

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 π -donor ligand**
- **the spectrochemical series and crystal field theory**
- **MO theory for a single π^* -acceptor ligand**
- **Summary of Δ_{oct} for different ligand types**

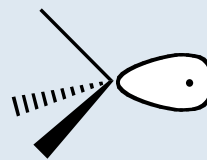
Revision: Ligands

3 key types of ligand

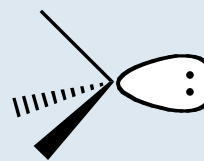
σ -donor ligands

- ◆ ligands with electrons in σ -type orbitals

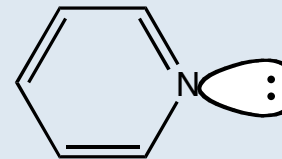
σ -donor ligands



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



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



Py

Fig. 2

reminder

Revision: Ligands

3 key types of ligand

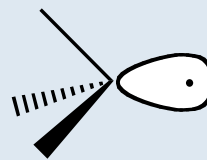
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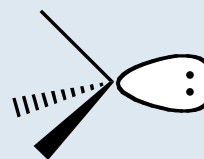
π -donor ligands

- ◆ ligands which have additional filled π orbitals

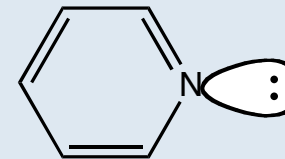
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Py

Fig. 2

π -donor ligands

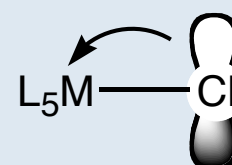
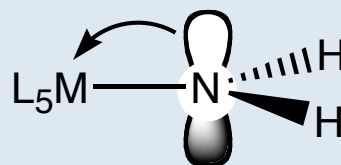


Fig. 2

Revision: Ligands

3 key types of ligand

σ -donor ligands

- ◆ ligands with an available lone pair

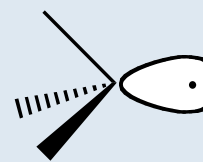
π -donor ligands

- ◆ ligands which have additional filled π orbitals

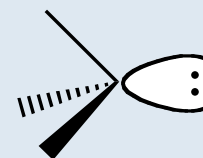
π -acceptor ligands

- ◆ ligands which have additional empty π orbitals

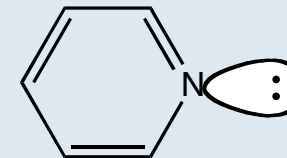
σ -donor ligands



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



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



Py

Fig. 2

π -acceptor ligands

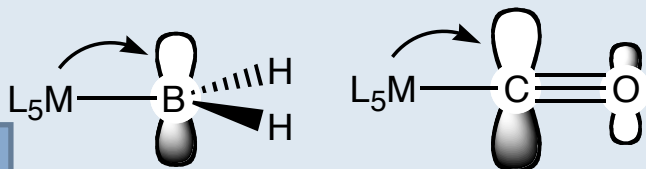


Fig. 2

π -donor ligands

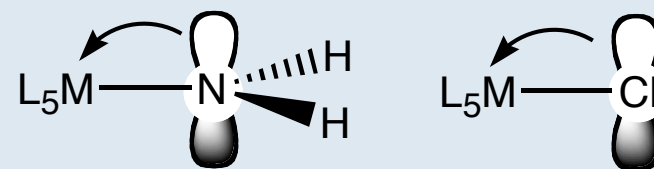


Fig. 2

Metal-Ligand Interactions

Dewar-Chatt-Duncanson bonding

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

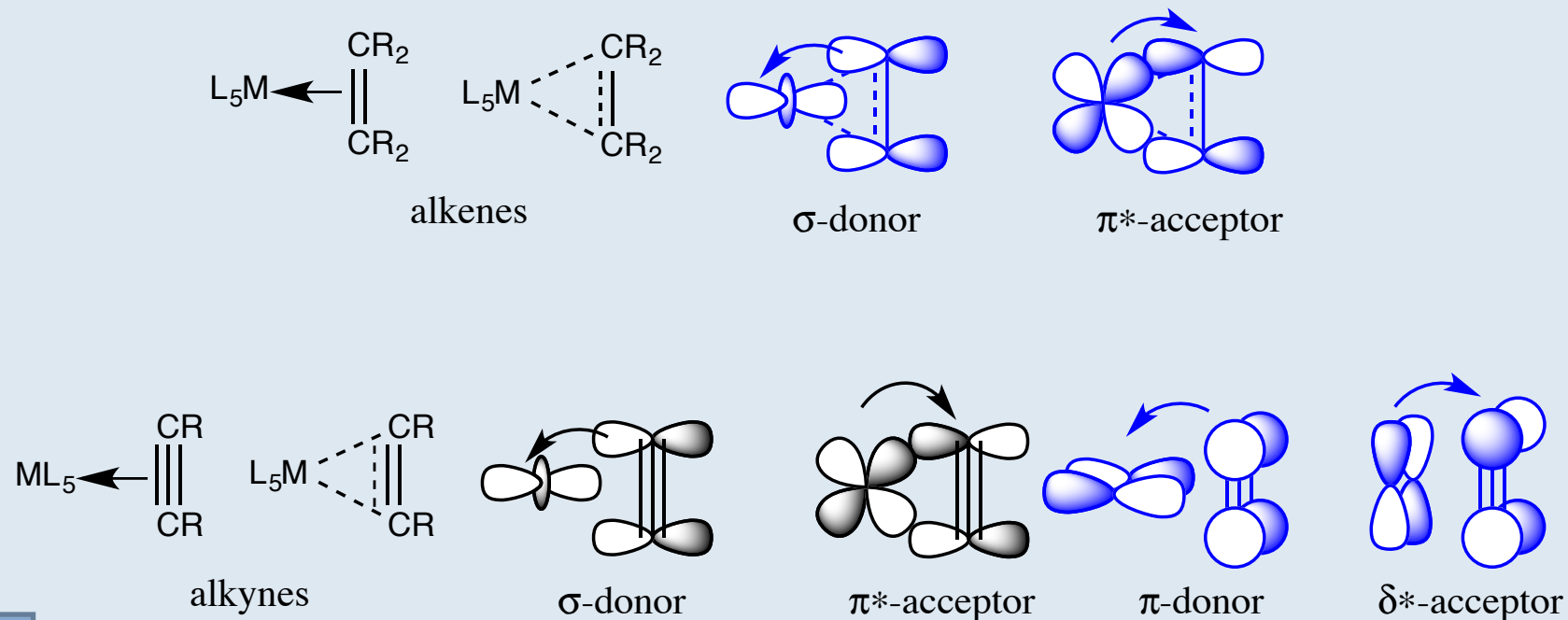
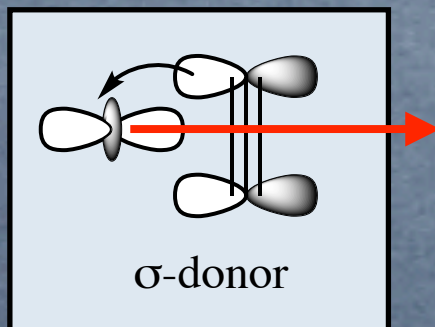
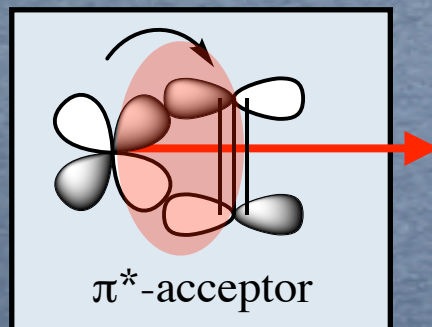


Fig. 3

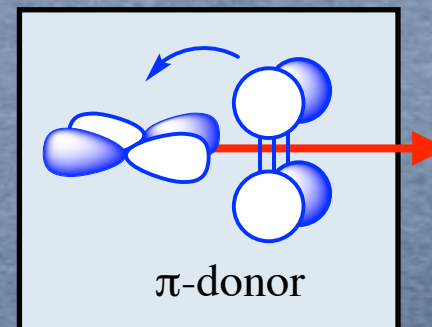
π - and δ - symmetry



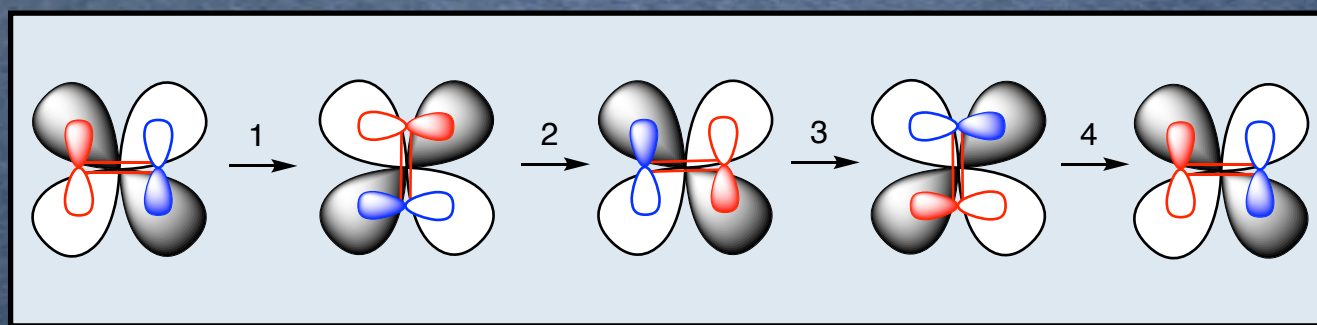
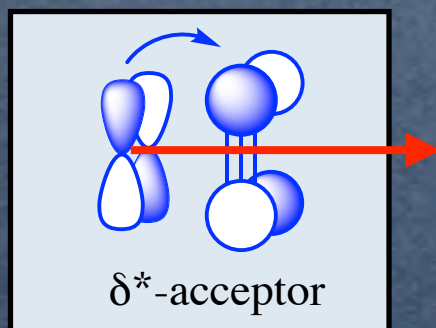
rotate about "bond"
no phase change $\Rightarrow \sigma$



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



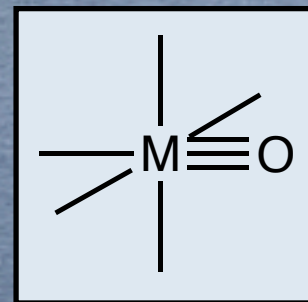
rotate about "bond"
2 phase changes $\Rightarrow \pi$



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-} ?

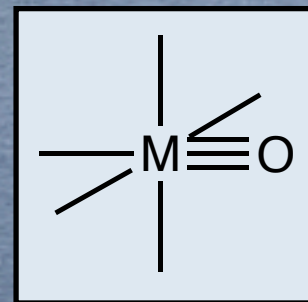


WHZ9KBWC3

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: π -Ligands

consider 6 ligands

- ♦ 1 is π -donor $\Rightarrow L'$
- ♦ 5 are σ -donor ligands $\Rightarrow L$

ALL ligands contribute to σ -framework

L' contributes additional π -orbitals

part of
 σ -framework

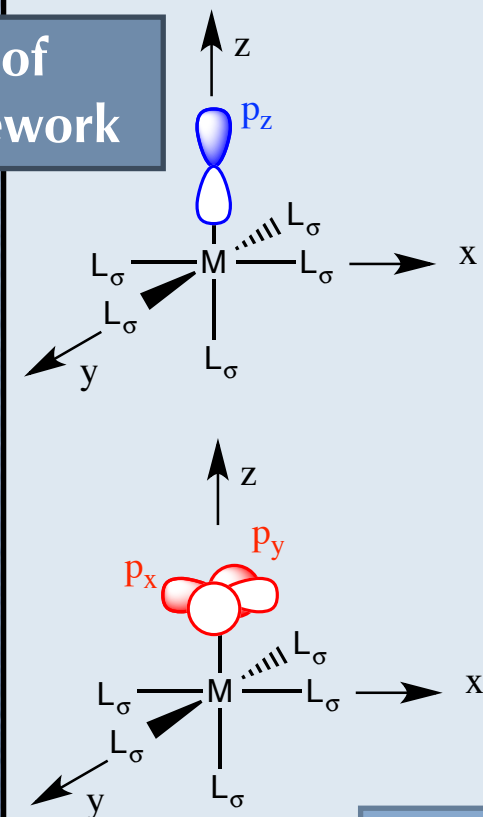


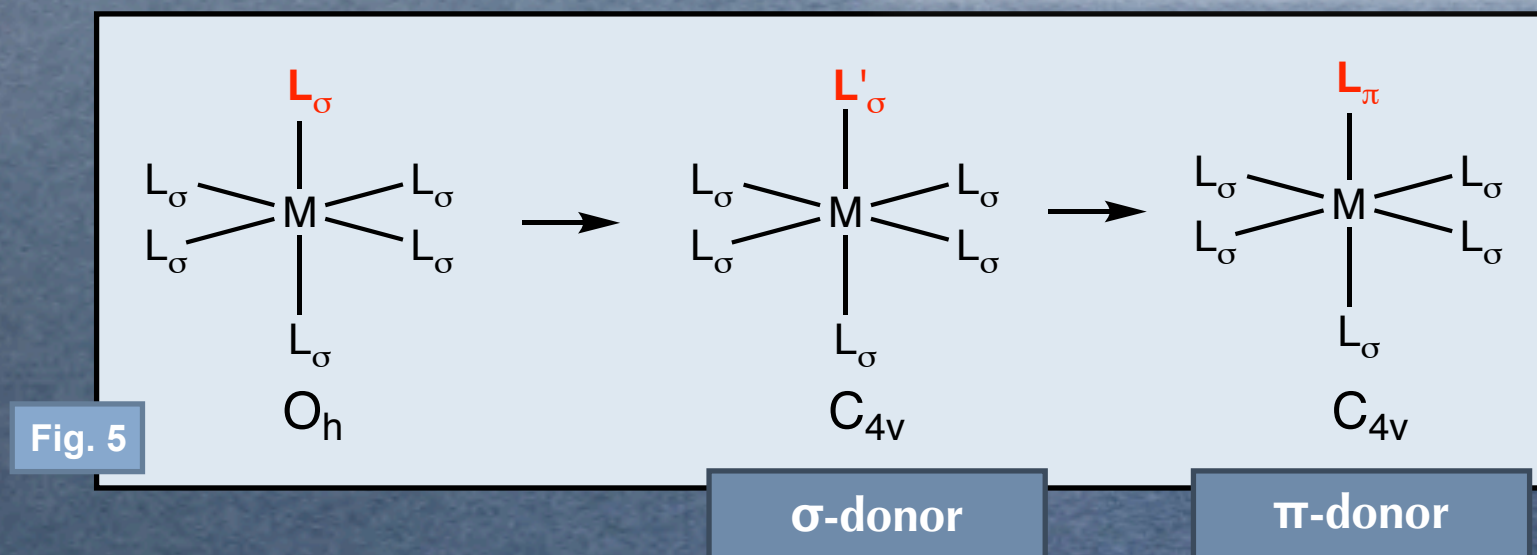
Fig. 4

π -donor
fragment orbitals

Method: π -Ligands

first: work out reduced symmetry

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



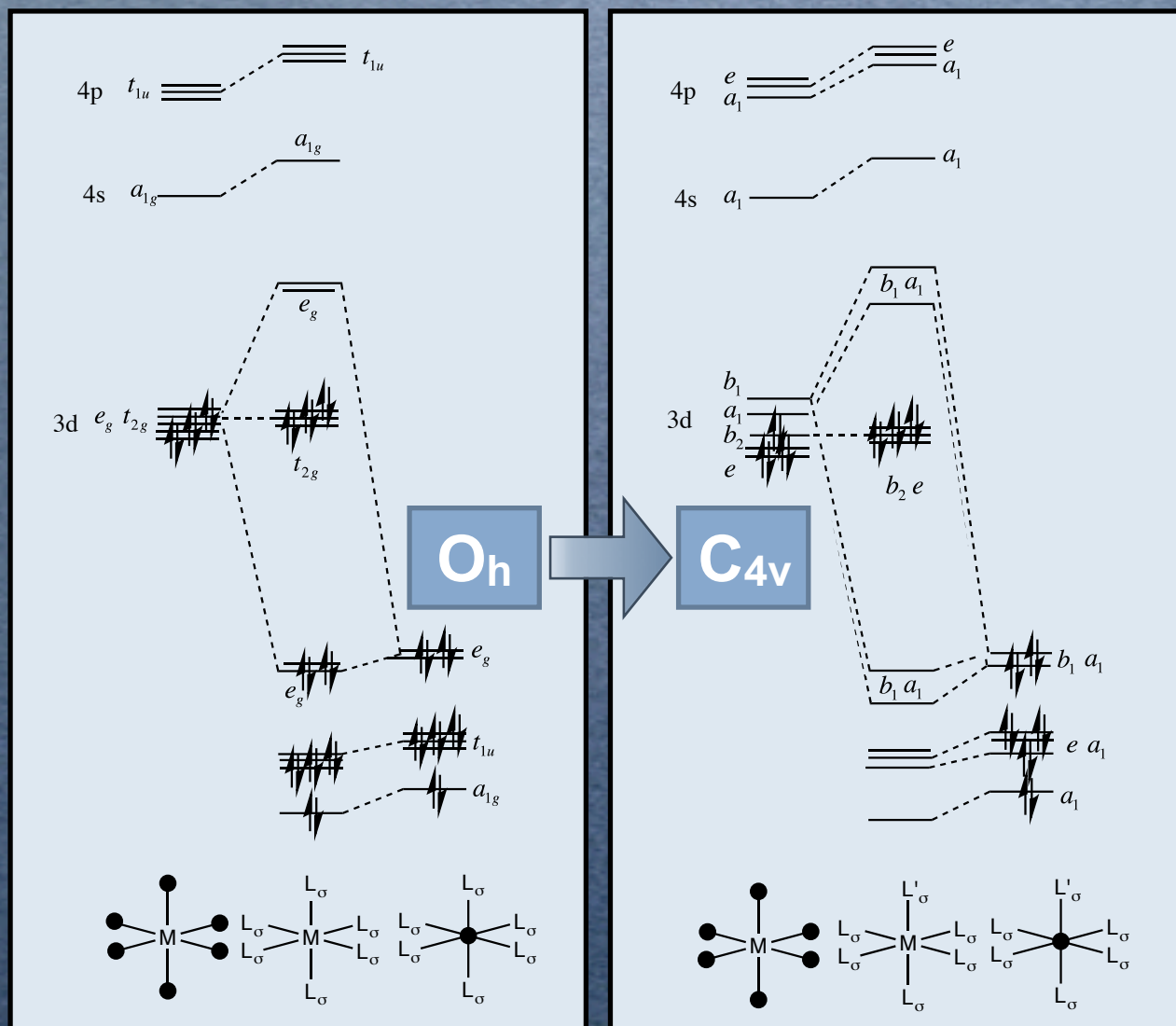
covered in L6!

Method: from last lecture

- start with the octahedral TM diagram
- for σ -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 σ -ligands

colour the L'
orbitals in your
notes BLUE

the remaining
orbitals are the L
ligands orbitals

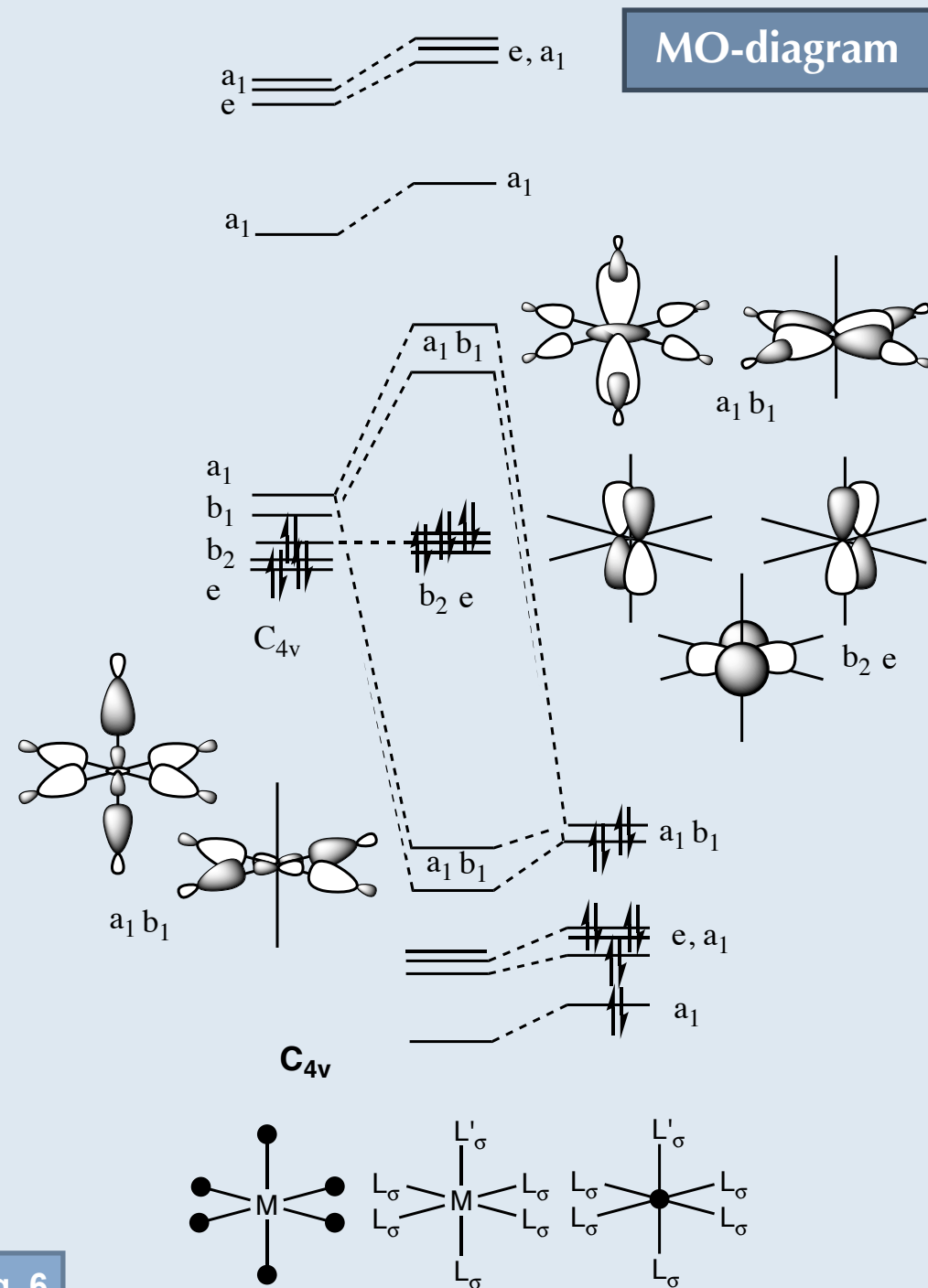


Fig. 6

π -Donor Ligand

● Cl is an example π -donor ligand

● p_z part σ -donor framework

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

colour the L'
 σ -energy
levels in your
notes BLUE

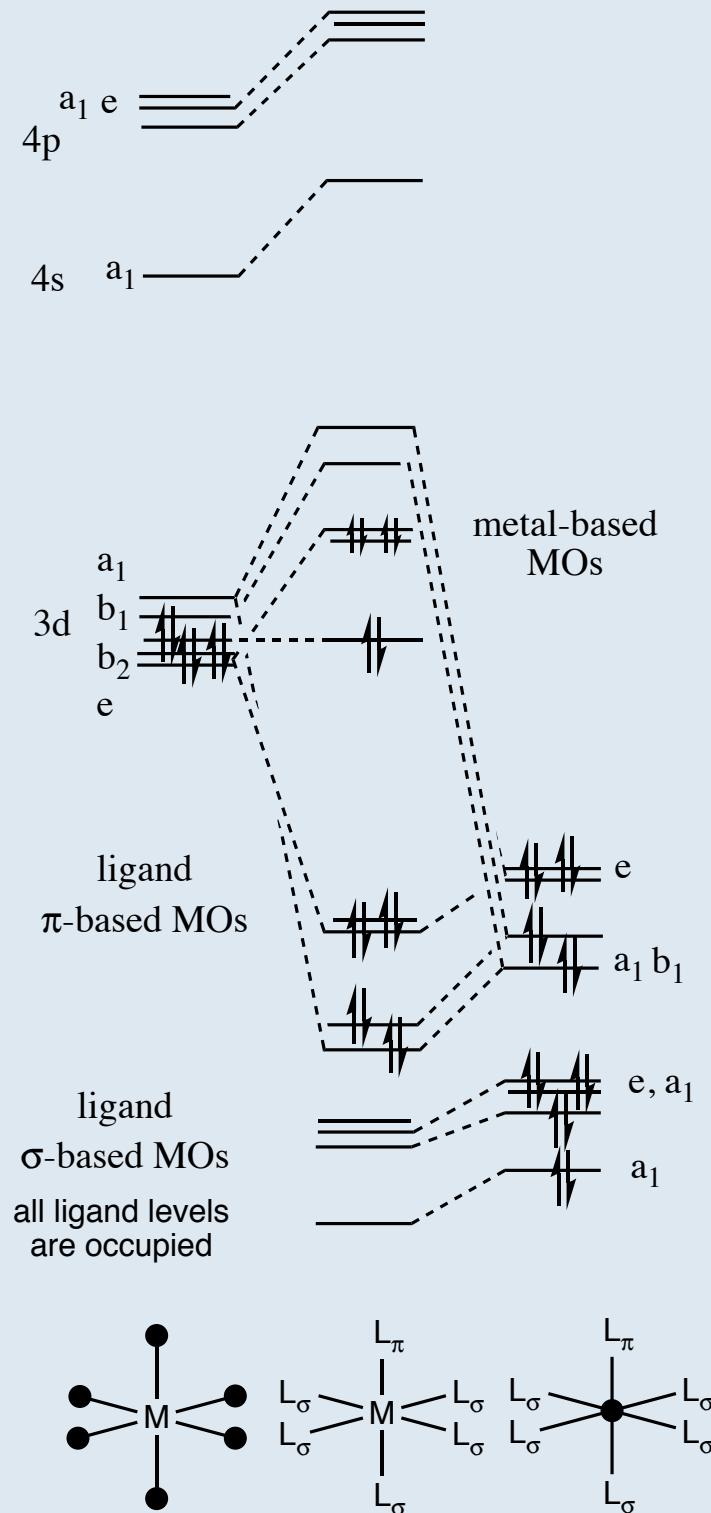
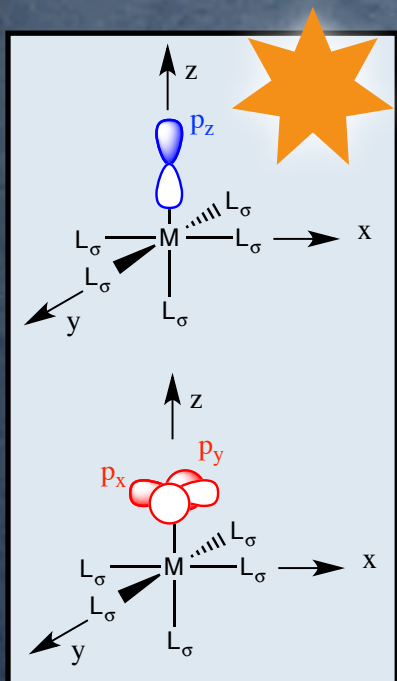


Fig. 7

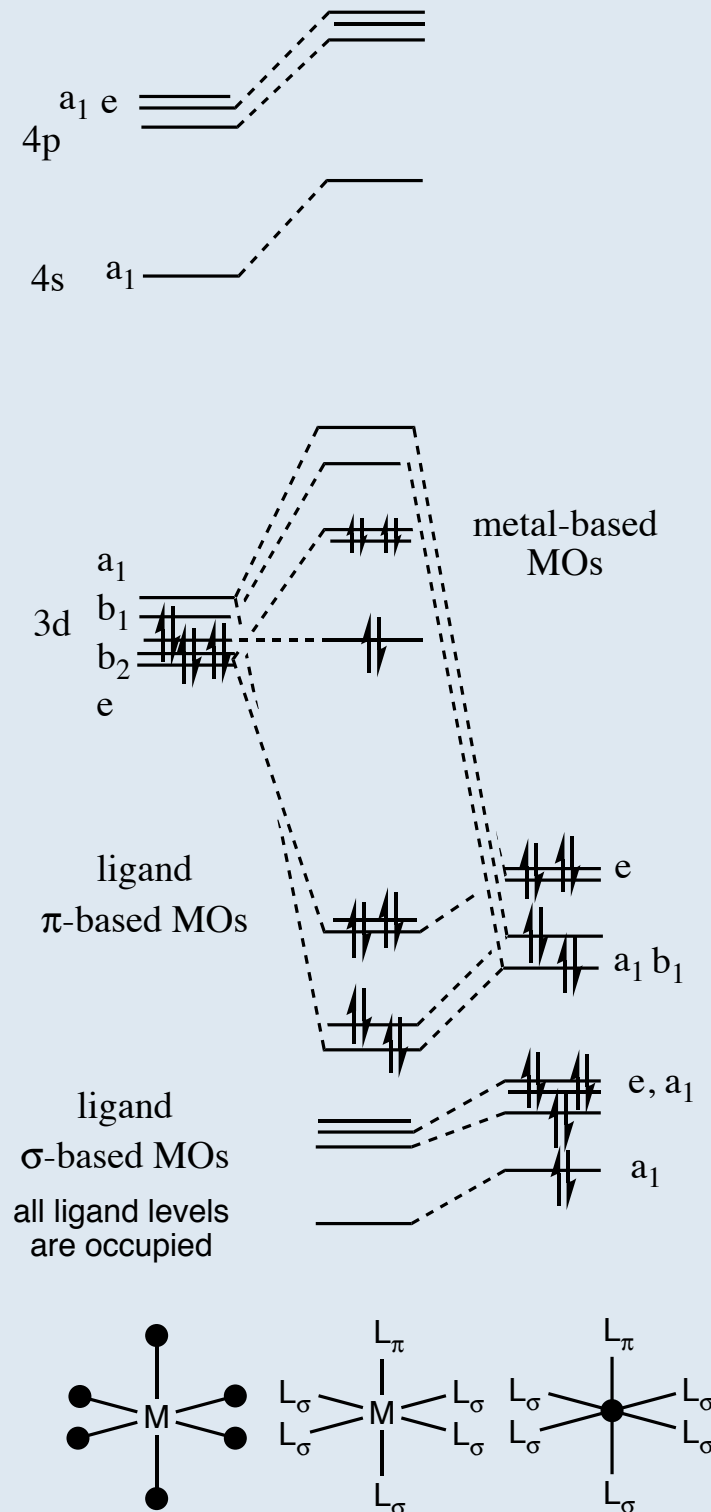
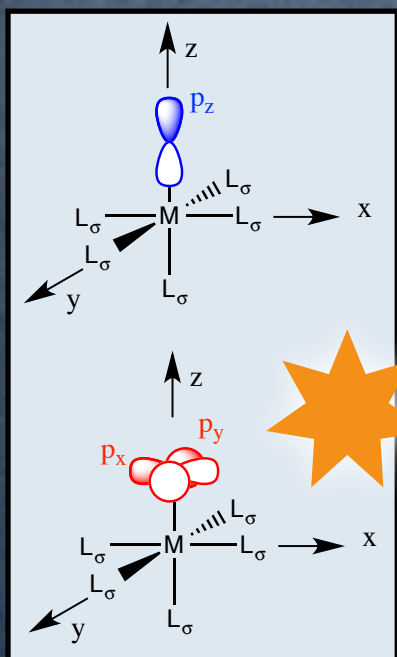
π -Donor Ligand

● Cl is an example π -donor ligand

● (p_x, p_y) degenerate π -donor FOs

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

colour the L'
 π -energy
levels in your
notes RED



π -Donor Ligand

where to position the FOs?

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

(p_x, p_y, p_z) degenerate in Cl

- ◆ p_z effects σ -donor framework slightly
- ◆ p_x, p_y slightly above

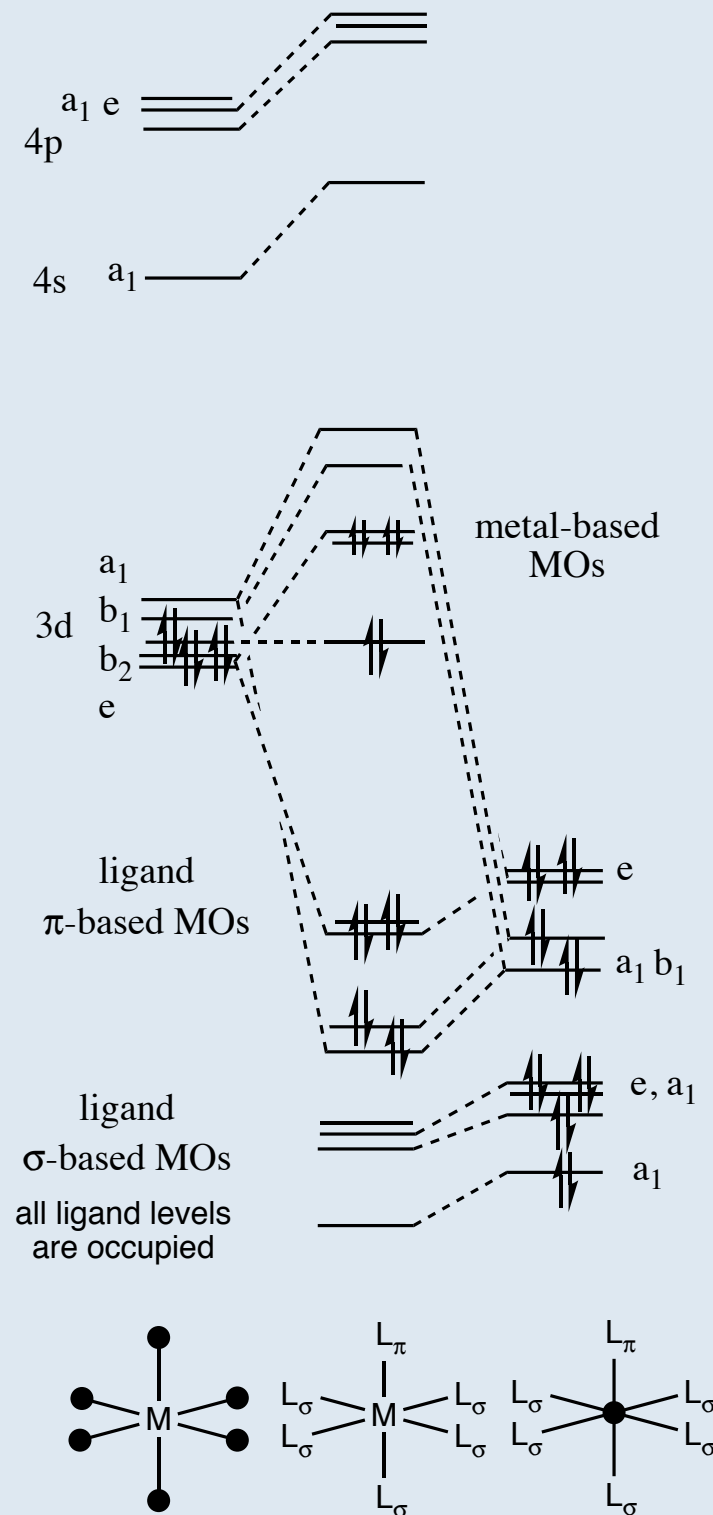


Fig. 7

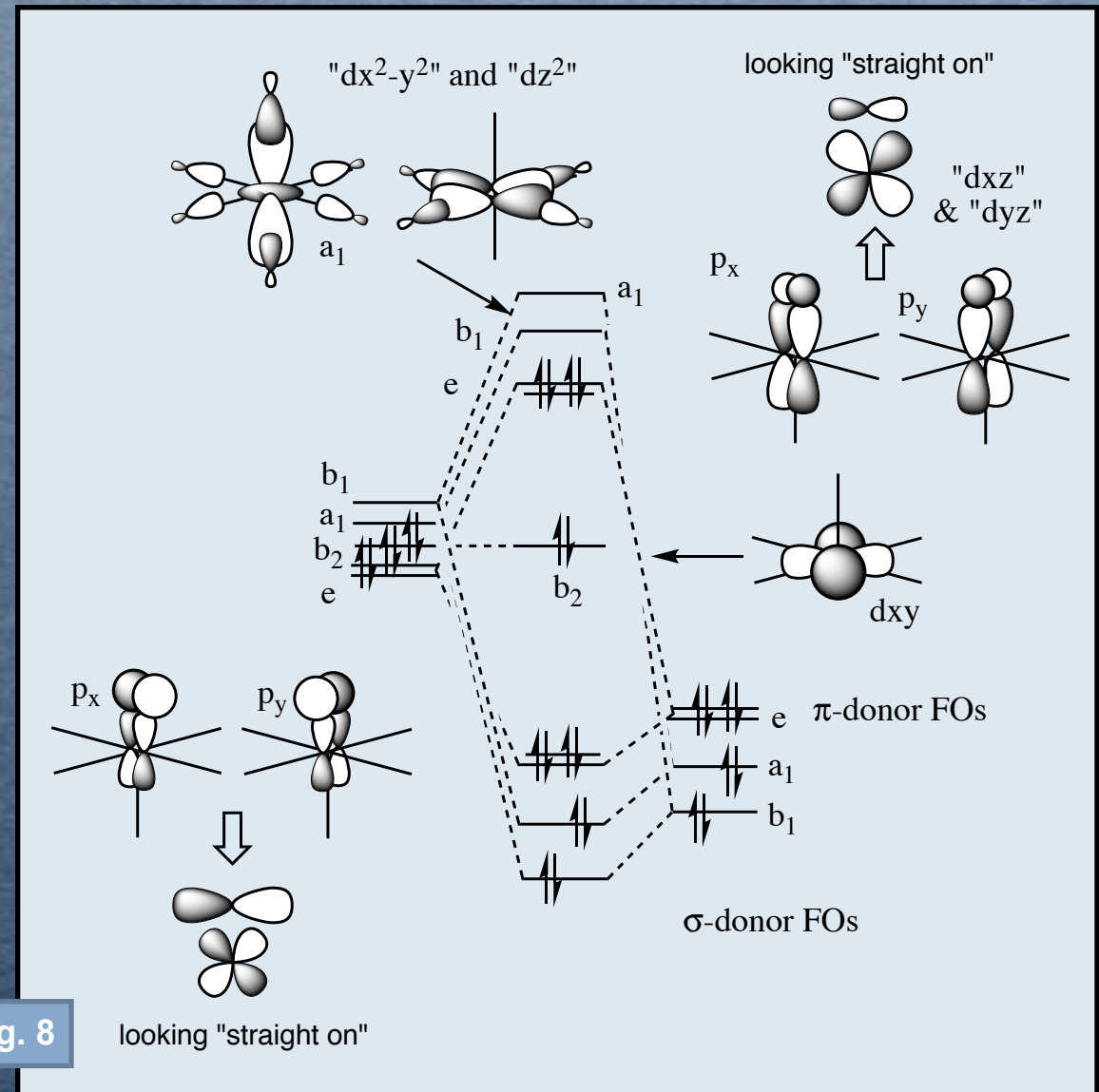
π -Donor Ligand

- new π -donor orbitals:
 - form a bonding/antibonding pair

interaction

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

colour the L'
orbitals in
your notes
BLUE/RED



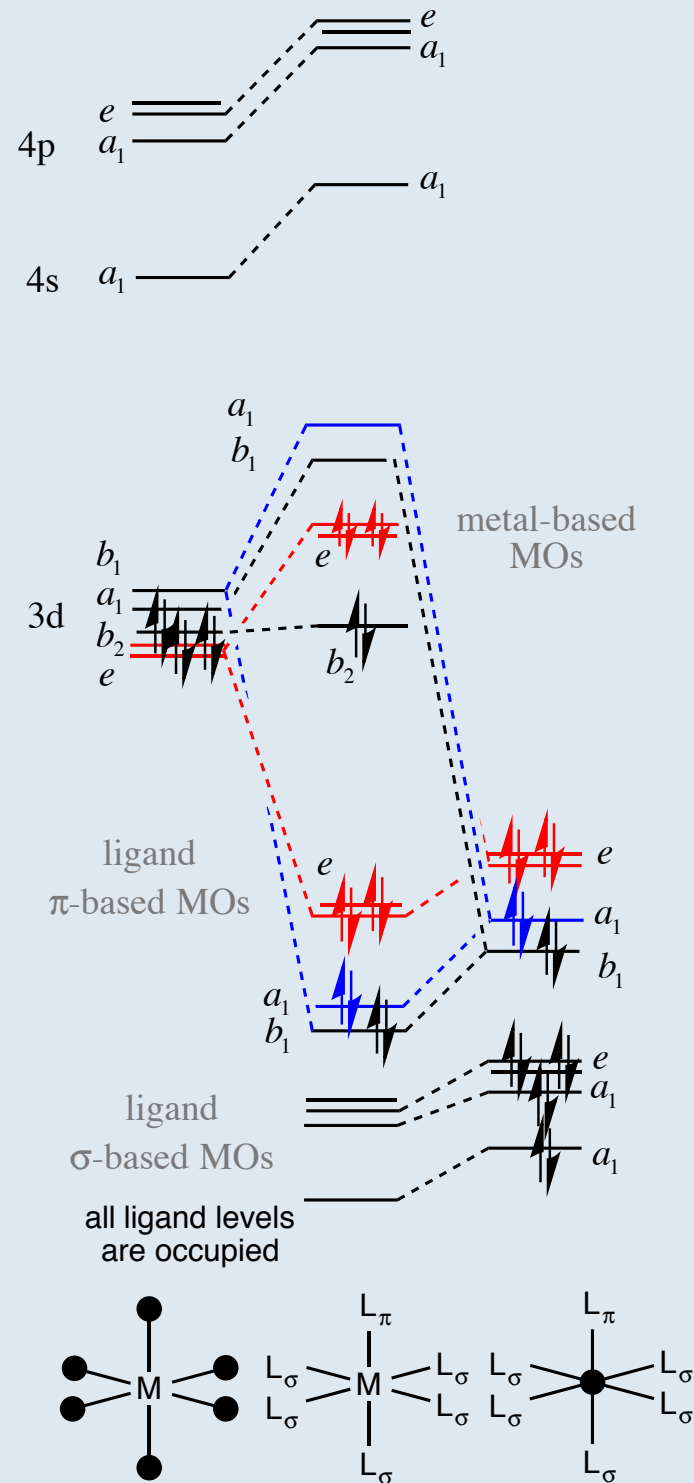
π-Donor Ligand

 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 Δ_{oct} ?

Δ_{oct}

- ◆ less well defined!
- ◆ often refer to “old” symmetry labels
- ◆ e and b₂ are “t_{2g}”
- ◆ a₁ and b₁ are “e_g”
- ◆ Δ_{oct} of σ -donor ligands (green)
- ◆ Δ_{oct} of π -donor ligand (pink)

π -donor ligand reduces Δ_{oct} because of destabilisation of “e” orbitals due to an antibonding interaction with π -FOs

Important!

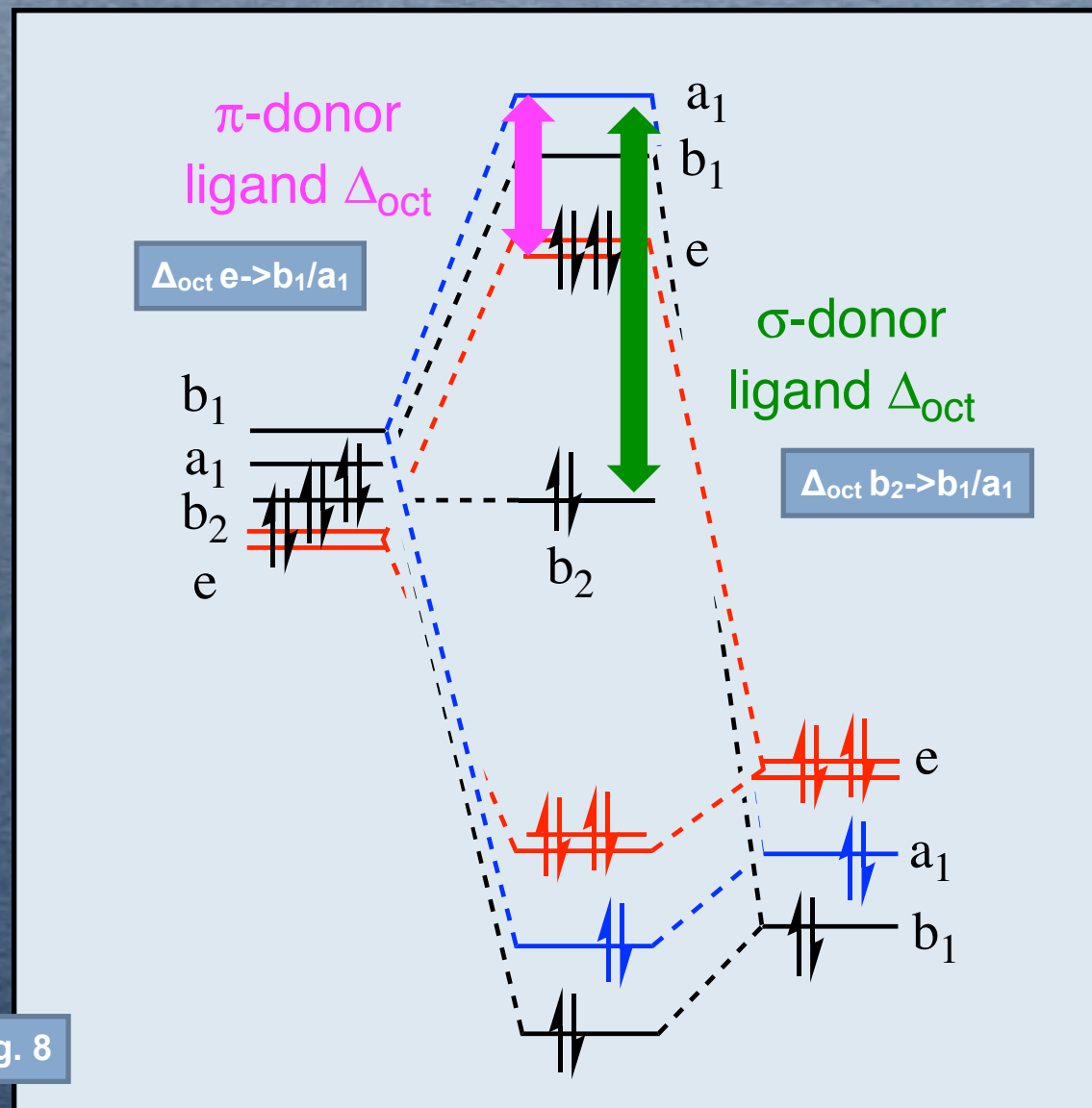


Fig. 8

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}

Δ_{oct} measures splitting of e_g and t_{2g}

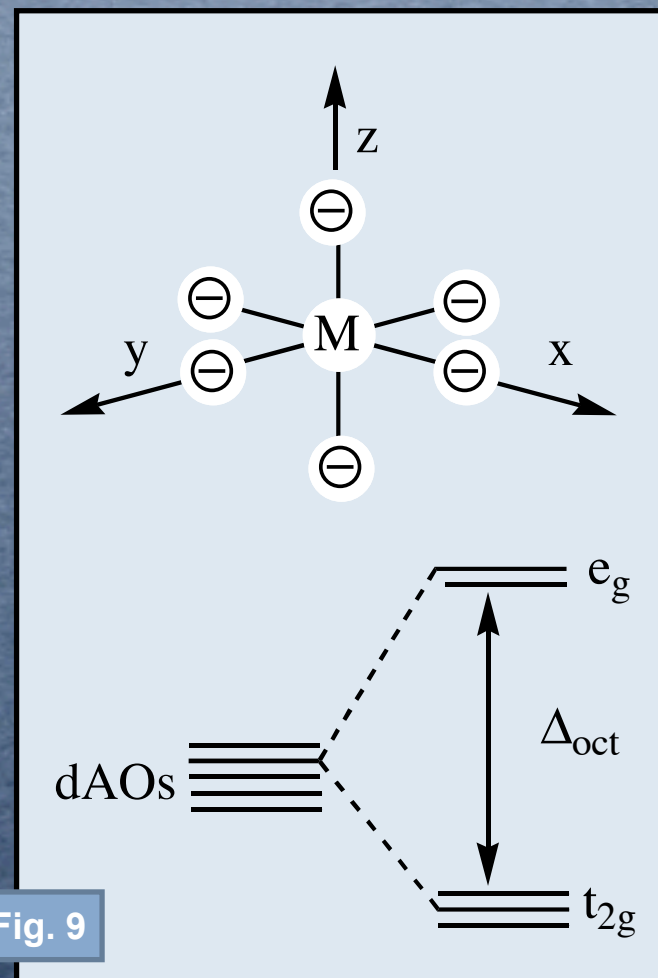


Fig. 9

Spectrochemical Series

O²⁻

- ◆ has a large charge => should generate a large Δ_{oct}
- ◆ colour of emeralds and rubies is due to Cr³⁺ in the octahedral field of six O²⁻ in the solid state

Removed due
to copyright

Emerald: Cr³⁺ in the
octahedral sites of Beryl
Be3Al2Si6O18

Fig. 10

Ruby: Cr³⁺
replaces Al³⁺
in Al₂O₃

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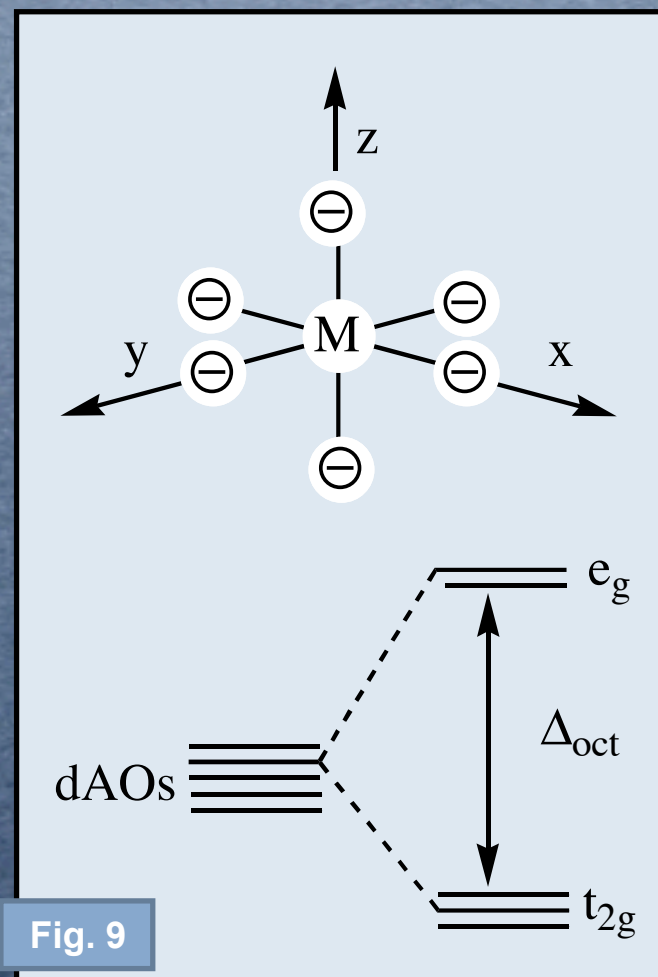
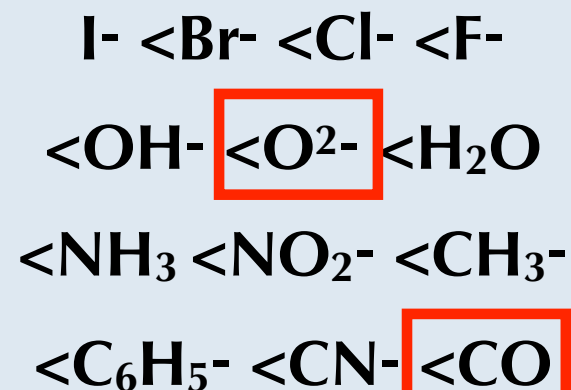


Fig. 9

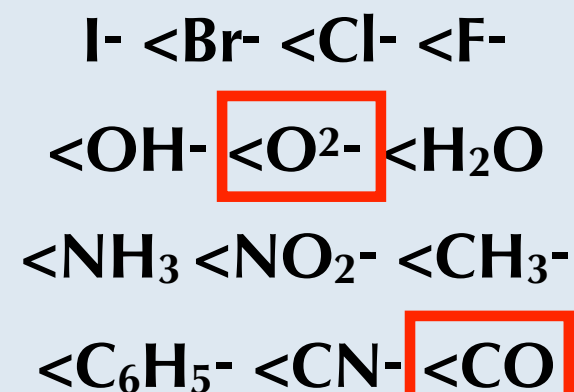
Spectrochemical Series

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



Spectrochemical Series

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

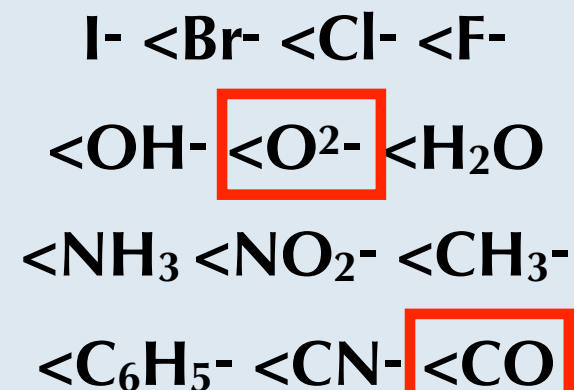


BUT:

- anions (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 Δ_{oct}
- order ligands from strong field (large Δ_{oct}) though to weak field (small Δ_{oct})
- CO has large Δ_{oct} and O^{2-} has small Δ_{oct}



BUT:

- anions (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

π -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 σ -donor orbitals (blue)
- ◆ has π -bonding orbitals (black)
- ◆ has π -antibonding orbitals (red)

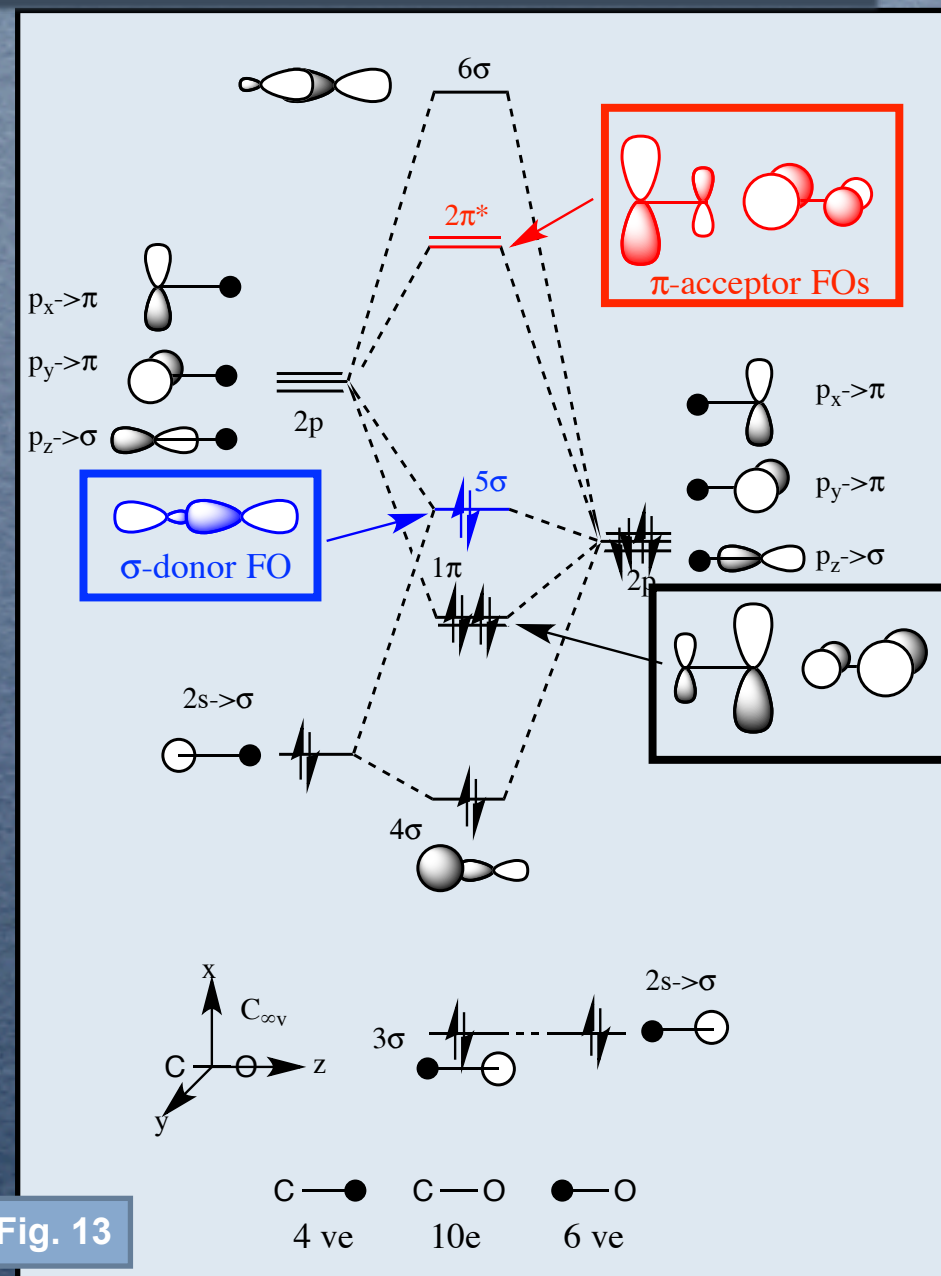


Fig. 13

π -Acceptor Ligand

- orbitals from MO diagram of CO
- σ -donor orbitals



contribute to
 σ -frame work

σ -bonding
orbitals

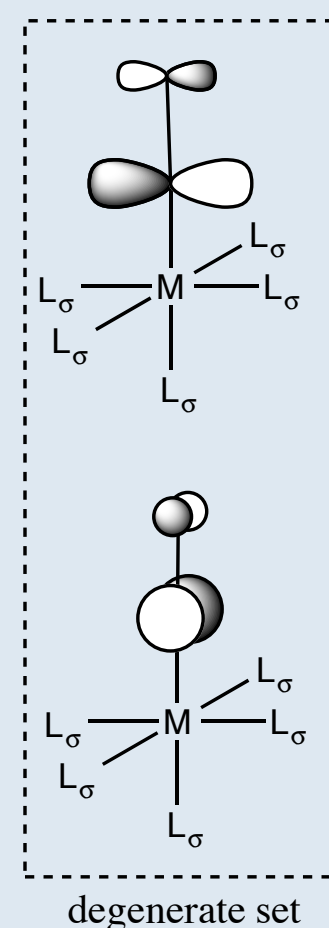
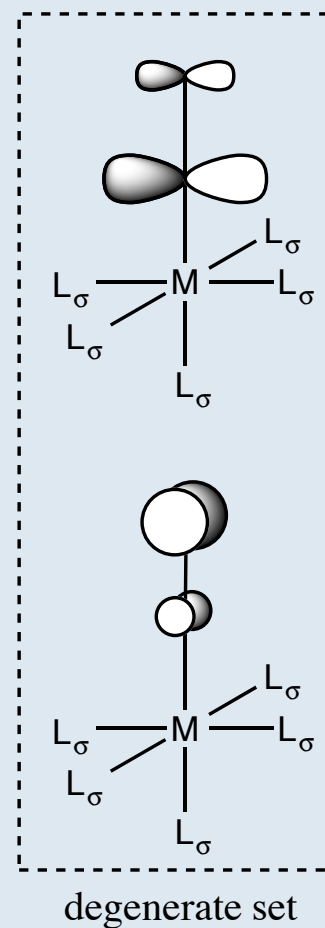
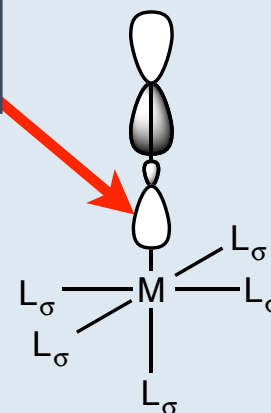
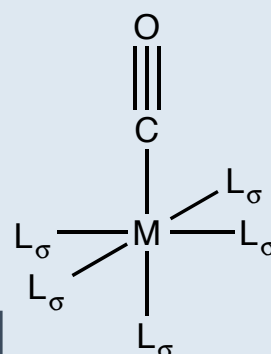


Fig. 14(a)

π -Acceptor Ligands

- orbitals from MO diagram of CO
- has σ -donor orbitals
- has π -bonding orbitals
- has π -antibonding orbitals

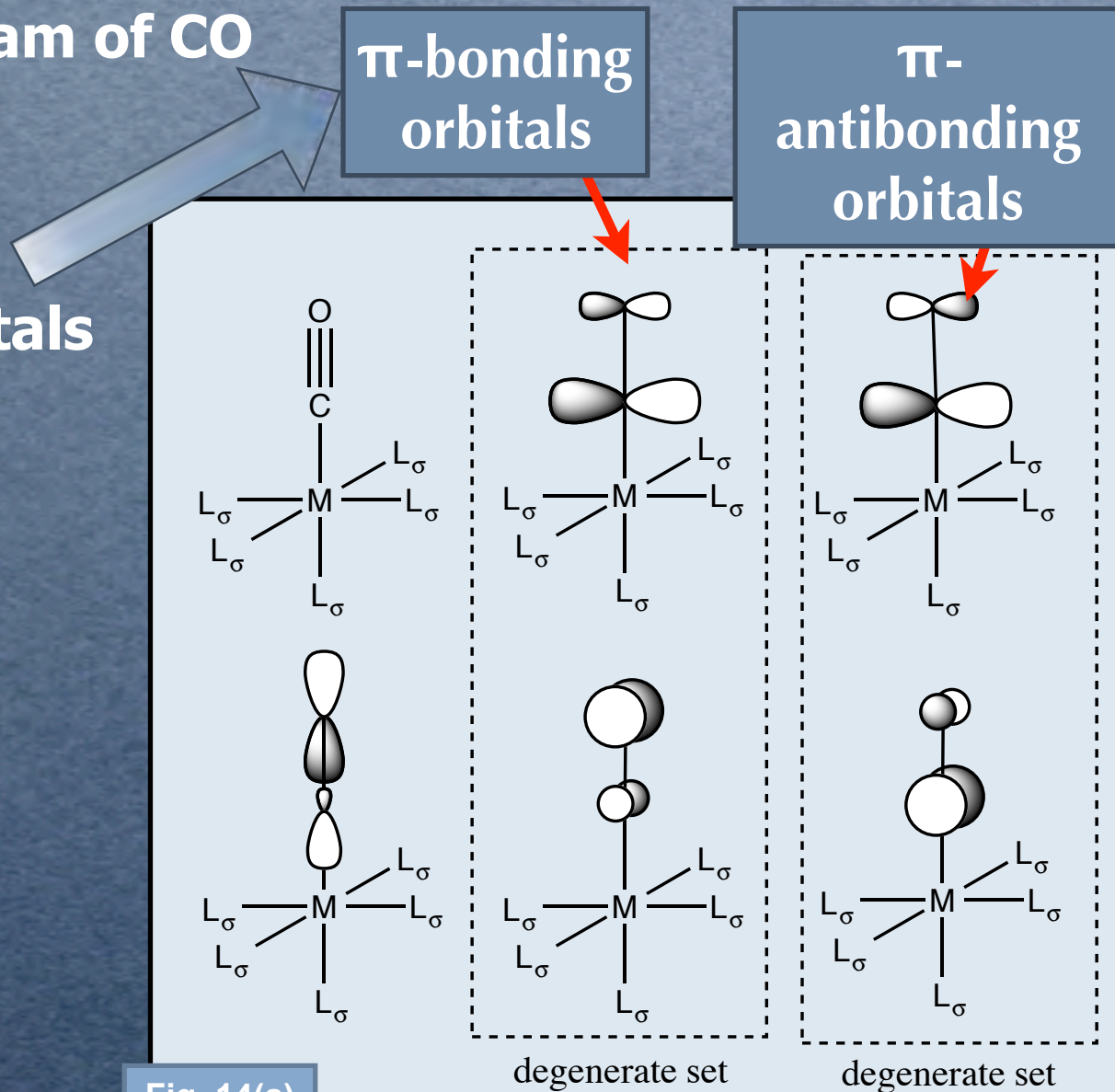


Fig. 14(a)

Symmetry Labels

π -orbitals

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

π^* -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

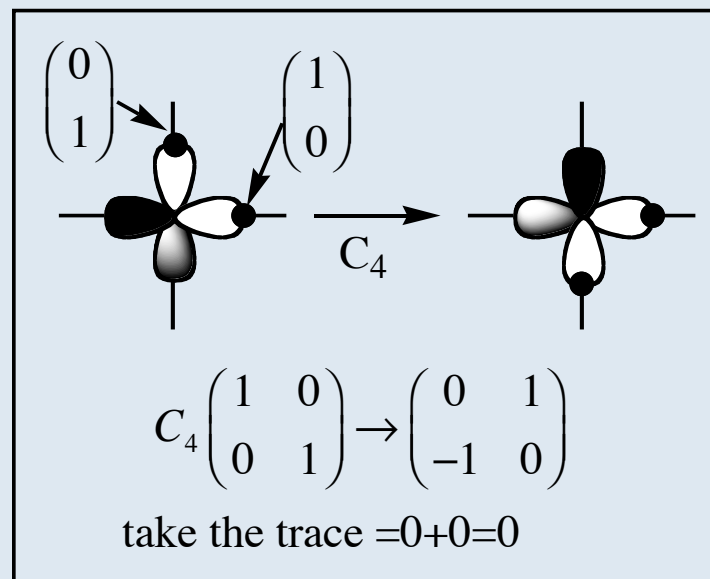
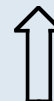


Fig. 14(b)

Energy Diagram

basic C_{4v} diagram for σ -ligands

add π -FOs (blue)

- ◆ π -orbitals have poor interaction with dAOs
- ◆ remain non-bonding

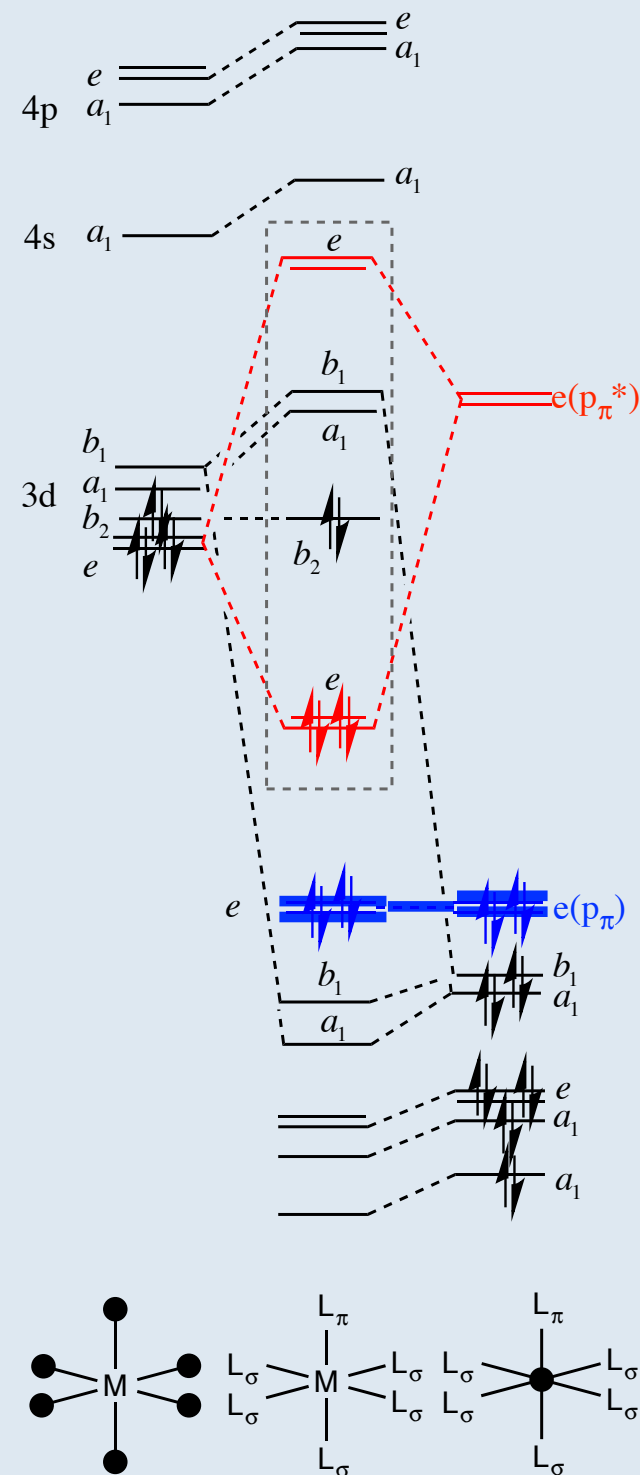
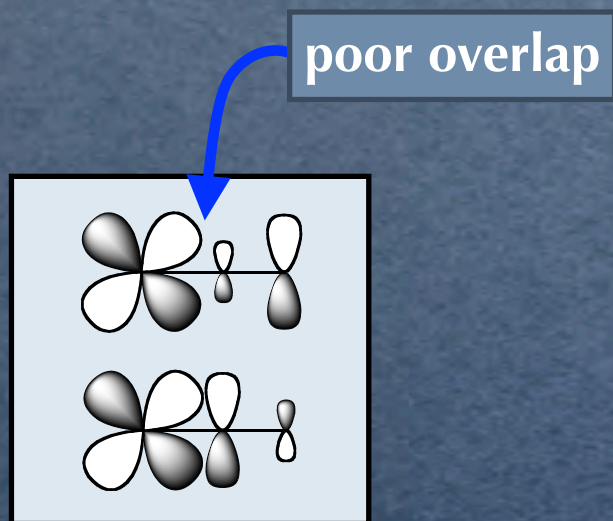


Fig. 15

Energy Diagram

basic C_{4v} diagram for σ -ligands

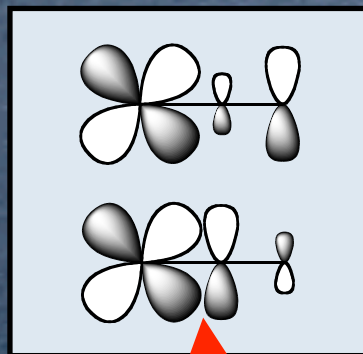
add π -FOs (blue)

- ◆ π -orbitals have poor interaction with dAOs
- ◆ remain non-bonding

add π^* -FOs (red)

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

- ⇒ close in energy
- ⇒ good overlap
- ⇒ still π -type interaction
- ⇒ strong splitting



good overlap

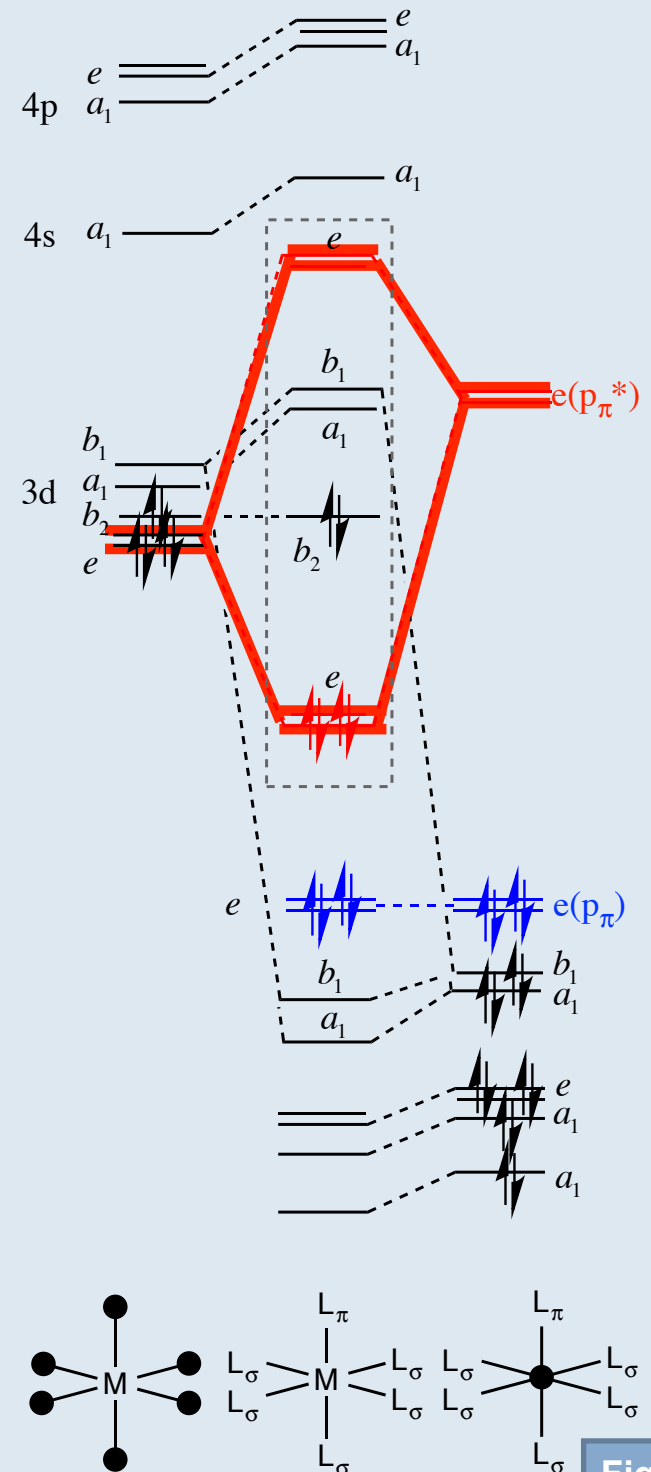
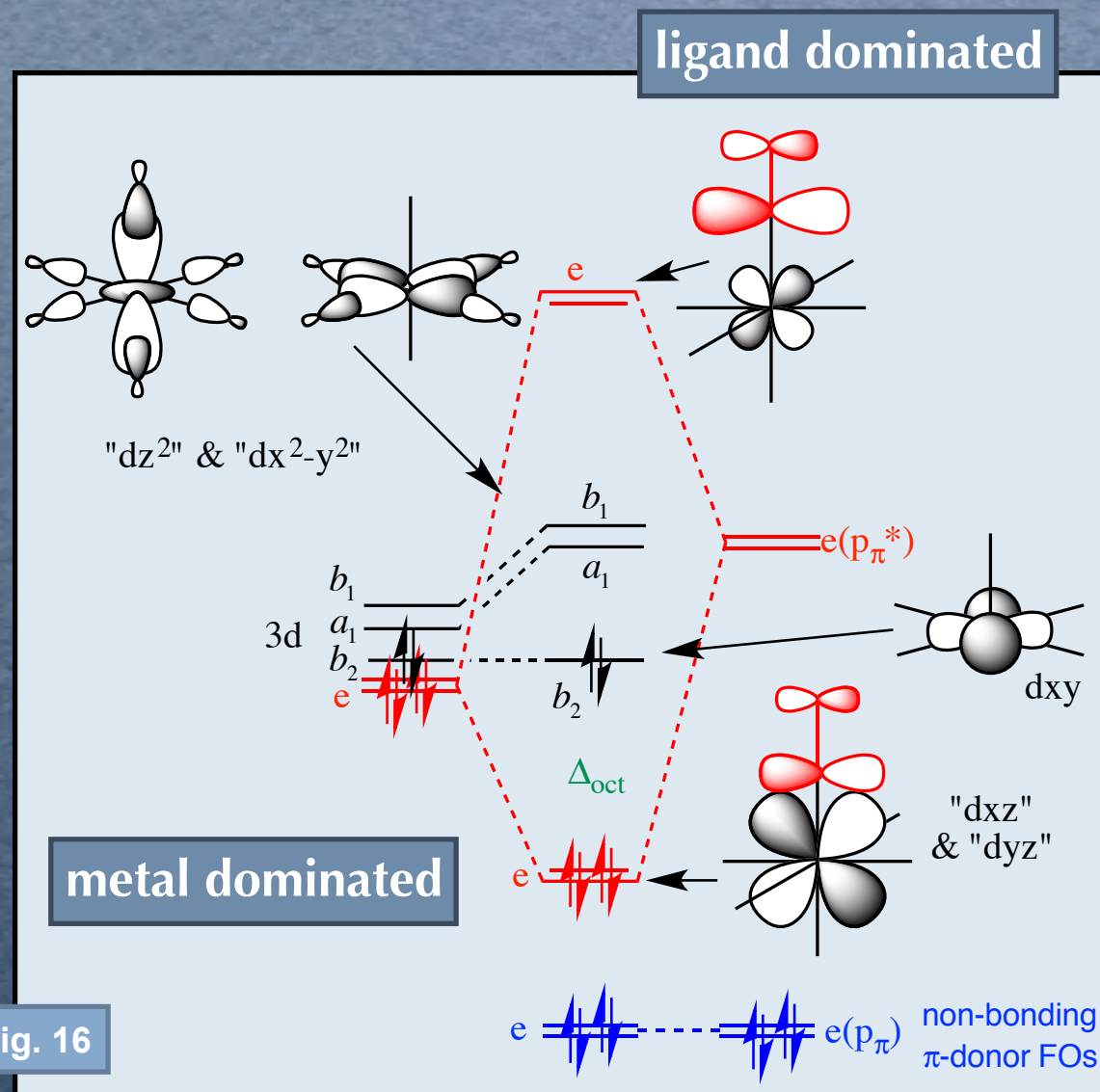


Fig. 15

The Important MOs

- focus in on π^* -dAO interactions
- dAO dominated MO is now the lower bonding MO

Important!



What about Δ_{oct} ?

 Δ_{oct} π -acceptor ligand

- ◆ less well defined!
- ◆ Δ_{oct} of σ -donor ligands (green)
- ◆ Δ_{oct} of π -acceptor ligand (pink)

 π -acceptor ligand increases Δ_{oct} because of stabilisation of e MOs due to a bonding interaction with π^* -FOs

Important!

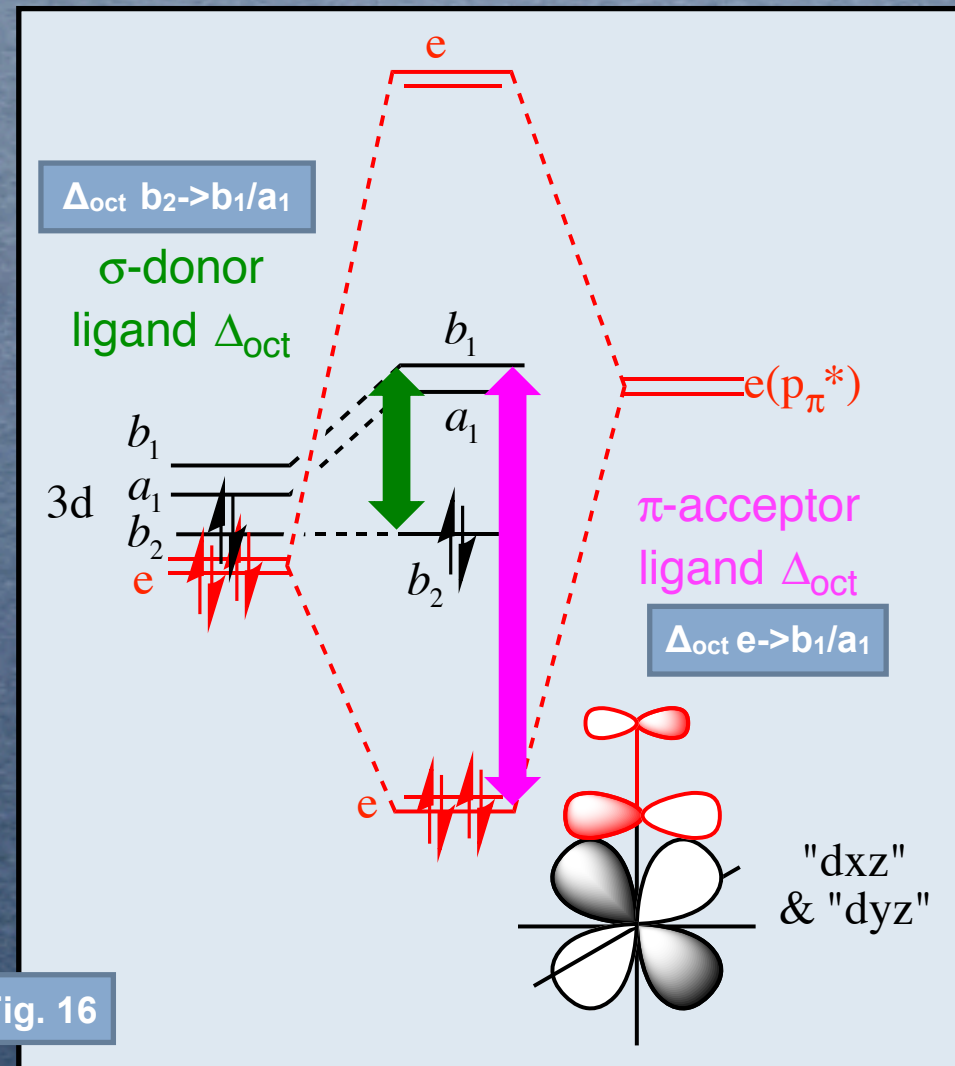


Fig. 16

Summary for Δ_{oct}

σ -donor ligands



π -donor ligands

π^* -acceptor ligands

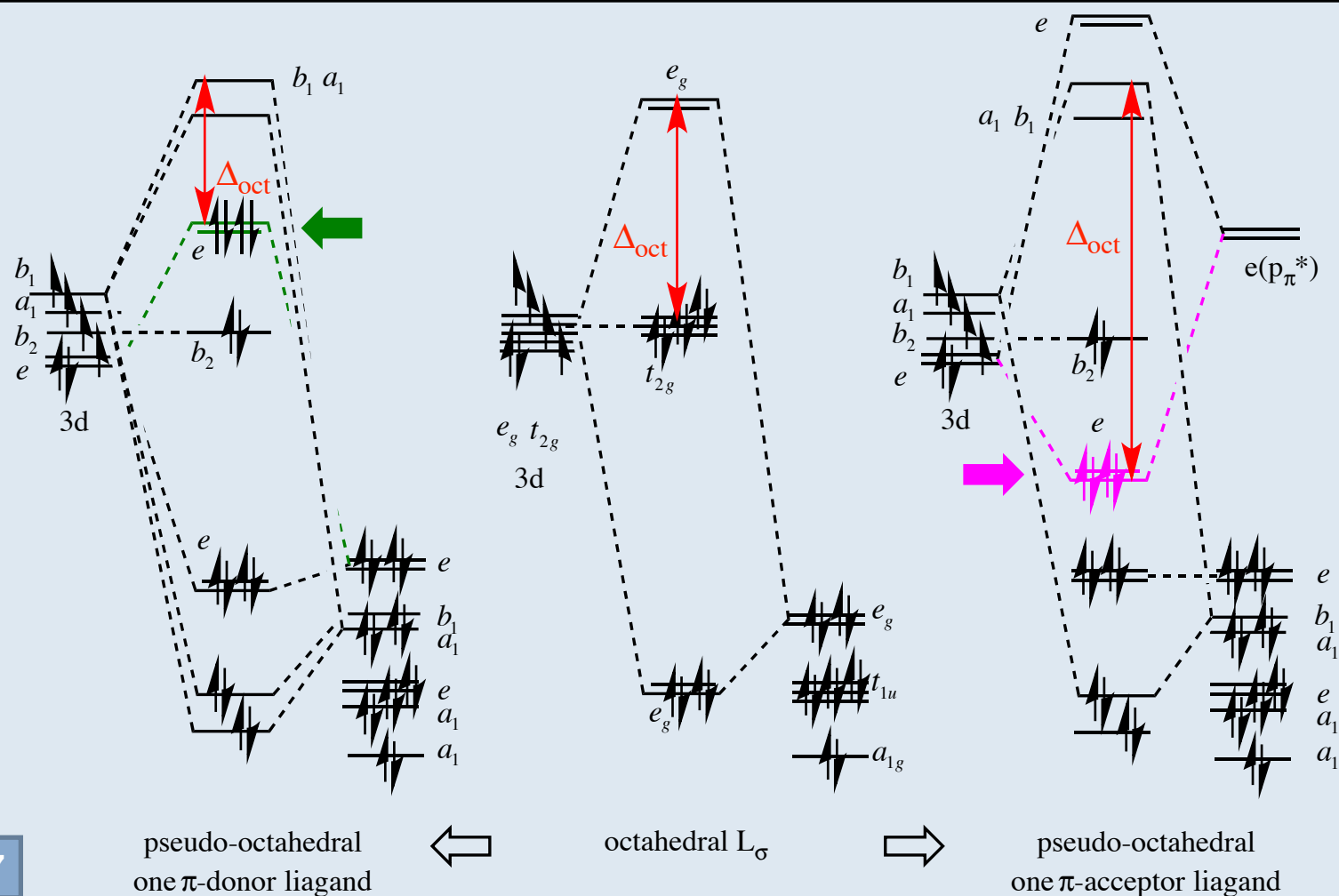


Fig. 17

Summary for Δ_{oct}

σ -donor ligands

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

π -donor ligands

π^* -acceptor ligands

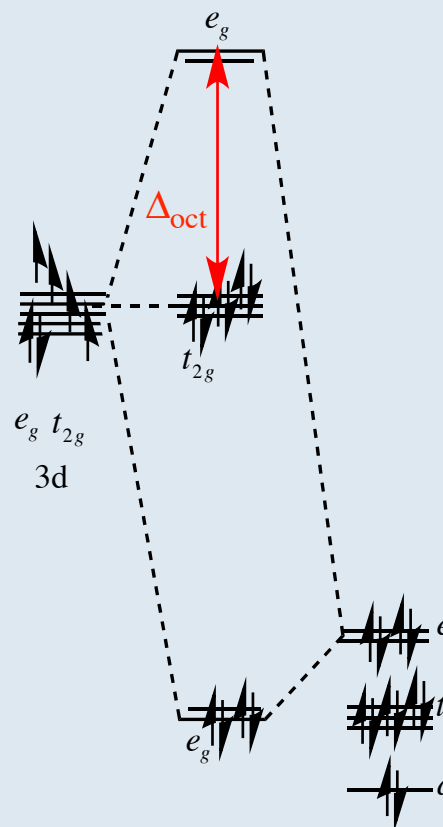


Fig. 17

σ -donor
"reference"

Summary for Δ_{oct}

σ -donor ligands

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

π -donor ligands

π^* -acceptor ligands

π -donor
dAO dominate
antibonding e MO
up $\uparrow\uparrow\uparrow$
 Δ_{oct} smaller

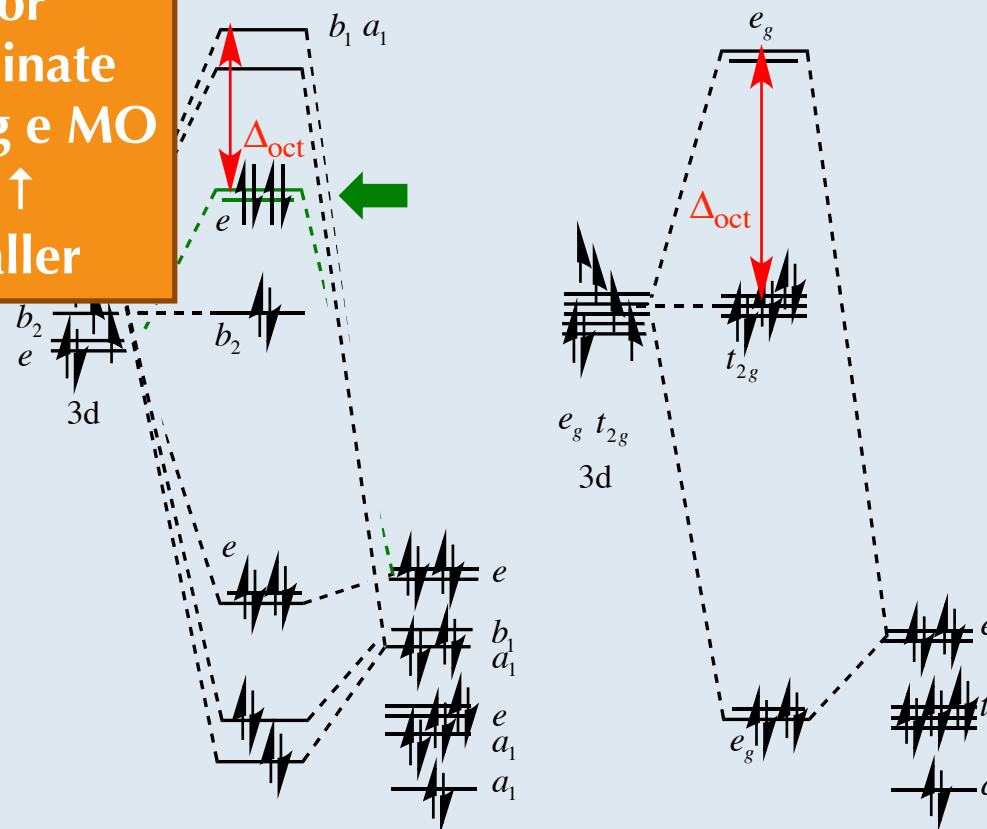


Fig. 17

pseudo-octahedral
one π -donor ligand

Summary for Δ_{oct}

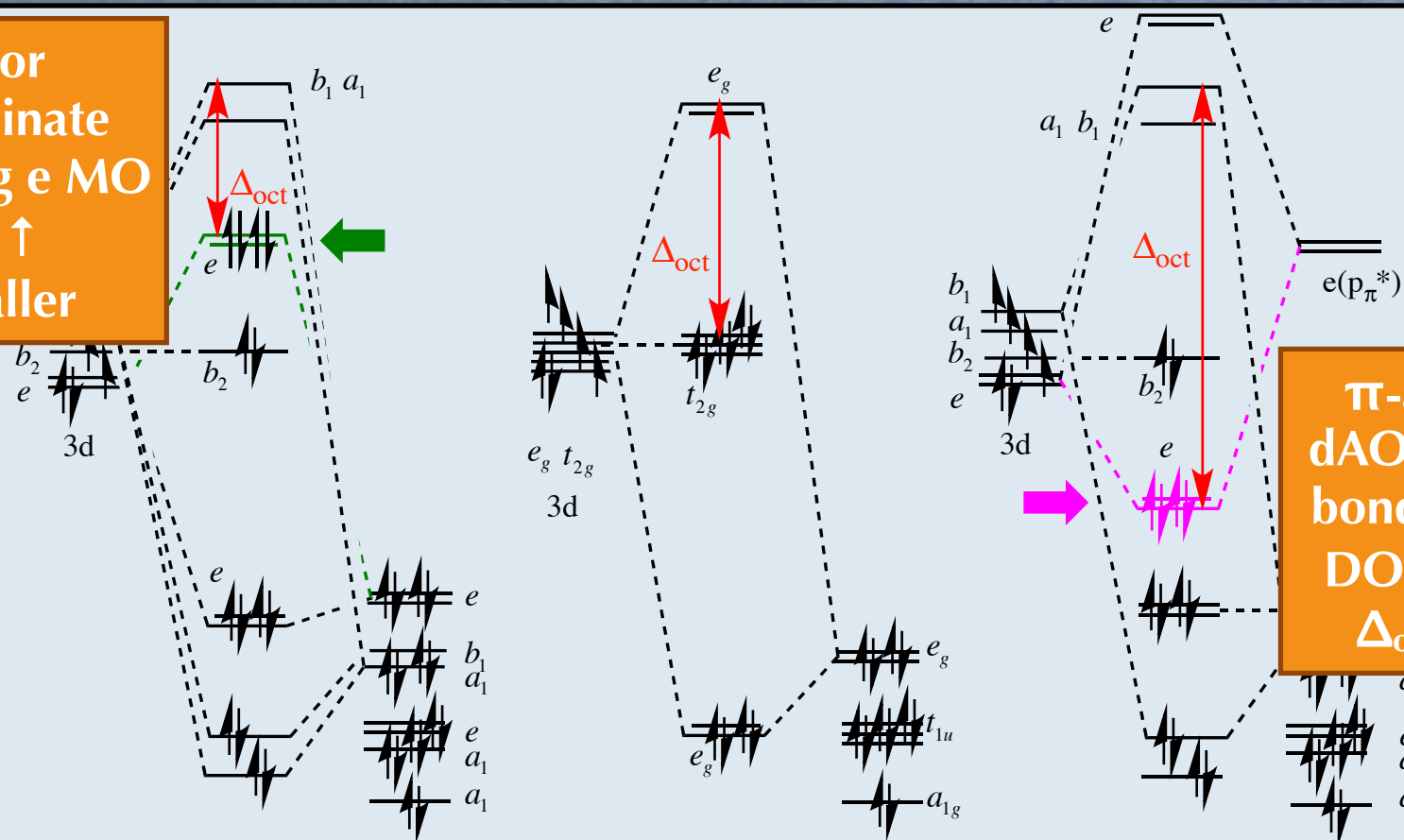
σ -donor ligands

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

π -donor ligands

π^* -acceptor ligands

π -donor
dAO dominate
antibonding e MO
up $\uparrow\uparrow\uparrow$
 Δ_{oct} smaller



π -acceptor
dAO dominate
bonding e MO
DOWN $\downarrow\downarrow\downarrow$
 Δ_{oct} larger

Fig. 17

pseudo-octahedral
one π -donor ligand

octahedral L_σ

pseudo-octahedral
one π -acceptor ligand

Key Points

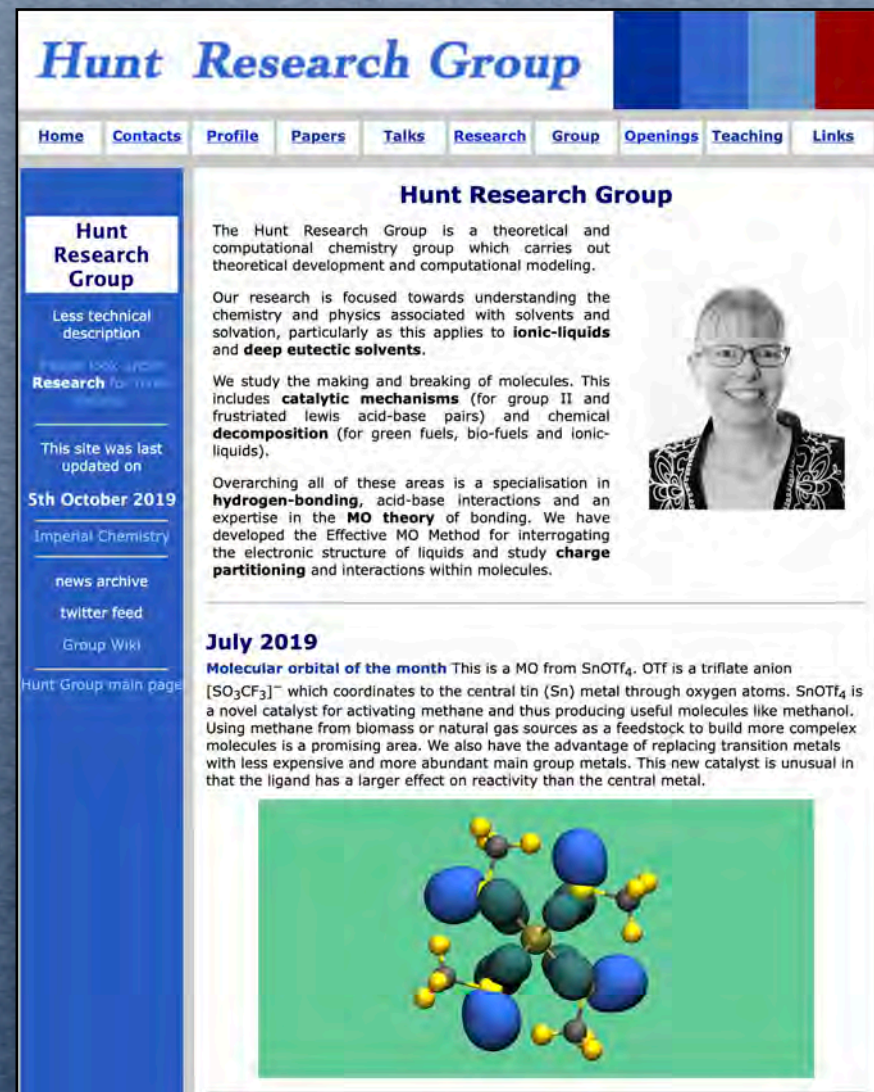
- be able to draw energy level diagrams for octahedral and square planar complexes with π -donor and π -acceptor ligands
- be able to draw and describe the important MOs
- be able to discuss key features of these diagrams
- be able to describe crystal field theory and discuss the empirical spectrochemical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



The screenshot shows the homepage of the Hunt Research Group website. The header features the group's name in a blue serif font. Below the header is a navigation menu with links to Home, Contacts, Profile, Papers, Talks, Research, Group, Openings, Teaching, and Links. The main content area is divided into two columns. The left column contains a sidebar with links to 'Less technical description', 'Research for...', 'This site was last updated on 5th October 2019', 'Imperial Chemistry', 'news archive', 'twitter feed', and 'Group Wiki'. The right column contains the main text, which includes a welcome message, a description of the group's research focus on solvents and solvation, a list of research areas (catalytic mechanisms, frustrated Lewis acid-base pairs, and chemical decomposition), and a section titled 'July 2019 Molecular orbital of the month' featuring a molecular orbital diagram of a tin complex. A portrait of a woman is also visible on the right side of the main text area.

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.

July 2019

Molecular orbital of the month This is a MO from SnOTf_4 . OTf is a triflate anion $[\text{SO}_3\text{CF}_3]^-$ which coordinates to the central tin (Sn) metal through oxygen atoms. 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.

