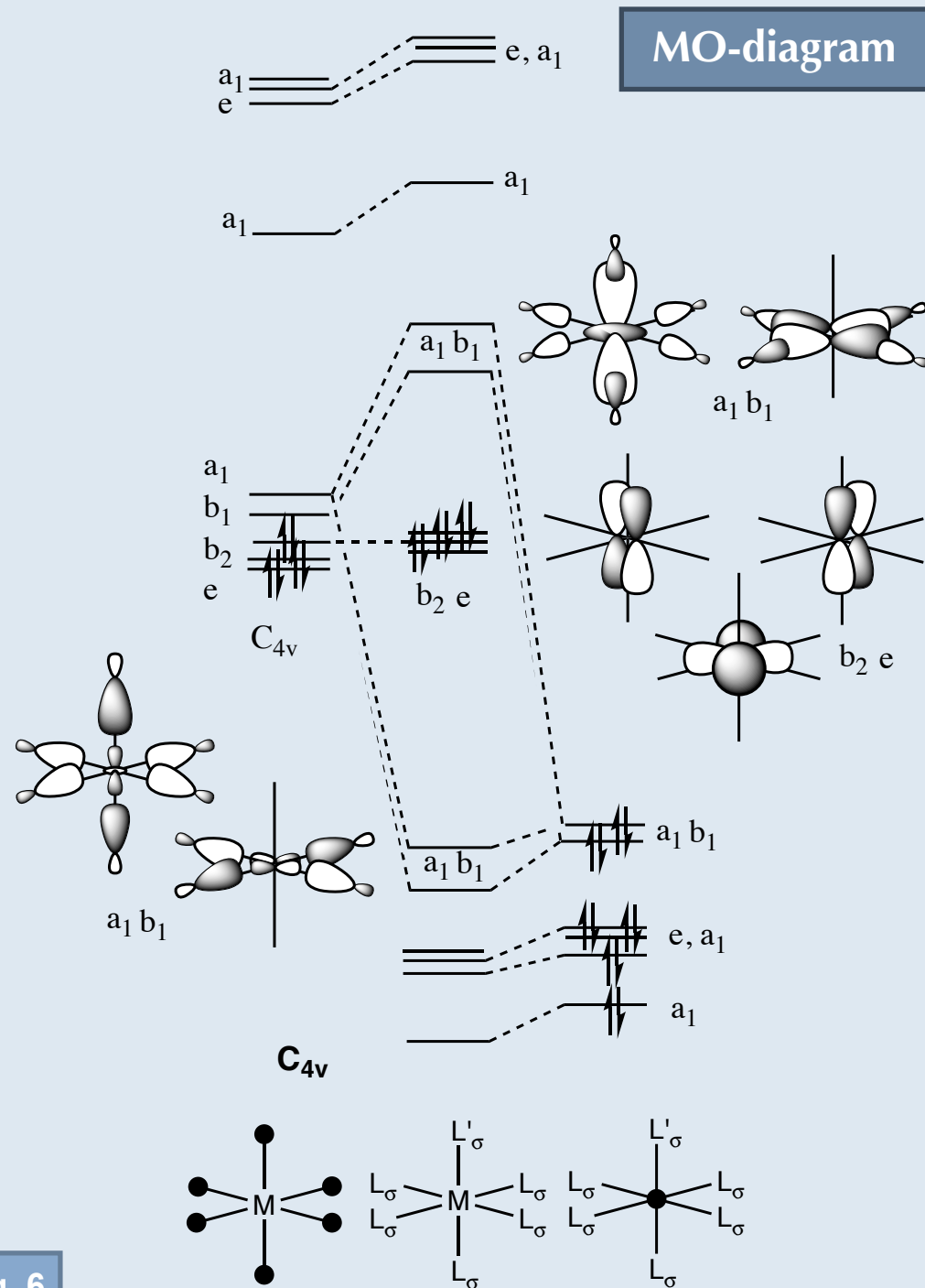


Fig. 6



# $\pi$ -Donor Ligand

● Cl is an example  $\pi$ -donor ligand

●  $p_z$  part  $\sigma$ -donor framework

- ◆ coloured blue on diagram
- ◆  $a_1$ -symmetry under  $C_{4v}$

colour the  $L'$   
 $\sigma$ -energy  
levels in your  
notes BLUE

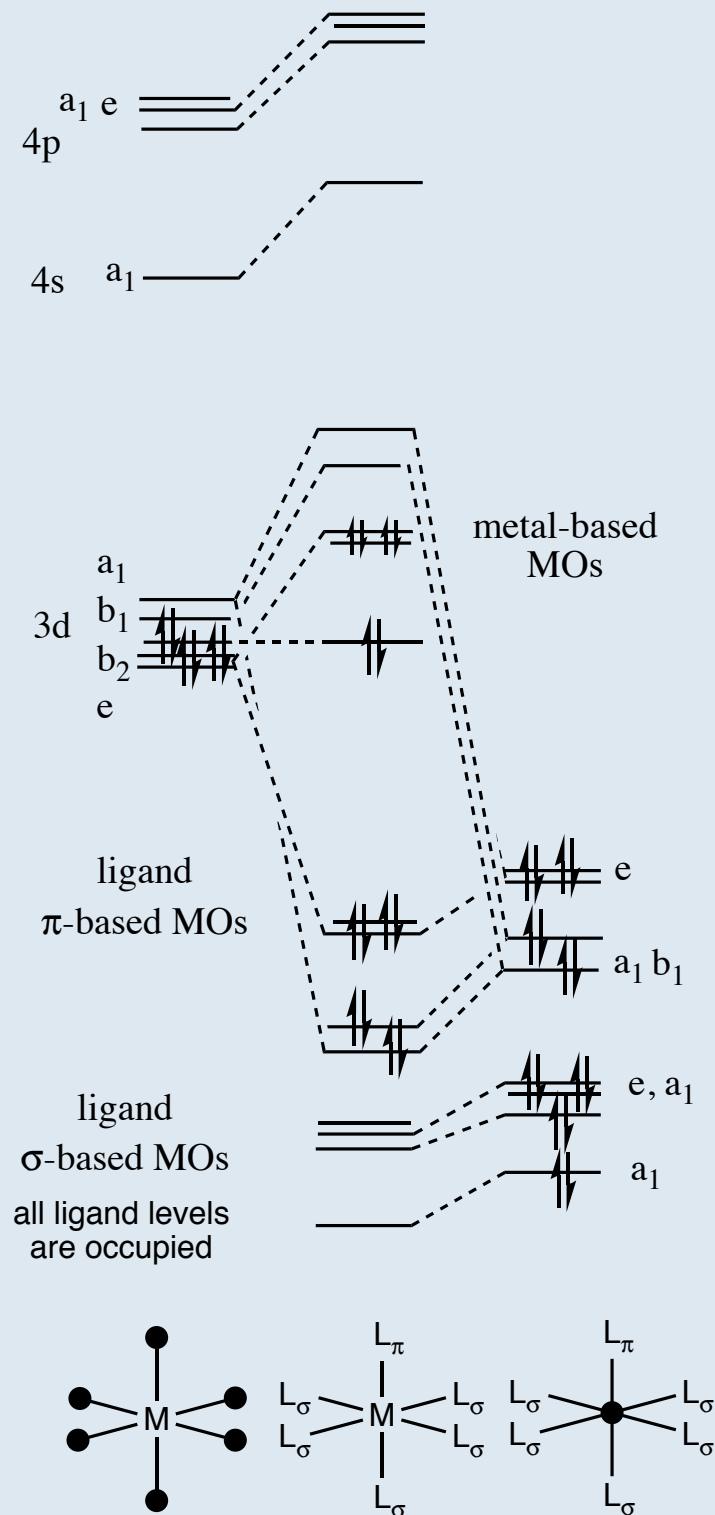
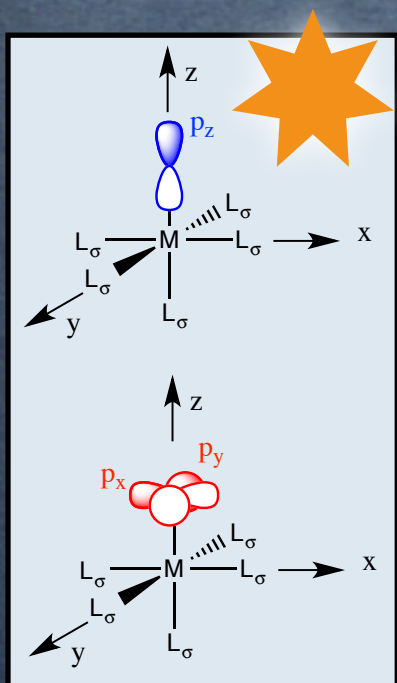


Fig. 7



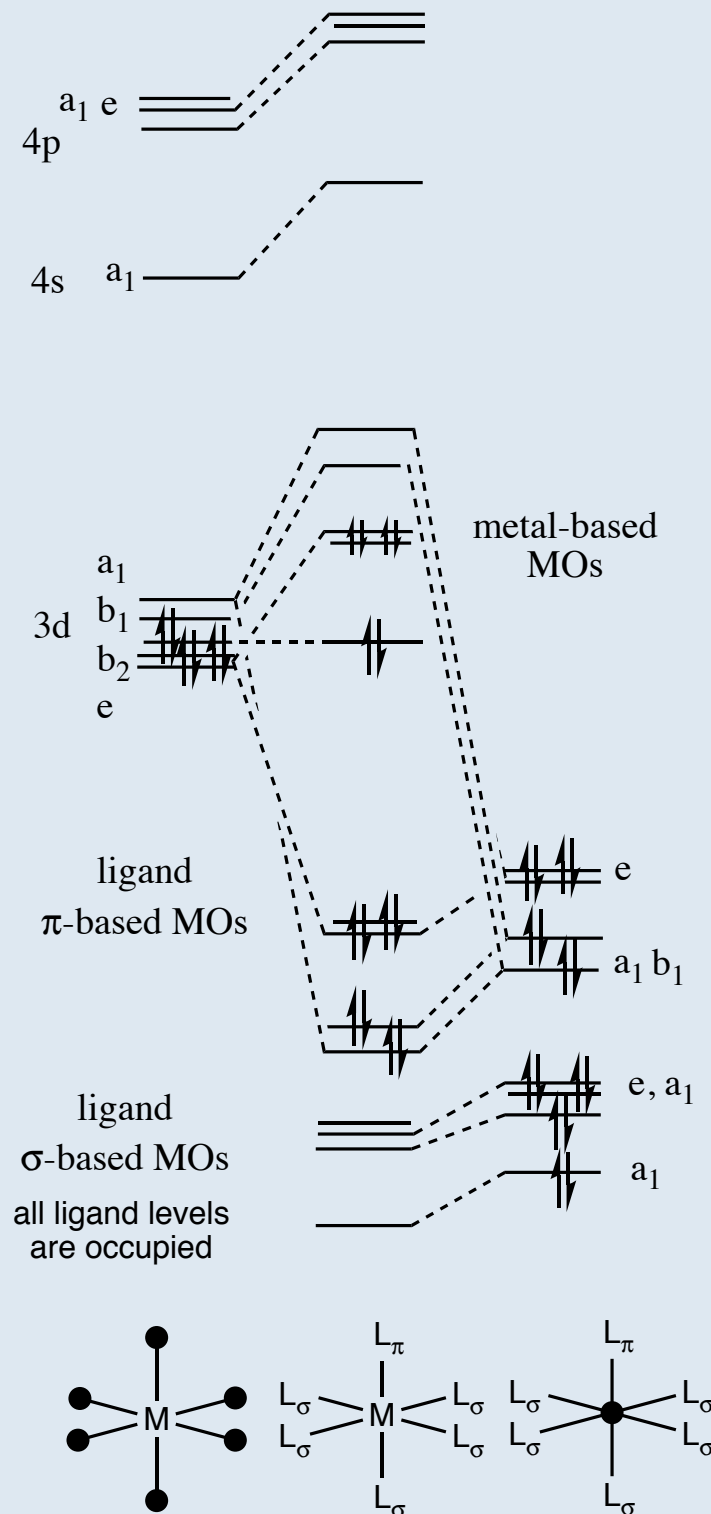
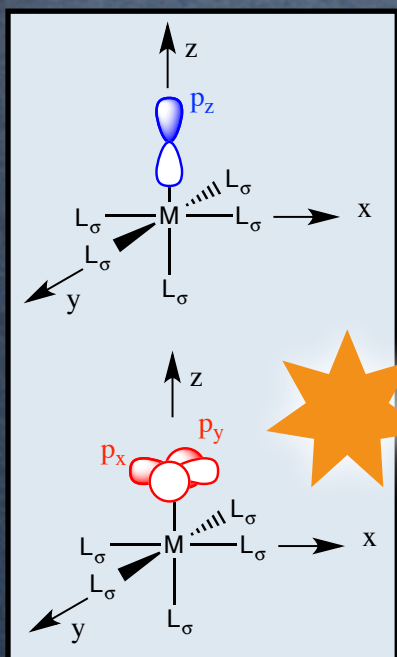
# $\pi$ -Donor Ligand

● Cl is an example  $\pi$ -donor ligand

●  $(p_x, p_y)$  degenerate  $\pi$ -donor FOs

- ◆ we simply add the extra  $\pi$ -donor FOs
- ◆ e-symmetry under  $C_{4v}$

colour the  $L'$   
 $\pi$ -energy  
levels in your  
notes RED





# $\pi$ -Donor Ligand

## where to position the FOs?

- ◆ Cl is electronegative FOs lie below TM orbitals
- ◆ pAOs non-bonding  $\rightarrow$  slightly above  $\sigma$ -donor FOs

## $(p_x, p_y, p_z)$ degenerate in Cl

- ◆  $p_z$  effects  $\sigma$ -donor framework slightly
- ◆  $p_x, p_y$  slightly above

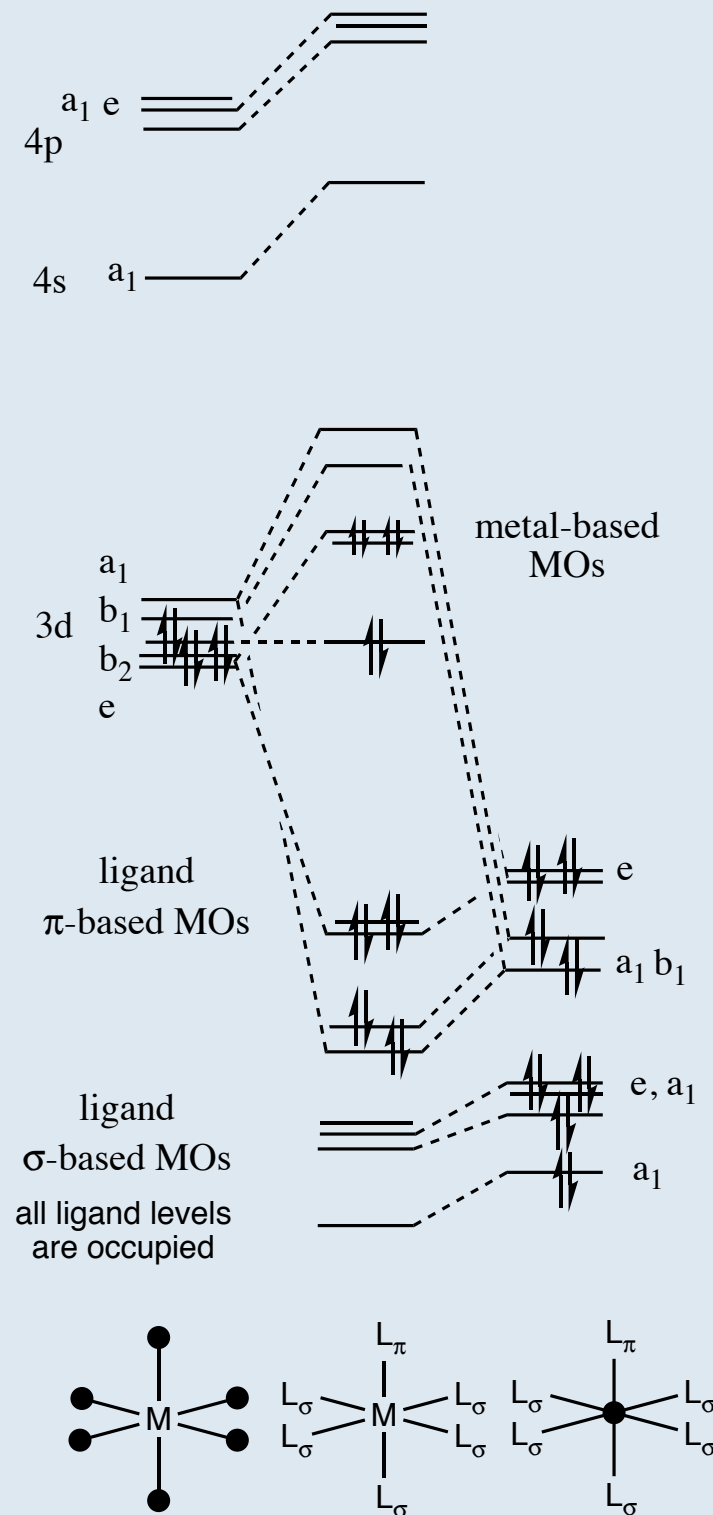


Fig. 7



# $\pi$ -Donor Ligand

## new $\pi$ -donor orbitals:

- ◆ form a bonding/antibonding pair

## interaction

- ◆  $\pi$ -orbitals higher energy
- ◆ smaller  $\Delta\epsilon$  leads to better interaction with metal dAOs
- ◆ BUT overlap d- $\pi$  is not as good as d- $\sigma$
- ◆ overall interaction is slightly less

colour the L'  
orbitals in  
your notes  
BLUE/RED

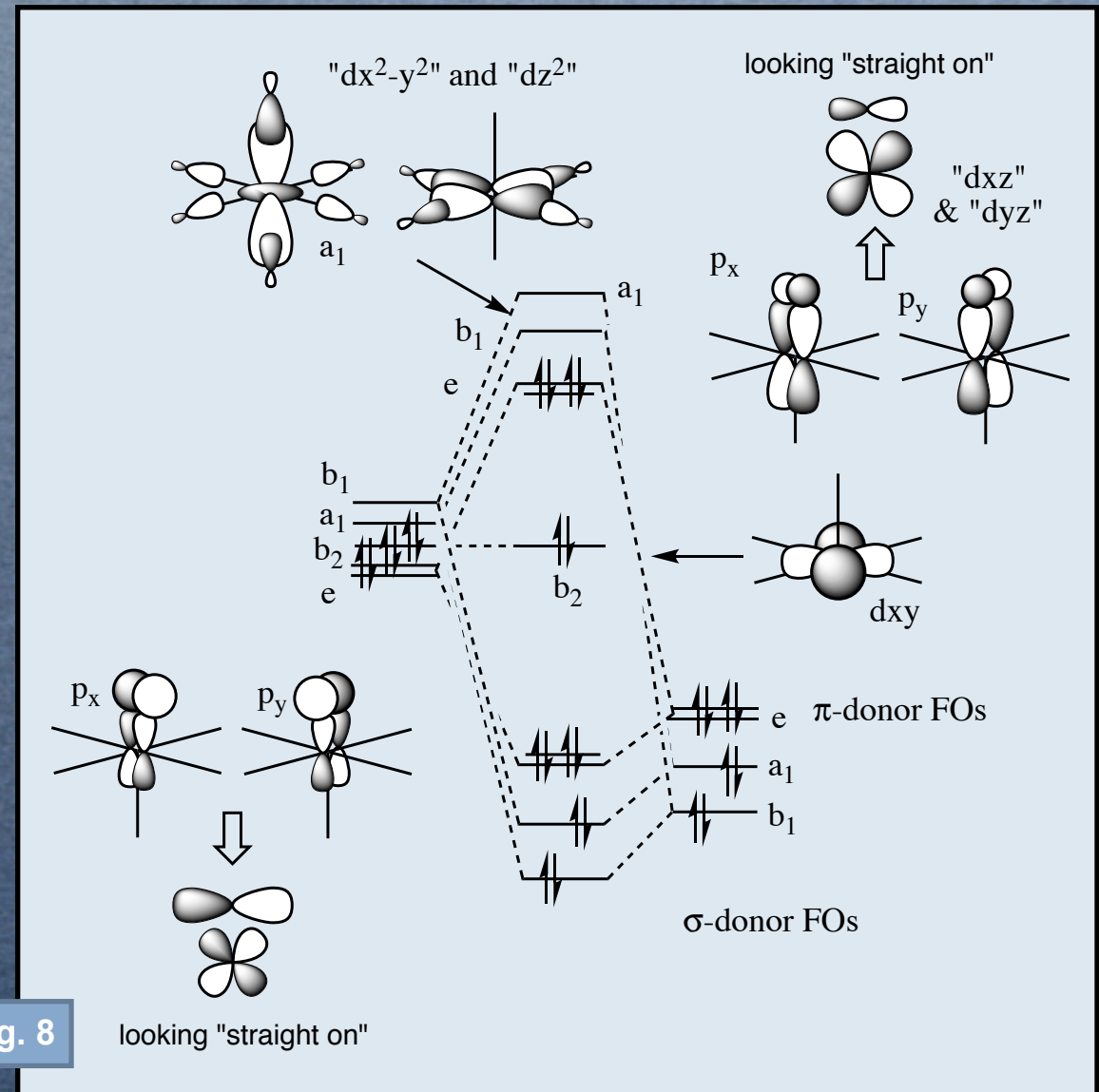


Fig. 8



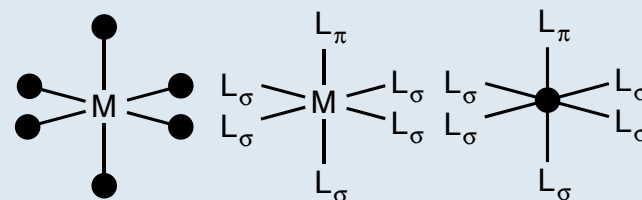
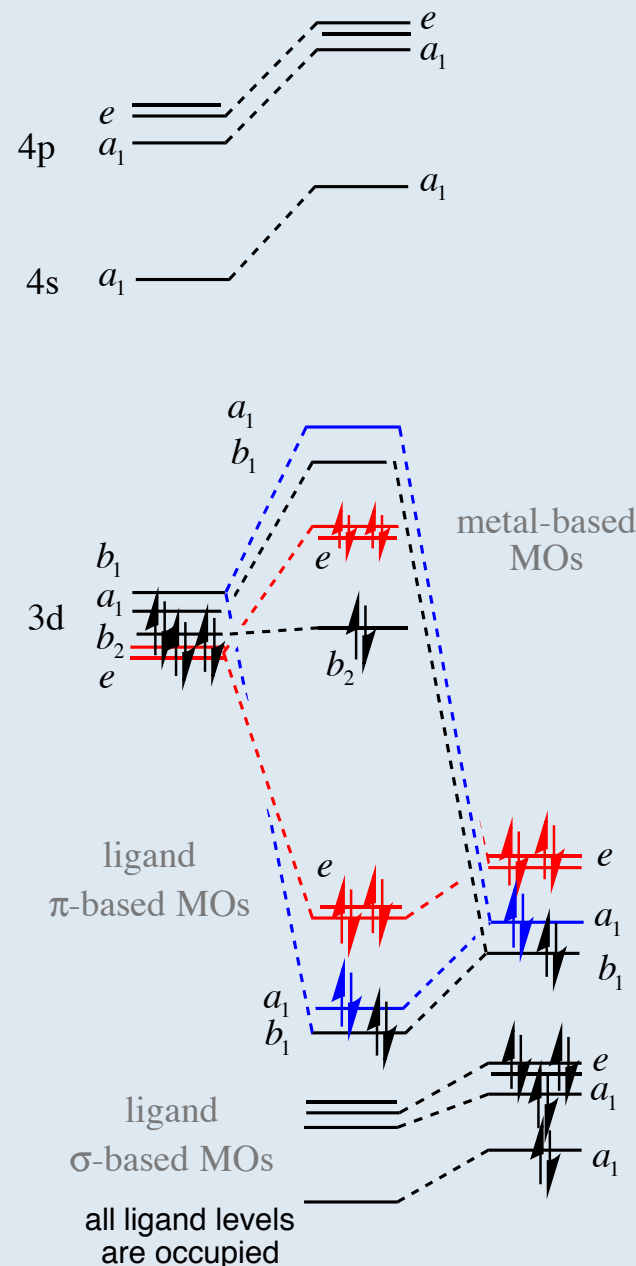
# $\pi$ -Donor Ligand

 I have simplified the diagram!

- ◆ dAOs are degenerate (slightly spread to show different symmetries)
- ◆ left off some of the interaction lines (high energy metal orbitals, low energy ligand orbitals)

answers to common questions

- ◆ left off some of the electrons! (occupied ligand levels)





# What about $\Delta_{\text{oct}}$ ?

## $\Delta_{\text{oct}}$

- ◆ less well defined!
- ◆ often refer to “old” symmetry labels
- ◆ e and b<sub>2</sub> are “t<sub>2g</sub>”
- ◆ a<sub>1</sub> and b<sub>1</sub> are “e<sub>g</sub>”
- ◆  $\Delta_{\text{oct}}$  of  $\sigma$ -donor ligands (green)
- ◆  $\Delta_{\text{oct}}$  of  $\pi$ -donor ligand (pink)

$\pi$ -donor ligand reduces  $\Delta_{\text{oct}}$  because of destabilisation of “e” orbitals due to an antibonding interaction with  $\pi$ -FOs

Important!

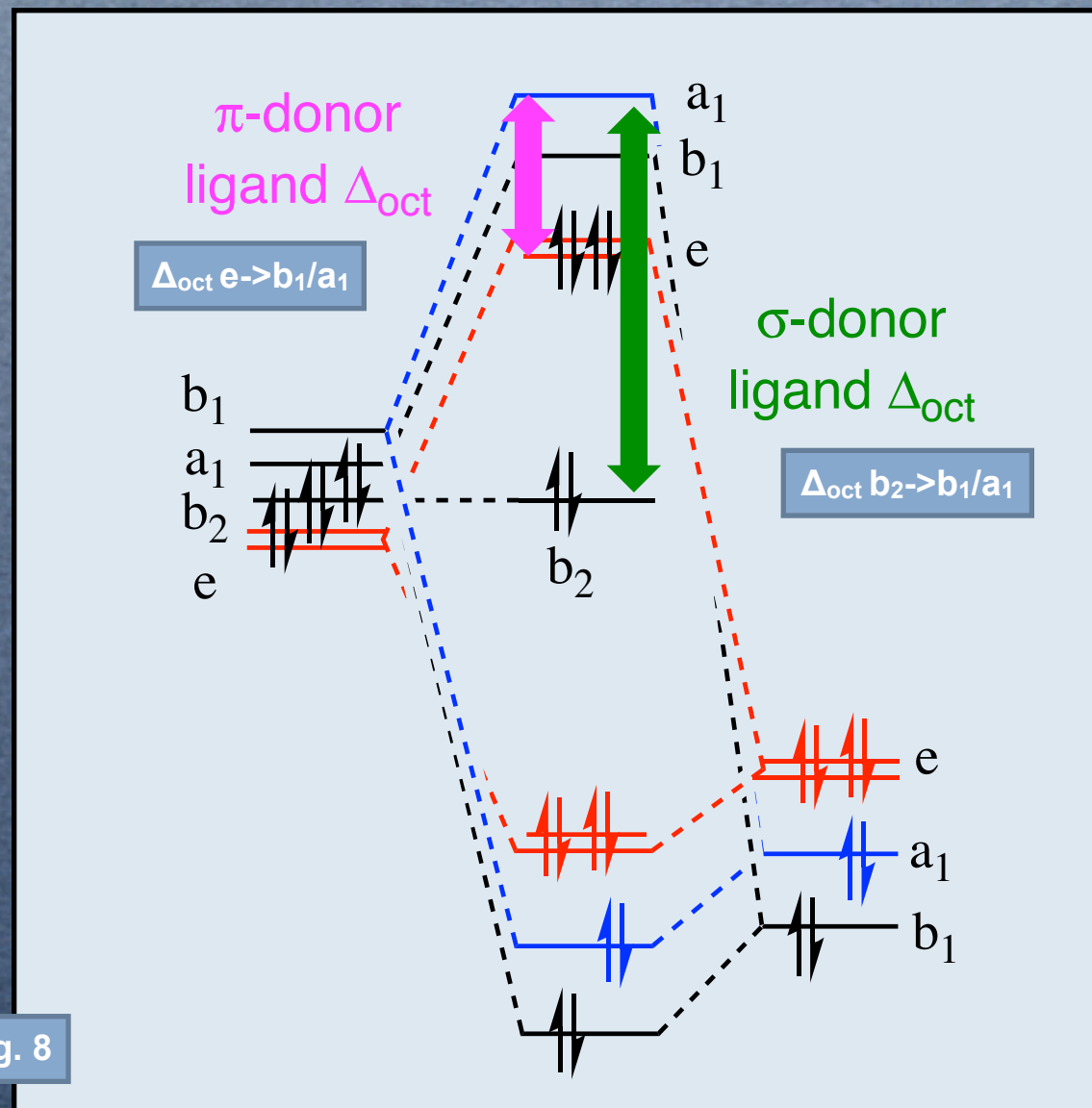


Fig. 8



# Spectrochemical Series

reminder

## Crystal field theory

- ◆ ligands modelled by six negative point charges
- ◆ equidistant along x, y and z axes
- ◆ repel electrons in the dAOs
- ◆ destabilisation of dAOs with lobes directed along the axes, ie  $d_{z^2}$   $d_{x^2-y^2}$
- ◆ stabilisation of the dAOs with lobes directed between the axes, ie  $d_{xy}$   $d_{xz}$   $d_{yz}$

◆  $\Delta_{\text{oct}}$  measures splitting of  $e_g$  and  $t_{2g}$

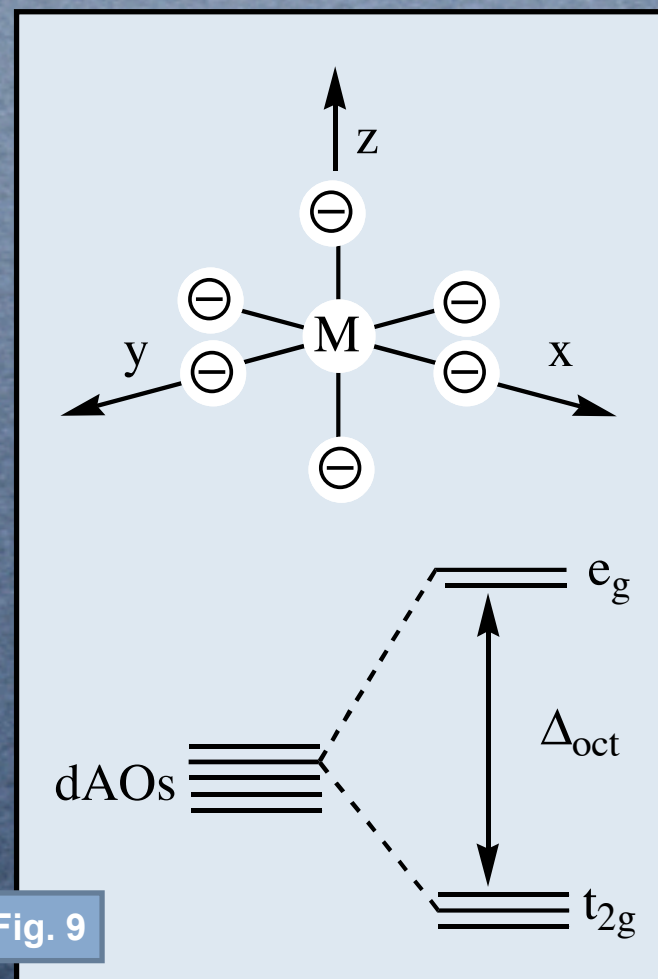


Fig. 9



# Spectrochemical Series

## $O^{2-}$

- ◆ has a large charge  $\Rightarrow$  should generate a large  $\Delta_{oct}$
- ◆ colour of emeralds and rubies is due to  $Cr^{3+}$  in the octahedral field of six  $O^{2-}$  in the solid state

Removed due to copyright

**Emerald:**  $Cr^{3+}$  in the octahedral sites of Beryl  
 $Be_3Al_2Si_6O_{18}$

Fig. 10

**Ruby:**  $Cr^{3+}$  replaces  $Al^{3+}$  in  $Al_2O_3$

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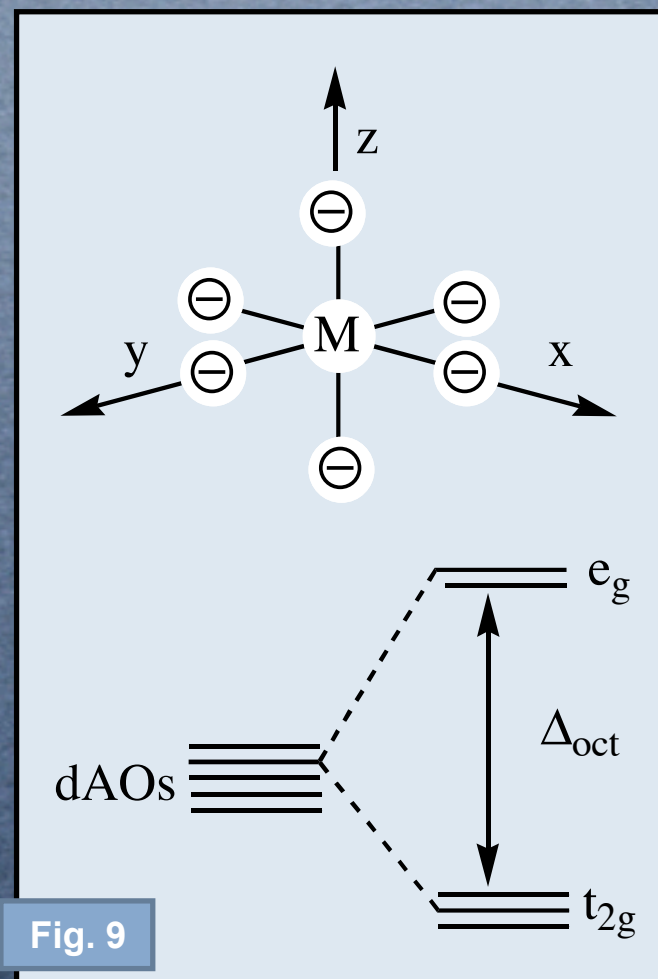
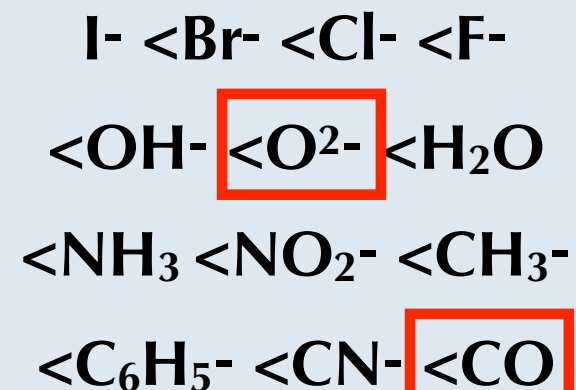


Fig. 9



# Spectrochemical Series

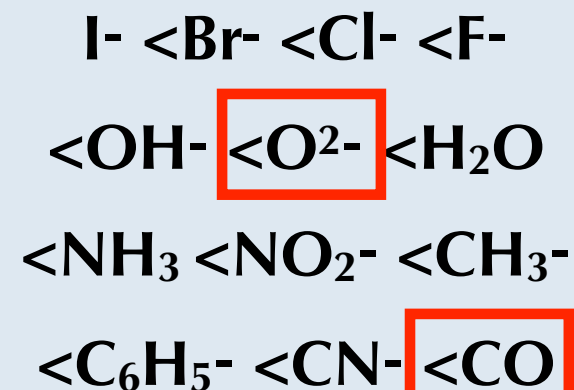
- experimentally measure  $\Delta_{\text{oct}}$
- order ligands from strong field (large  $\Delta_{\text{oct}}$ ) though to weak field (small  $\Delta_{\text{oct}}$ )
- CO has large  $\Delta_{\text{oct}}$  and  $\text{O}^{2-}$  has small  $\Delta_{\text{oct}}$





# Spectrochemical Series

- experimentally measure  $\Delta_{\text{oct}}$
- order ligands from strong field (large  $\Delta_{\text{oct}}$ ) though to weak field (small  $\Delta_{\text{oct}}$ )
- CO has large  $\Delta_{\text{oct}}$  and  $\text{O}^{2-}$  has small  $\Delta_{\text{oct}}$



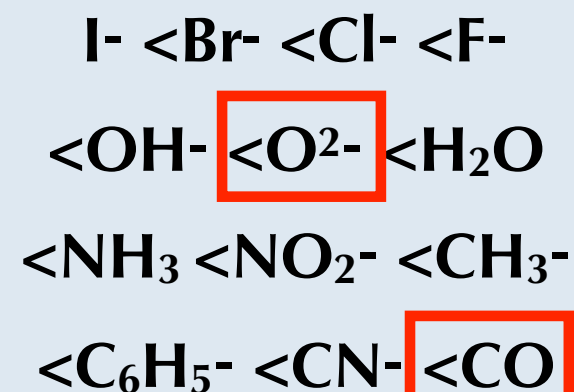
**BUT:**

- anions ( $\text{O}^{2-}$ ) should produce largest splitting (due to e-e repulsion)
- and neutral ligands like CO should have the smallest splitting!



# Spectrochemical Series

- experimentally measure  $\Delta_{\text{oct}}$
- order ligands from strong field (large  $\Delta_{\text{oct}}$ ) though to weak field (small  $\Delta_{\text{oct}}$ )
- CO has large  $\Delta_{\text{oct}}$  and  $\text{O}^{2-}$  has small  $\Delta_{\text{oct}}$



**BUT:**

- anions ( $\text{O}^{2-}$ ) should produce largest splitting (due to e-e repulsion)
- and neutral ligands like CO should have the smallest splitting!

There is a miss-match between experiment and crystal field theory!

**USE MO theory**



# $\pi$ -Acceptor Ligand

## CO common TM ligand

- ◆ you will study many CO complexes in your “TM and Organometallic Chemistry” course

## ligand orbitals come from the MO diagram of CO

- ◆ has  $\sigma$ -donor orbitals (blue)
- ◆ has  $\pi$ -bonding orbitals (black)
- ◆ has  $\pi$ -antibonding orbitals (red)

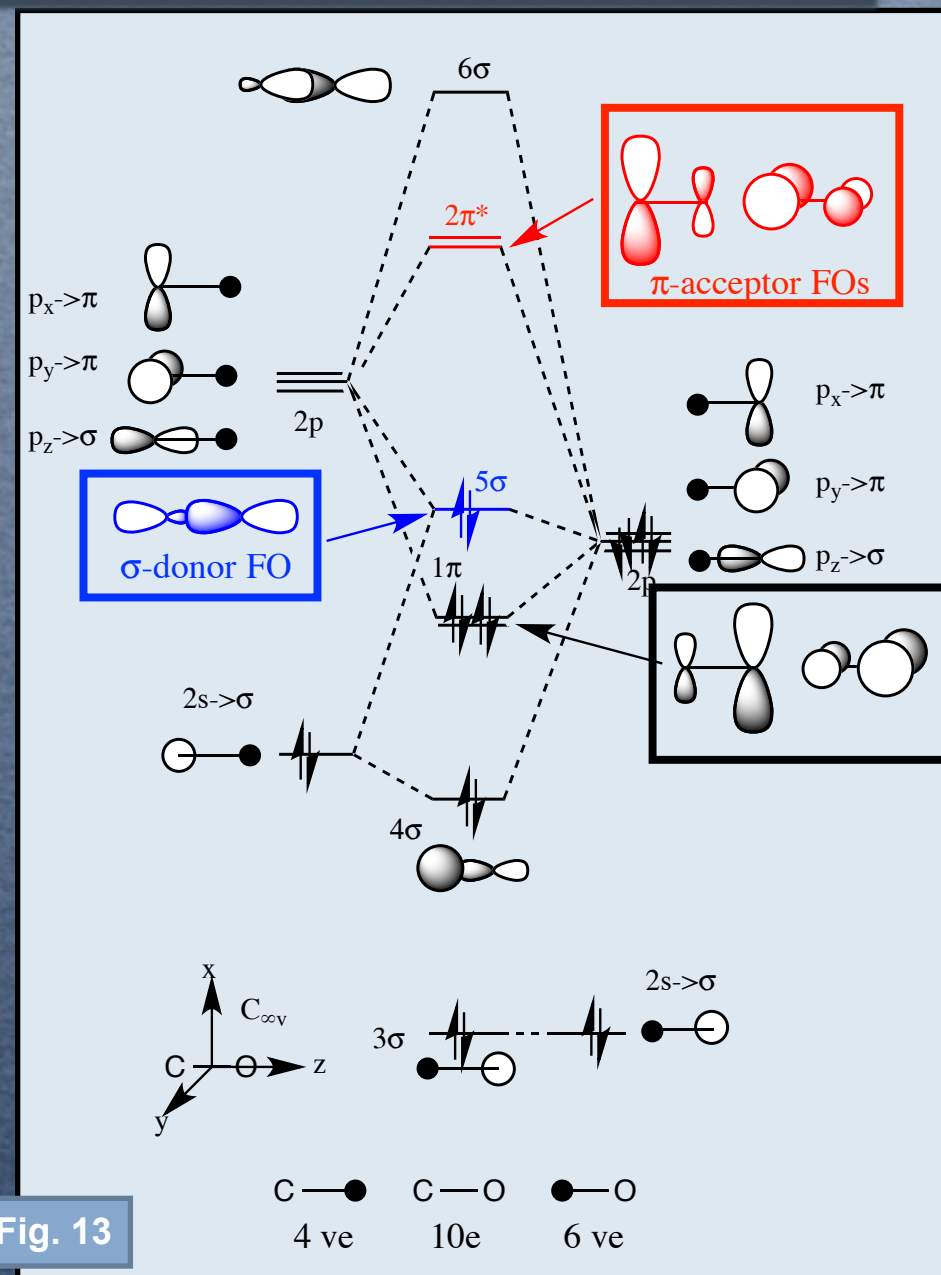
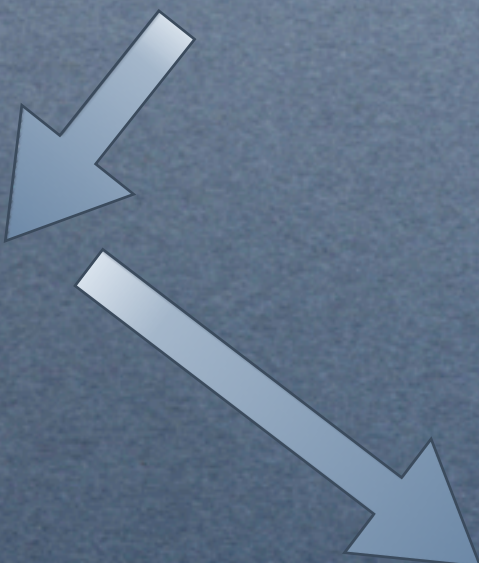


Fig. 13



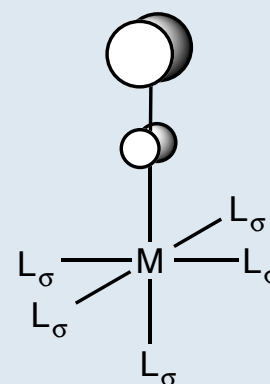
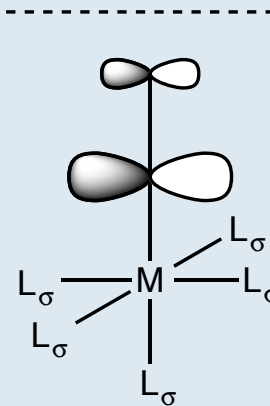
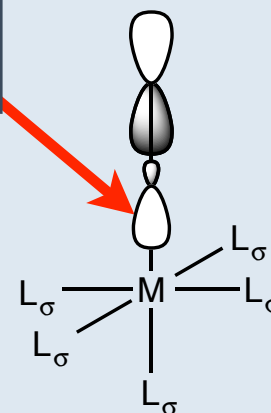
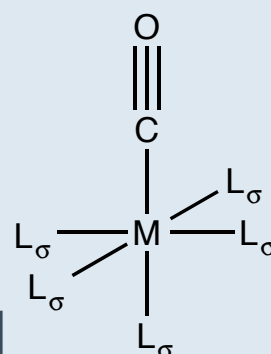
# $\pi$ -Acceptor Ligand

- orbitals from MO diagram of CO
- $\sigma$ -donor orbitals

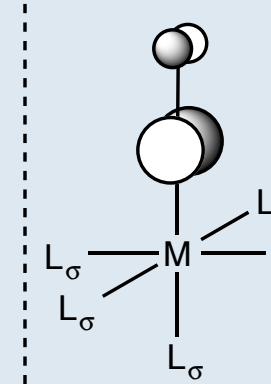
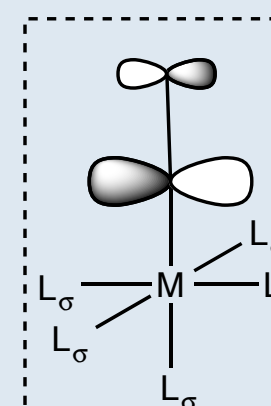


contribute to  
 $\sigma$ -frame work

$\sigma$ -bonding  
orbitals



degenerate set



degenerate set

Fig. 14(a)



# $\pi$ -Acceptor Ligands

- orbitals from MO diagram of CO
- has  $\sigma$ -donor orbitals
- has  $\pi$ -bonding orbitals
- has  $\pi$ -antibonding orbitals

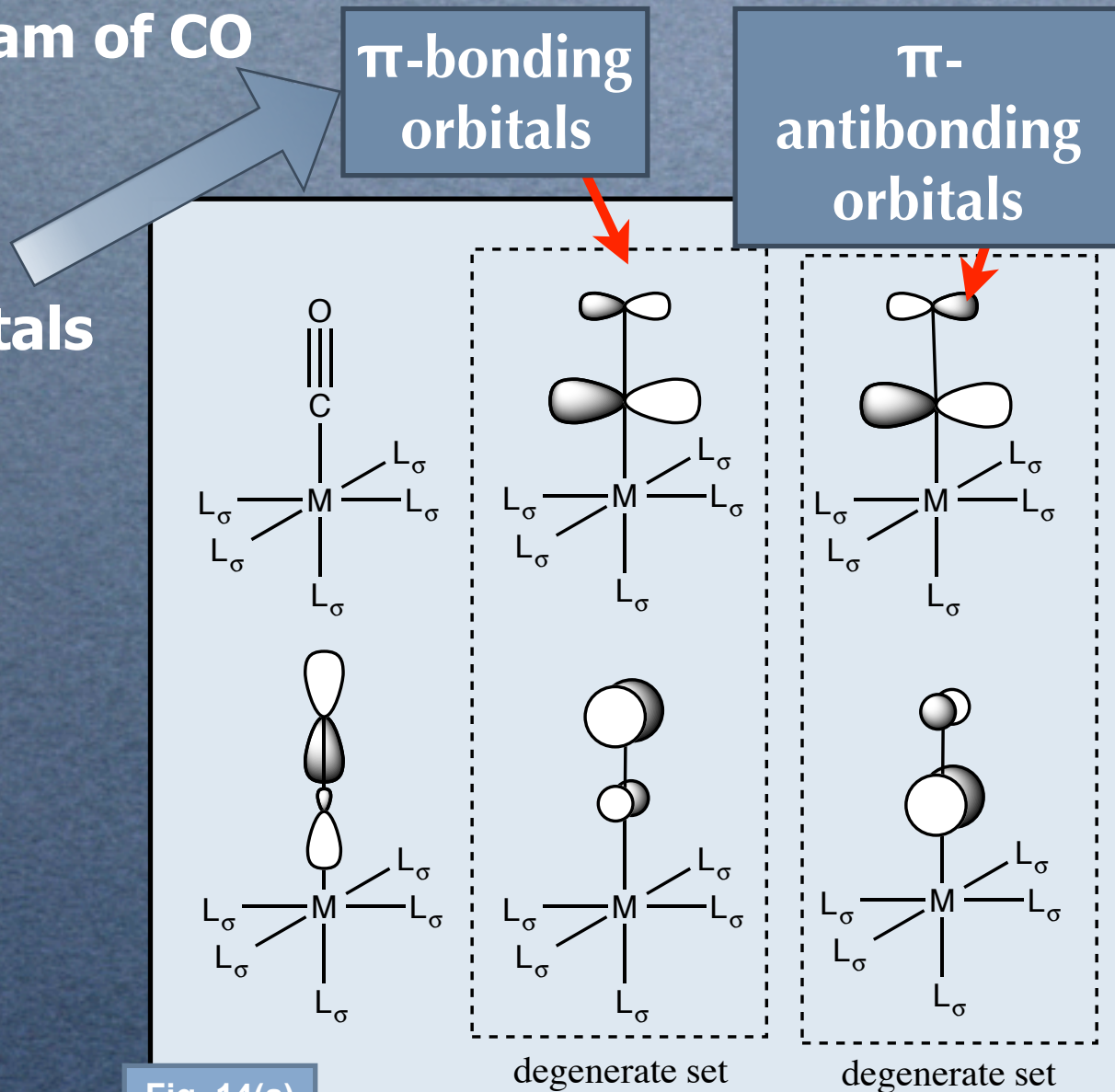


Fig. 14(a)



# Symmetry Labels

## $\pi$ -orbitals

- ◆ are the  $p_x$  and  $p_y$  orbitals
- ◆ have the same symmetry as the axes
- ◆ e symmetry label

## $\pi^*$ -orbitals

- ◆ more difficult to determine
- ◆ find the representation of the orbitals
- ◆ use a matrix for the degenerate components
- ◆ has e symmetry

$C_{4v}$	E	$2C_4$	$C_2$	$2\sigma_v$	$2\sigma_d$
$\Gamma(p_{\pi}^*)$	2	0	-2	0	0

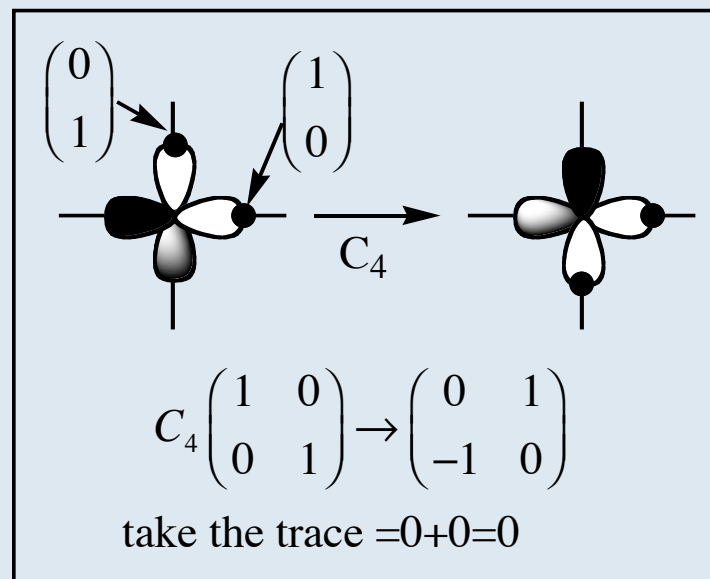
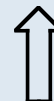


Fig. 14(b)

# Energy Diagram

● basic  $C_{4v}$  diagram for  $\sigma$ -ligands

● add  $\pi$ -FOs (blue)

- ◆  $\pi$ -orbitals have poor interaction with dAOs
- ◆ remain non-bonding

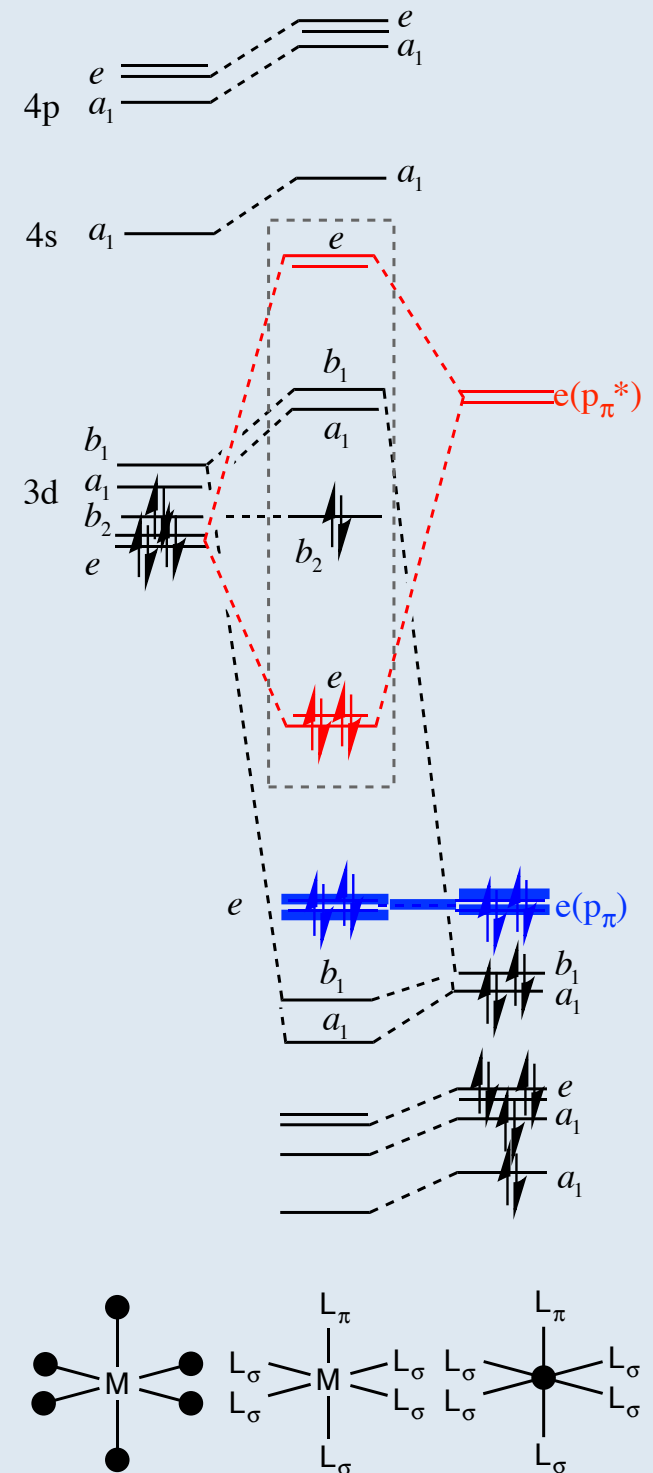
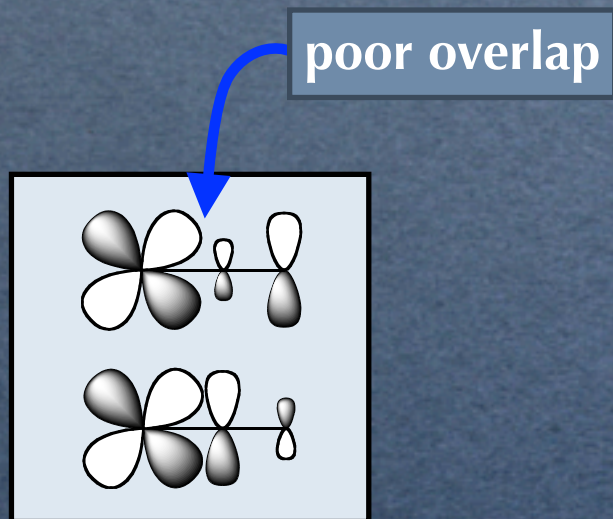


Fig. 15



# Energy Diagram

## basic $C_{4v}$ diagram for $\sigma$ -ligands

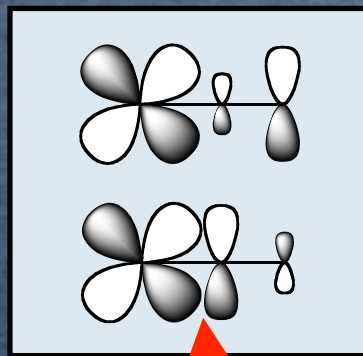
## add $\pi$ -FOs (blue)

- ◆  $\pi$ -orbitals have poor interaction with dAOs
- ◆ remain non-bonding

## add $\pi^*$ -FOs (red)

- ◆  $\pi$ -acceptor FOs lie above the dAOs
- ◆ strongly interact with e-dAOs forming a bonding/antibonding pair

- ⇒ close in energy
- ⇒ good overlap
- ⇒ still  $\pi$ -type interaction
- ⇒ strong splitting



good overlap

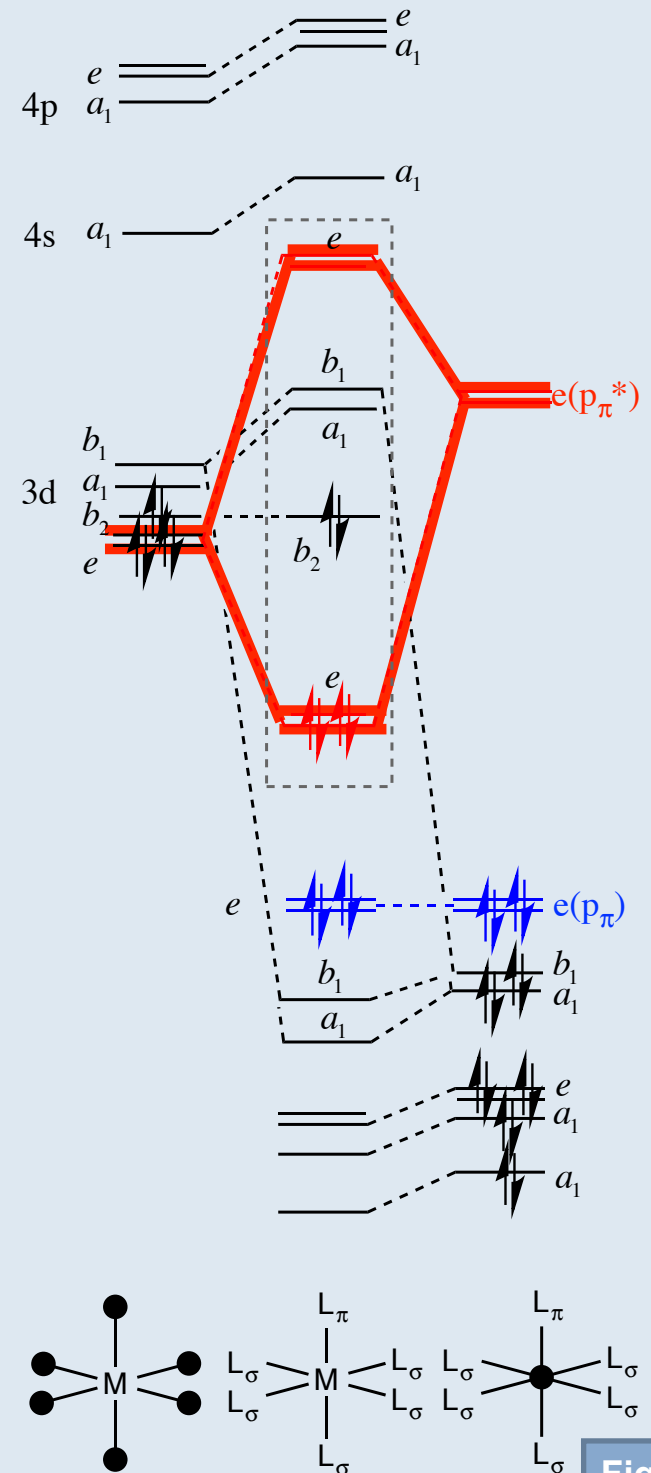


Fig. 15

# The Important MOs

- focus in on  $\pi^*$ -dAO interactions
- dAO dominated MO is now the lower bonding MO

Important!

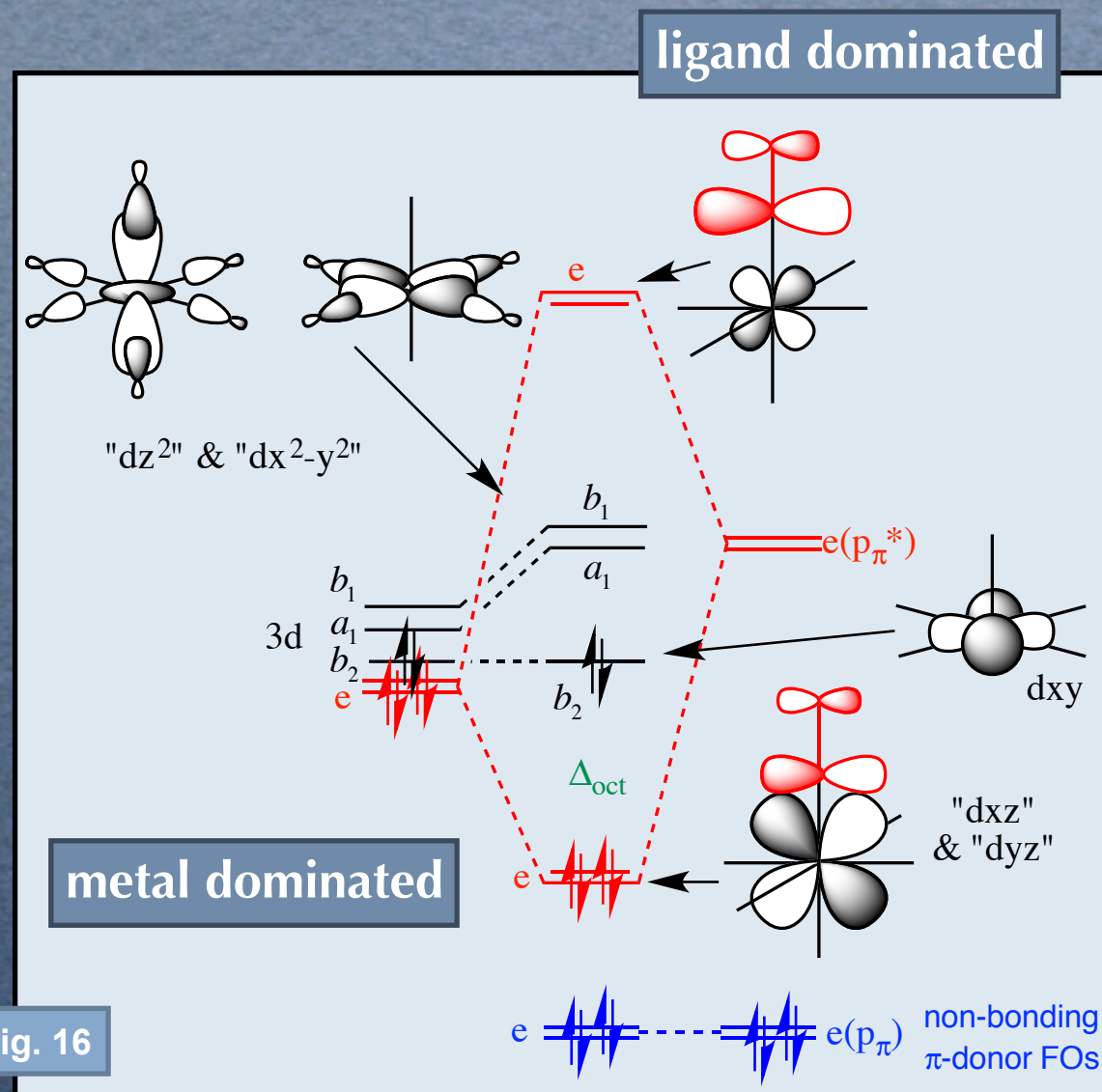


Fig. 16



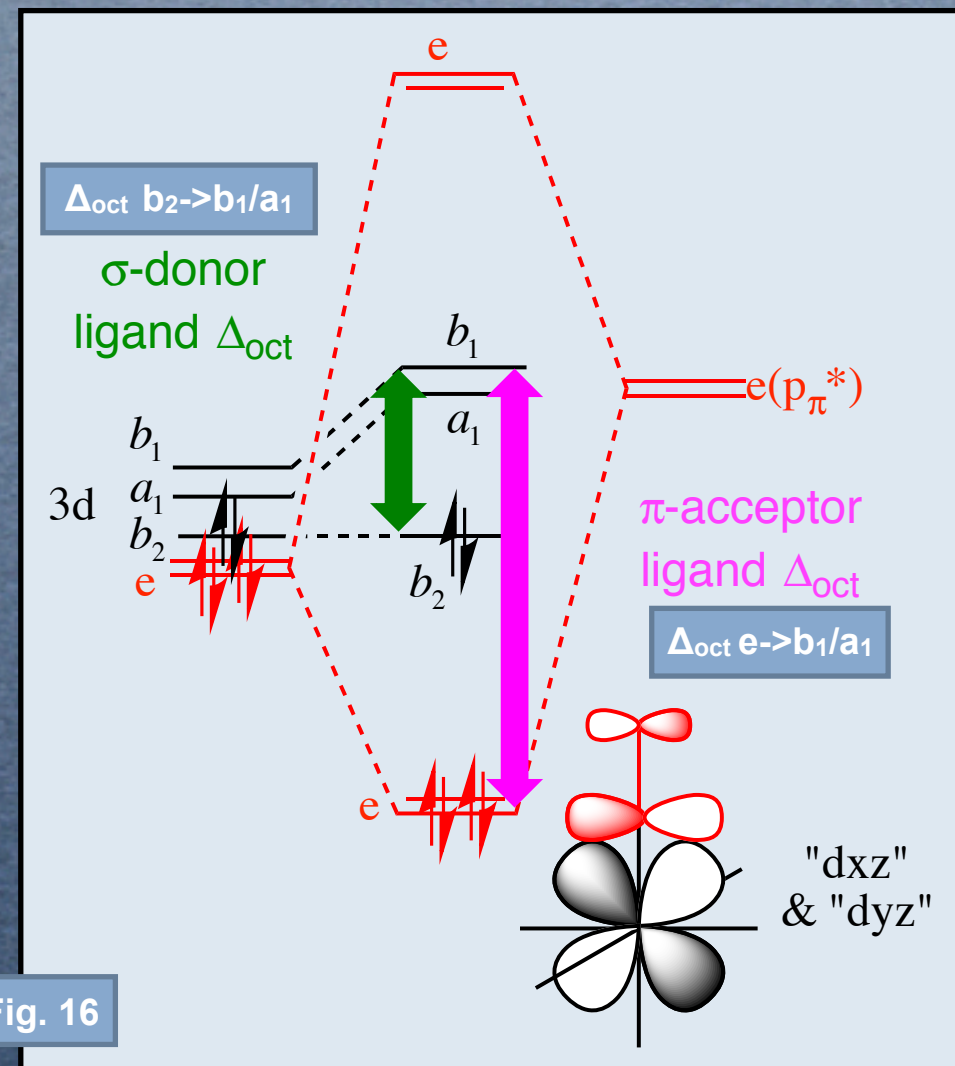
# What about $\Delta_{\text{oct}}$ ?

## $\Delta_{\text{oct}}$ $\pi$ -acceptor ligand

- ◆ less well defined!
- ◆  $\Delta_{\text{oct}}$  of  $\sigma$ -donor ligands (green)
- ◆  $\Delta_{\text{oct}}$  of  $\pi$ -acceptor ligand (pink)

$\pi$ -acceptor ligand increases  $\Delta_{\text{oct}}$  because of stabilisation of e MOs due to a bonding interaction with  $\pi^*$ -FOs

Important!



# Summary for $\Delta_{\text{oct}}$

$\sigma$ -donor ligands



$\pi$ -donor ligands

$\pi^*$ -acceptor ligands

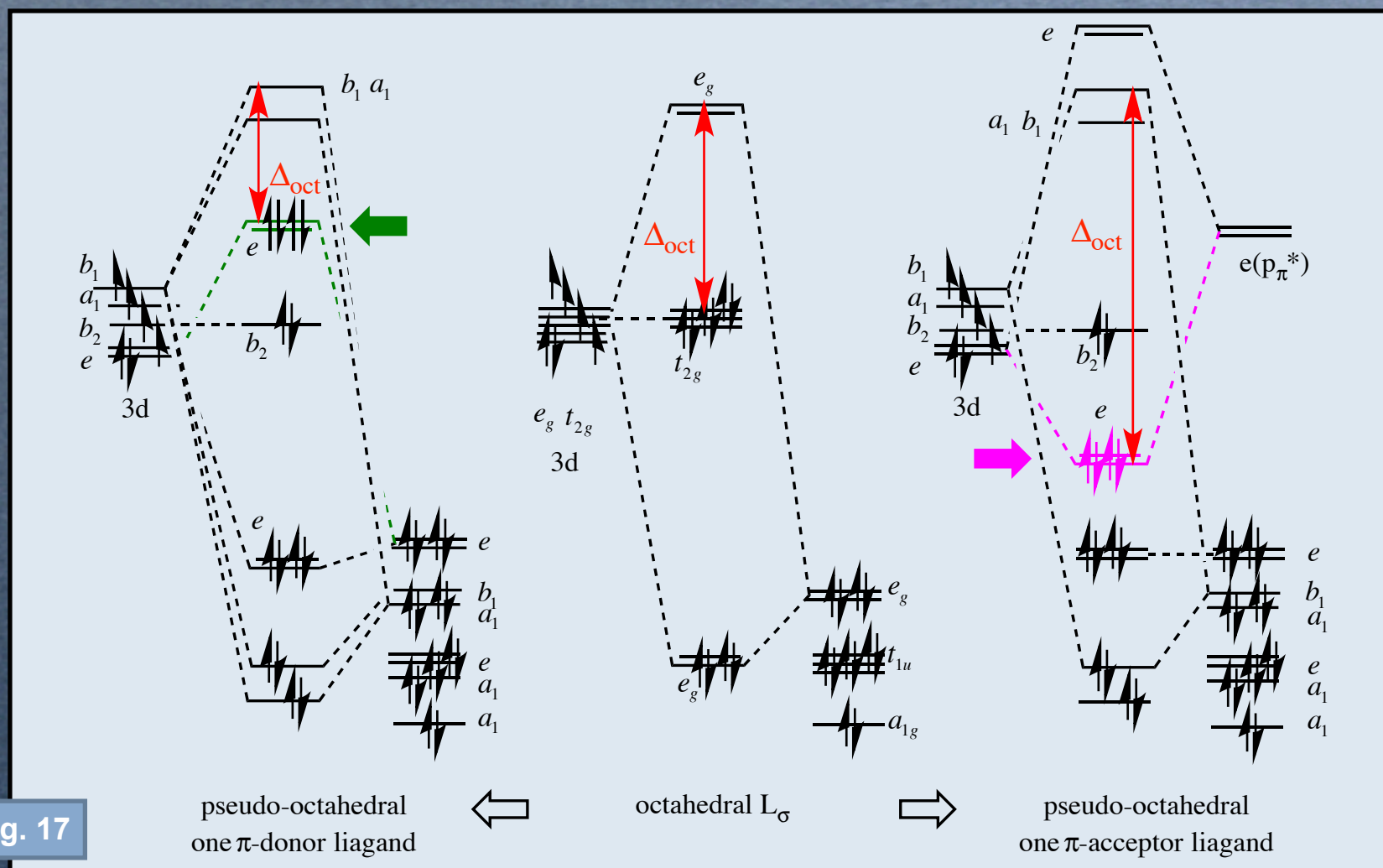


Fig. 17



# Summary for $\Delta_{\text{oct}}$

$\sigma$ -donor ligands



$\pi$ -donor ligands

$\pi^*$ -acceptor ligands

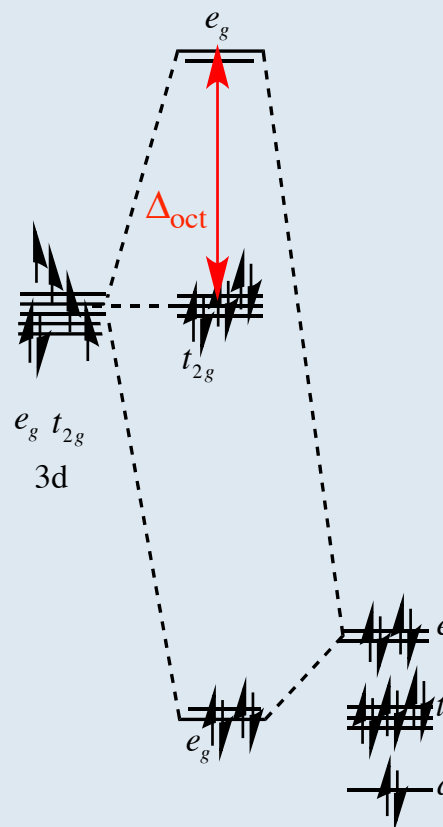


Fig. 17

$\sigma$ -donor  
"reference"

# Summary for $\Delta_{\text{oct}}$

$\sigma$ -donor ligands

$\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{NO}_3^- < \text{F}^- < \text{OH}^- < \text{O}^{2-} < \text{H}_2\text{O} < \text{NH}_3 < \text{en} < \text{NO}_2^- < \text{CH}_3^- < \text{C}_6\text{H}_5^- < \text{PPh}_3 < \text{CN}^- < \text{CO}$

$\pi$ -donor ligands

$\pi^*$ -acceptor ligands

$\pi$ -donor  
dAO dominate  
antibonding e MO  
up  $\uparrow\uparrow\uparrow$   
 $\Delta_{\text{oct}}$  smaller

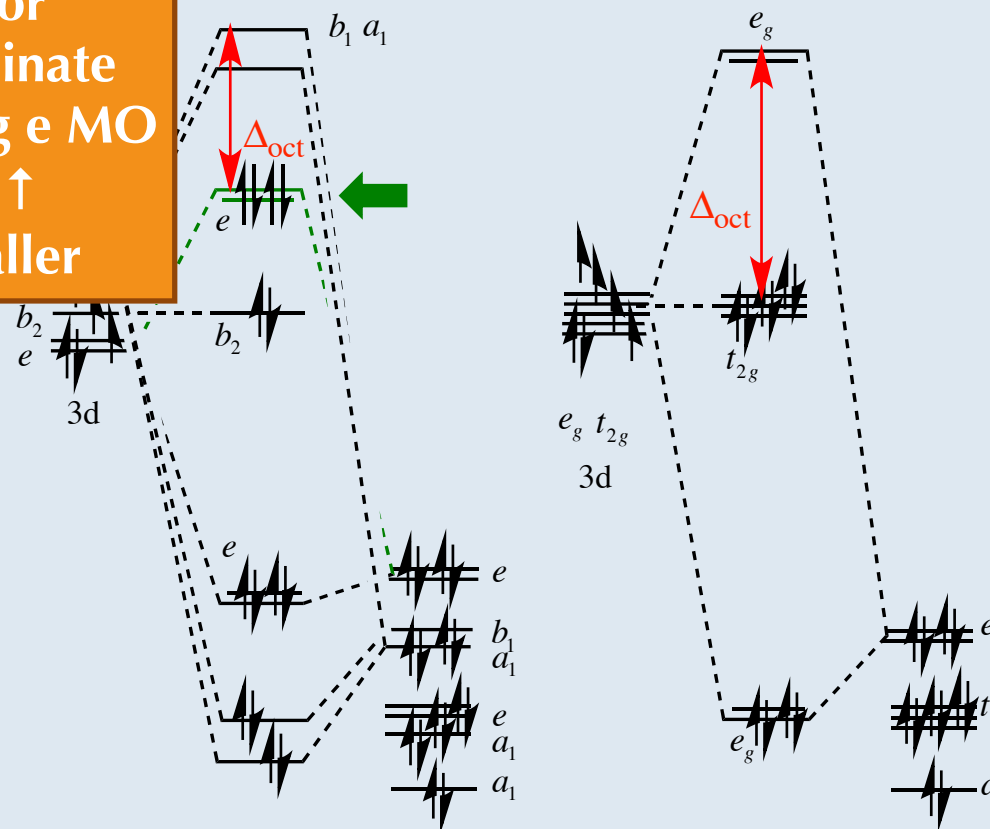


Fig. 17

pseudo-octahedral  
one  $\pi$ -donor ligand



# Summary for $\Delta_{\text{oct}}$

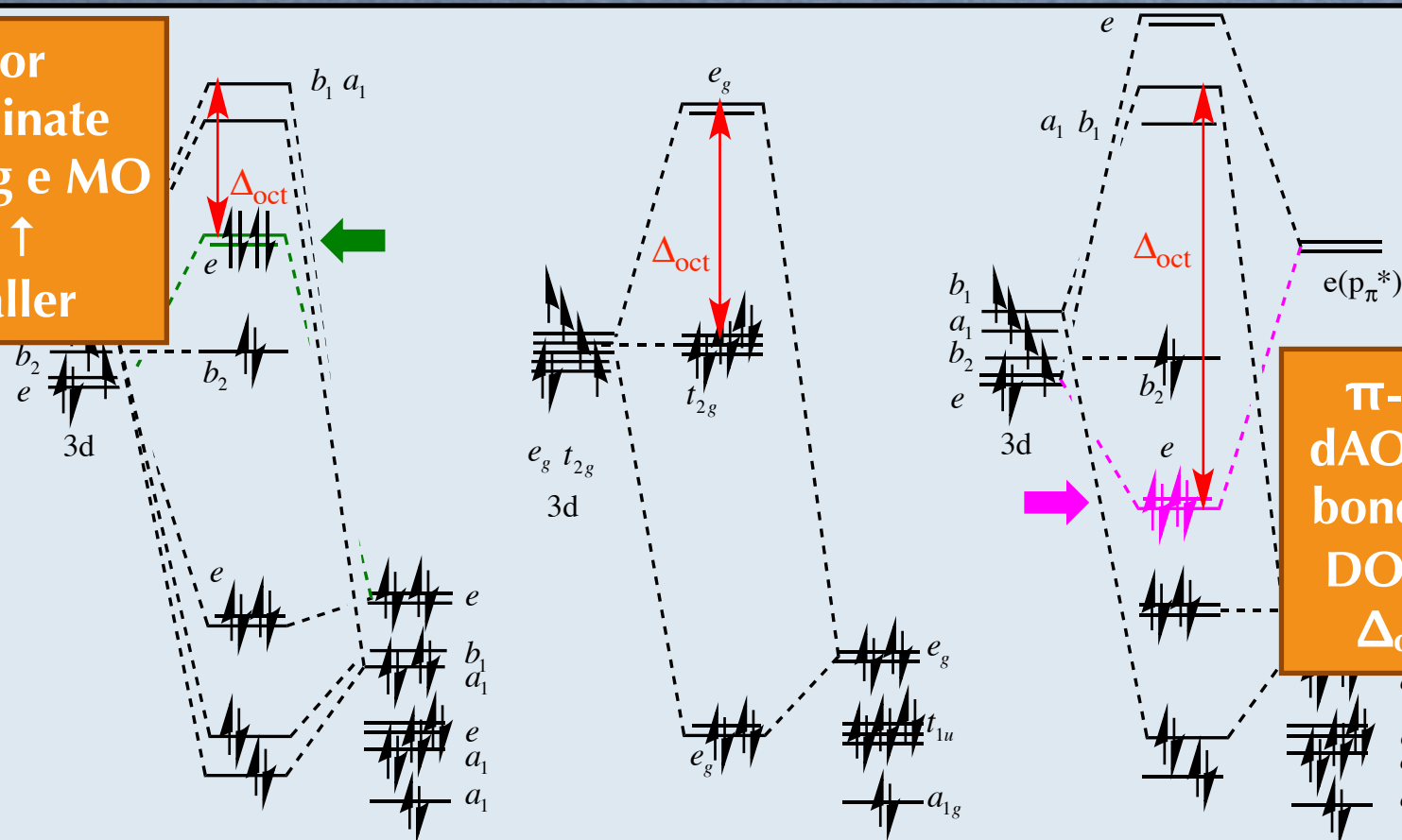
$\sigma$ -donor ligands

$\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{NO}_3^- < \text{F}^- < \text{OH}^- < \text{O}^{2-} < \text{H}_2\text{O} < \text{NH}_3 < \text{en} < \text{NO}_2^- < \text{CH}_3^- < \text{C}_6\text{H}_5^- < \text{PPh}_3 < \text{CN}^- < \text{CO}$

$\pi$ -donor ligands

$\pi^*$ -acceptor ligands

$\pi$ -donor  
dAO dominate  
antibonding e MO  
up  $\uparrow\uparrow\uparrow$   
 $\Delta_{\text{oct}}$  smaller



$\pi$ -acceptor  
dAO dominate  
bonding e MO  
DOWN  $\downarrow\downarrow\downarrow$   
 $\Delta_{\text{oct}}$  larger

Fig. 17

pseudo-octahedral  
one  $\pi$ -donor ligand

octahedral  $L_\sigma$

pseudo-octahedral  
one  $\pi$ -acceptor ligand

# Key Points

- be able to draw energy level diagrams for octahedral and square planar complexes with  $\pi$ -donor and  $\pi$ -acceptor ligands
- be able to draw and describe the important MOs
- be able to discuss key features of these diagrams
- be able to describe crystal field theory and discuss the empirical spectrochemical series and be able to explain the contradiction between the two
- be able to discuss key properties that impact on or affect  $\Delta_{\text{oct}}$  (such as energy alignment, orbital overlap, symmetry and  $\pi$ -ligands)
- be able to compare and contrast the size of  $\Delta_{\text{oct}}$  for different types of ligands and relate this information back to the spectrochemical series



# Finally

<http://www.huntresearchgroup.org.uk/>

## See my web-site

- ♦ notes AND slides
- ♦ link to panopto when it becomes available
- ♦ optional background support for beginners
- ♦ optional material to take you a little further
- ♦ links to interesting people and web-sites
- ♦ links to relevant research papers on MOs
- ♦ model answers!!

## Hunt Research Group

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### Hunt Research Group

The Hunt Research Group is a theoretical and computational chemistry group which carries out theoretical development and computational modeling.

Our research is focused towards understanding the chemistry and physics associated with solvents and solvation, particularly as this applies to **ionic-liquids** and **deep eutectic solvents**.

We study the making and breaking of molecules. This includes **catalytic mechanisms** (for group II and frustrated Lewis acid-base pairs) and chemical **decomposition** (for green fuels, bio-fuels and ionic-liquids).

Overarching all of these areas is a specialisation in **hydrogen-bonding**, acid-base interactions and an expertise in the **MO theory** of bonding. We have developed the Effective MO Method for interrogating the electronic structure of liquids and study **charge partitioning** and interactions within molecules.



**5th October 2019**

Imperial Chemistry

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### July 2019

**Molecular orbital of the month** This is a MO from  $\text{SnOTf}_4$ . OTf is a triflate anion  $[\text{SO}_3\text{CF}_3]^-$  which coordinates to the central tin (Sn) metal through oxygen atoms.  $\text{SnOTf}_4$  is a novel catalyst for activating methane and thus producing useful molecules like methanol. Using methane from biomass or natural gas sources as a feedstock to build more complex molecules is a promising area. We also have the advantage of replacing transition metals with less expensive and more abundant main group metals. This new catalyst is unusual in that the ligand has a larger effect on reactivity than the central metal.

