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

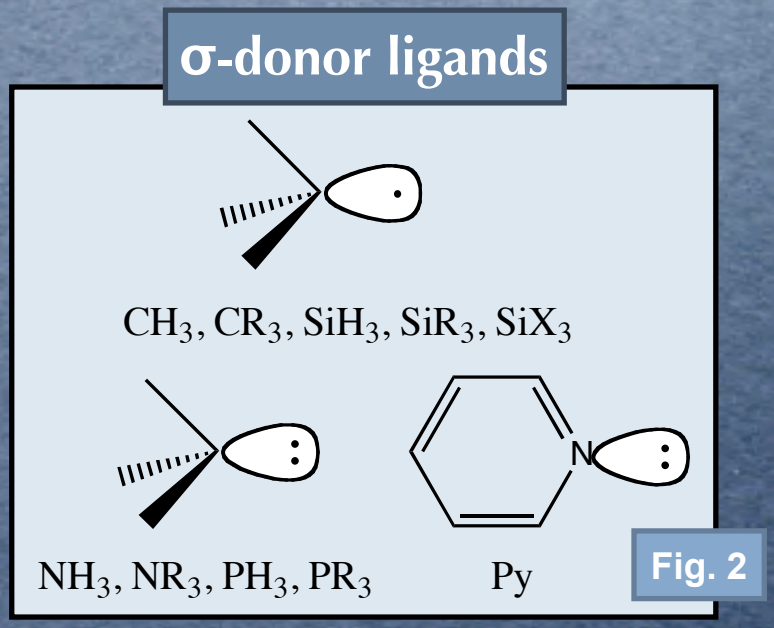
socrative quiz!

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

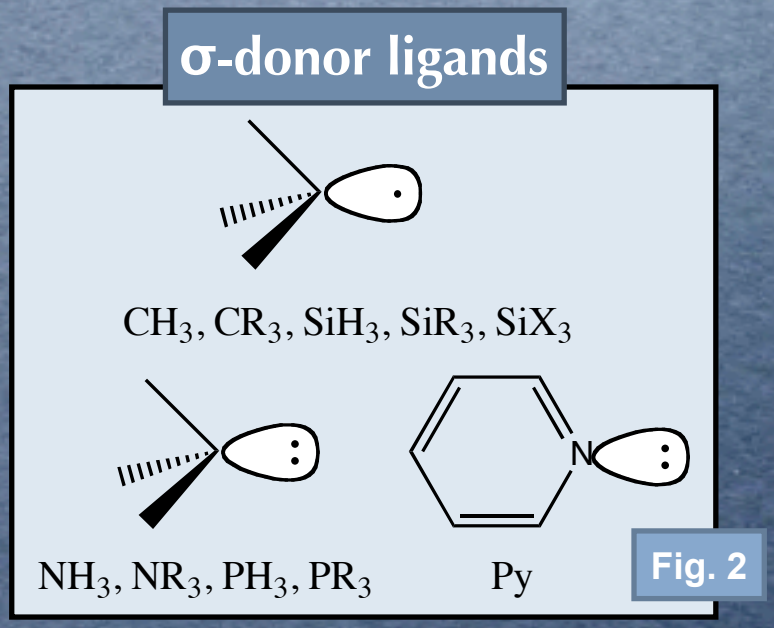
- 3 key types of ligand
- σ-donor ligands
  - ligands with electrons in σ-type orbitals

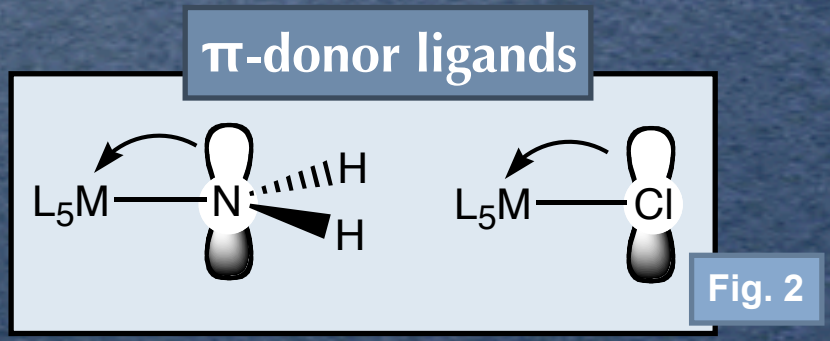


reminder

Revision: Ligands

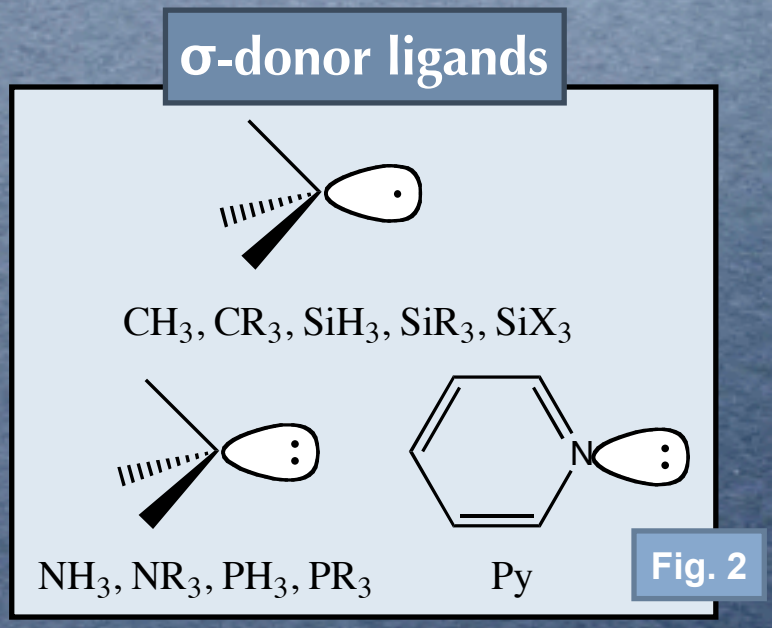
- 3 key types of ligand
- σ-donor ligands
  - ligands with electrons in σ-type orbitals
- π-donor ligands
  - ligands which have additional filled π orbitals

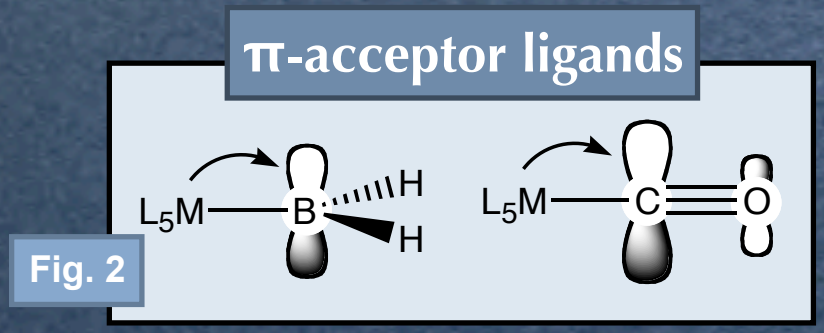


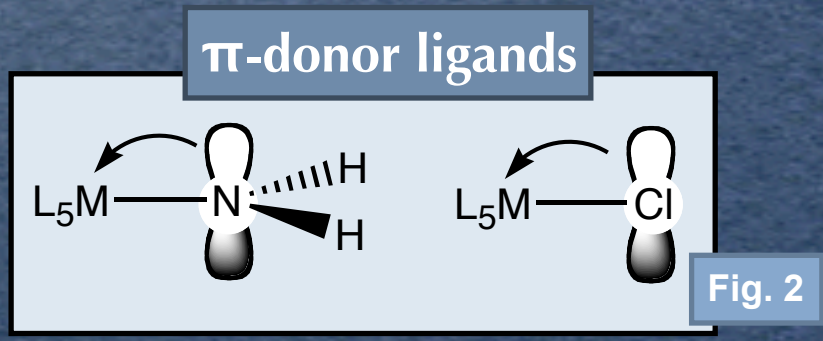


Revision: Ligands

- 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







Metal-Ligand Interactions

Dewar-Chatt-Duncanson bonding

- alkenes, alkynes => double or triple bond

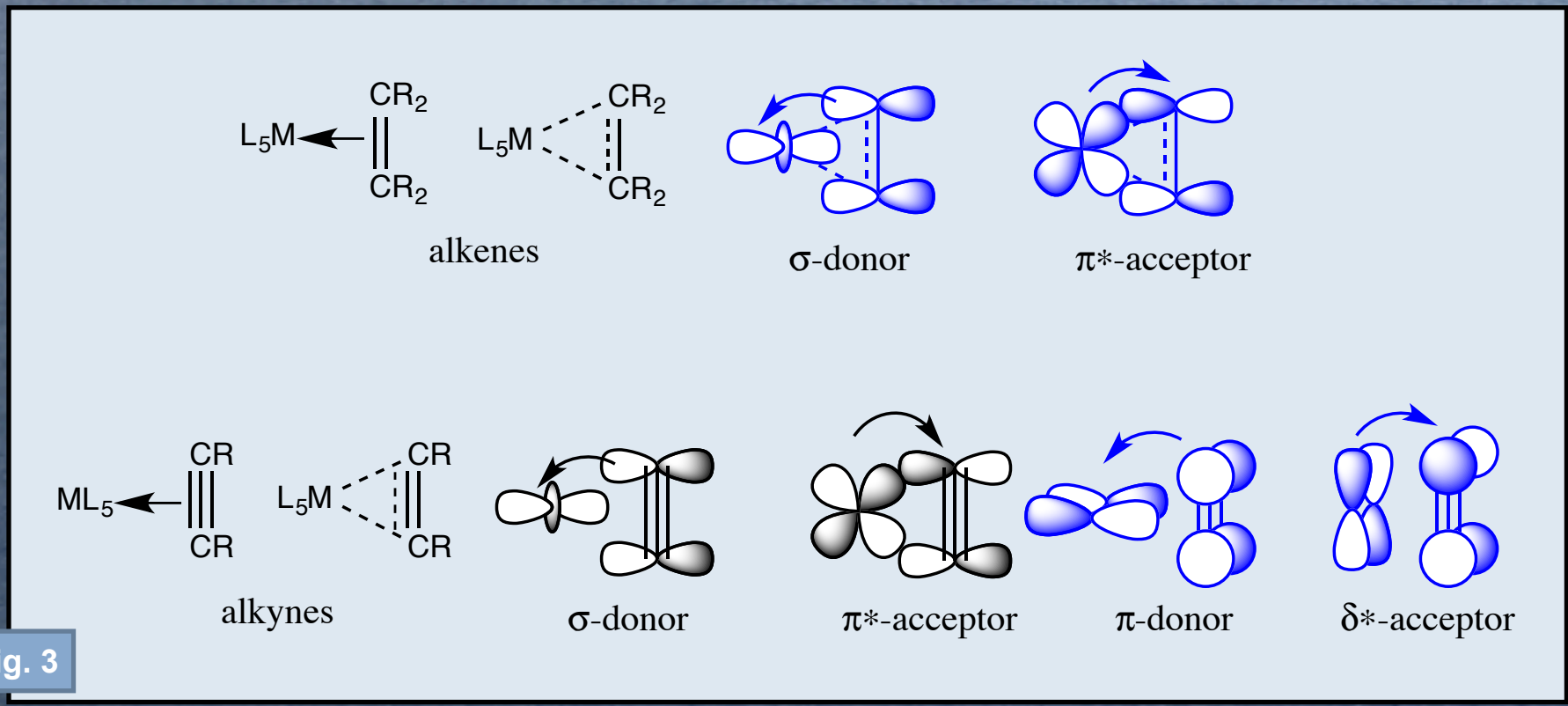
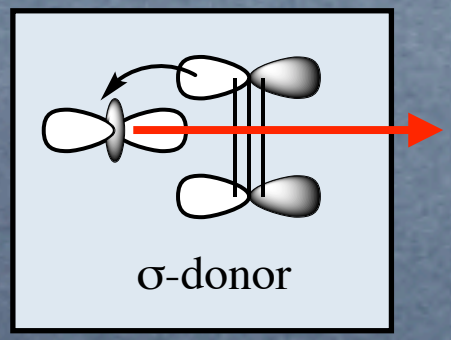
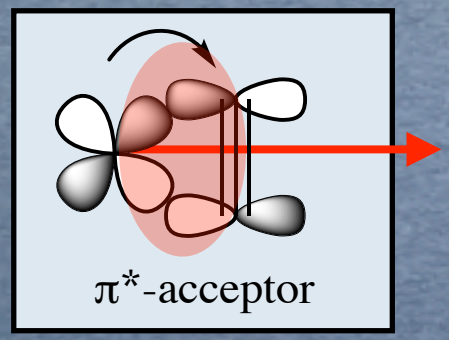


Fig. 3

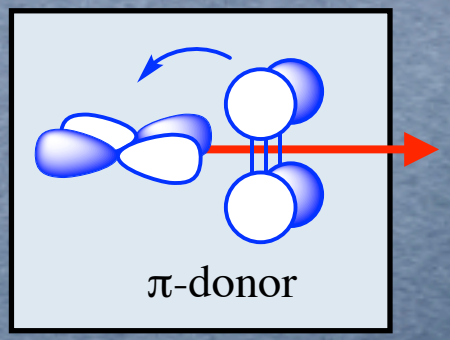
π- and δ- symmetry



rotate about "bond"
no phase change => σ



rotate about "bond"
2 phase changes => π



rotate about "bond"
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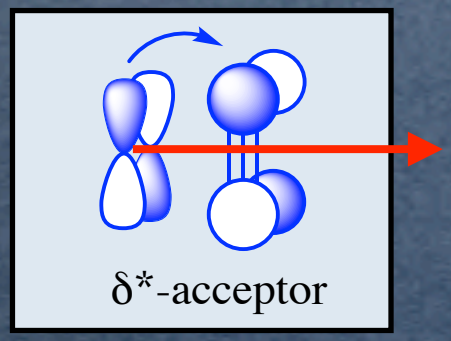
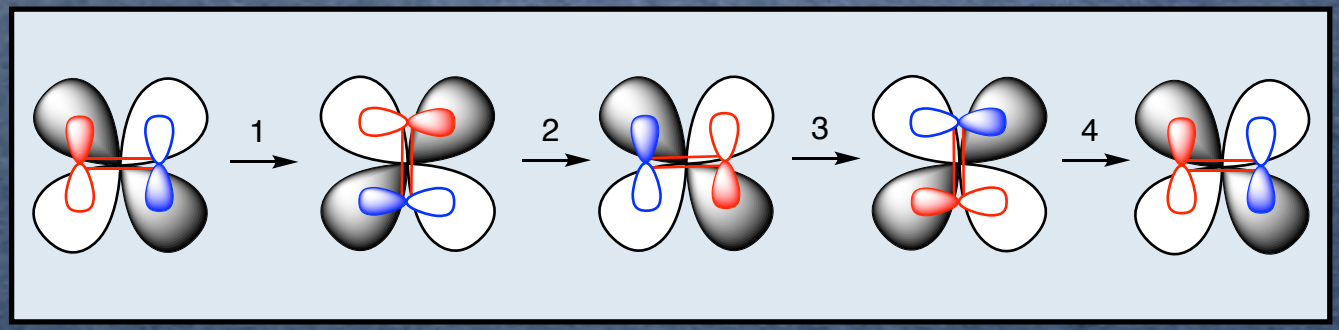
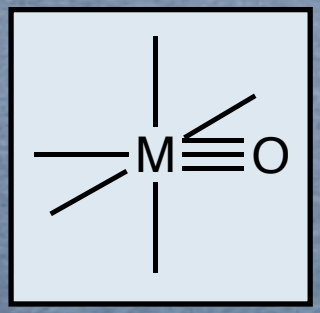




rotate about "bond"
4 phase changes => δ

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-}?

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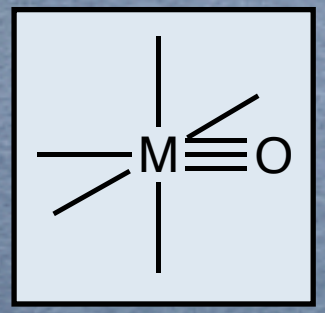
socrative quiz!

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 =>L'
  - 5 are σ-donor ligands =>L
- ALL ligands contribute to σ-framework
- L' contributes additional π-orbitals

part of σ-framework

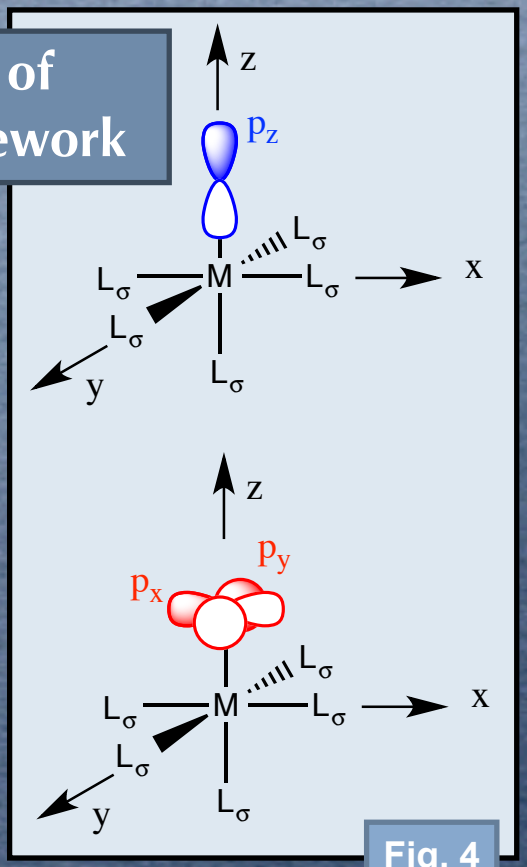


Fig. 4

π-donor fragment orbitals

Method: π-Ligands

- **first: work out reduced symmetry**

descent in symmetry O_h -> C_{4v}

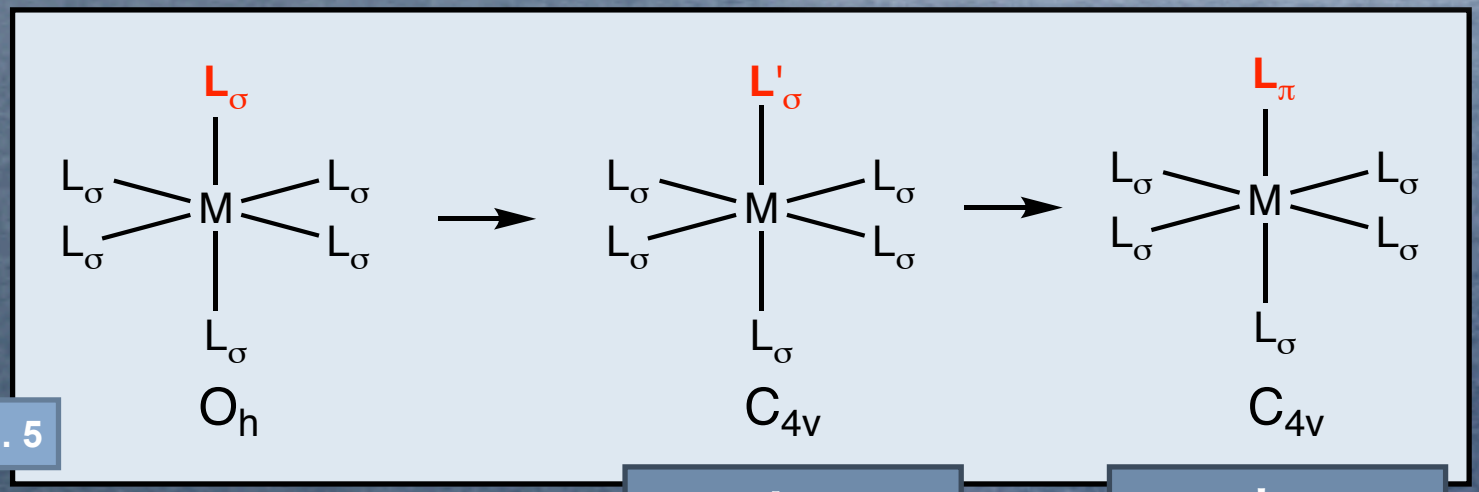


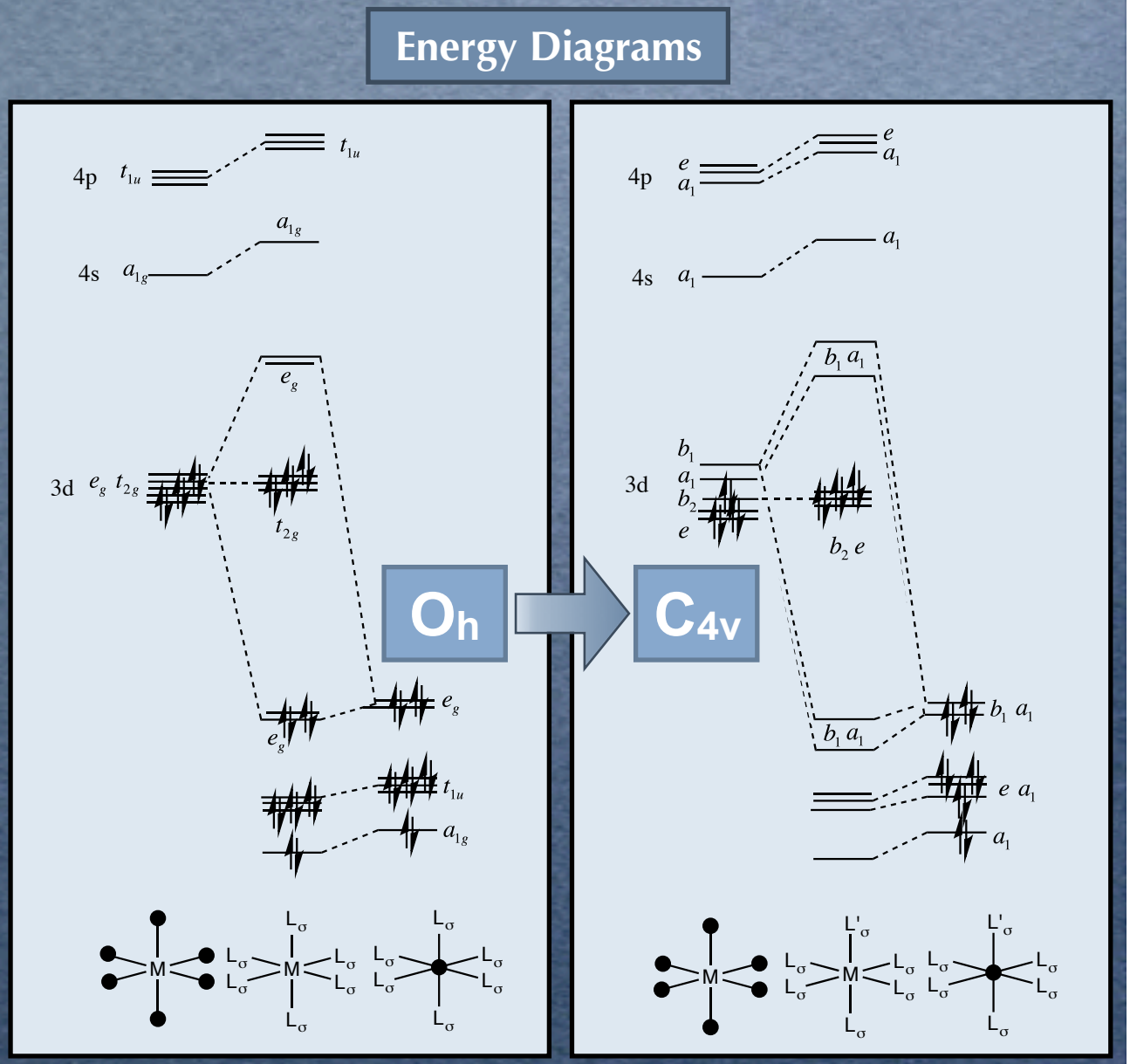
Fig. 5

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!



Reduce Symmetry

- C_{4v} diagram for σ-ligands

colour the L′ orbitals in your notes BLUE

the remaining orbitals are the L ligands orbitals

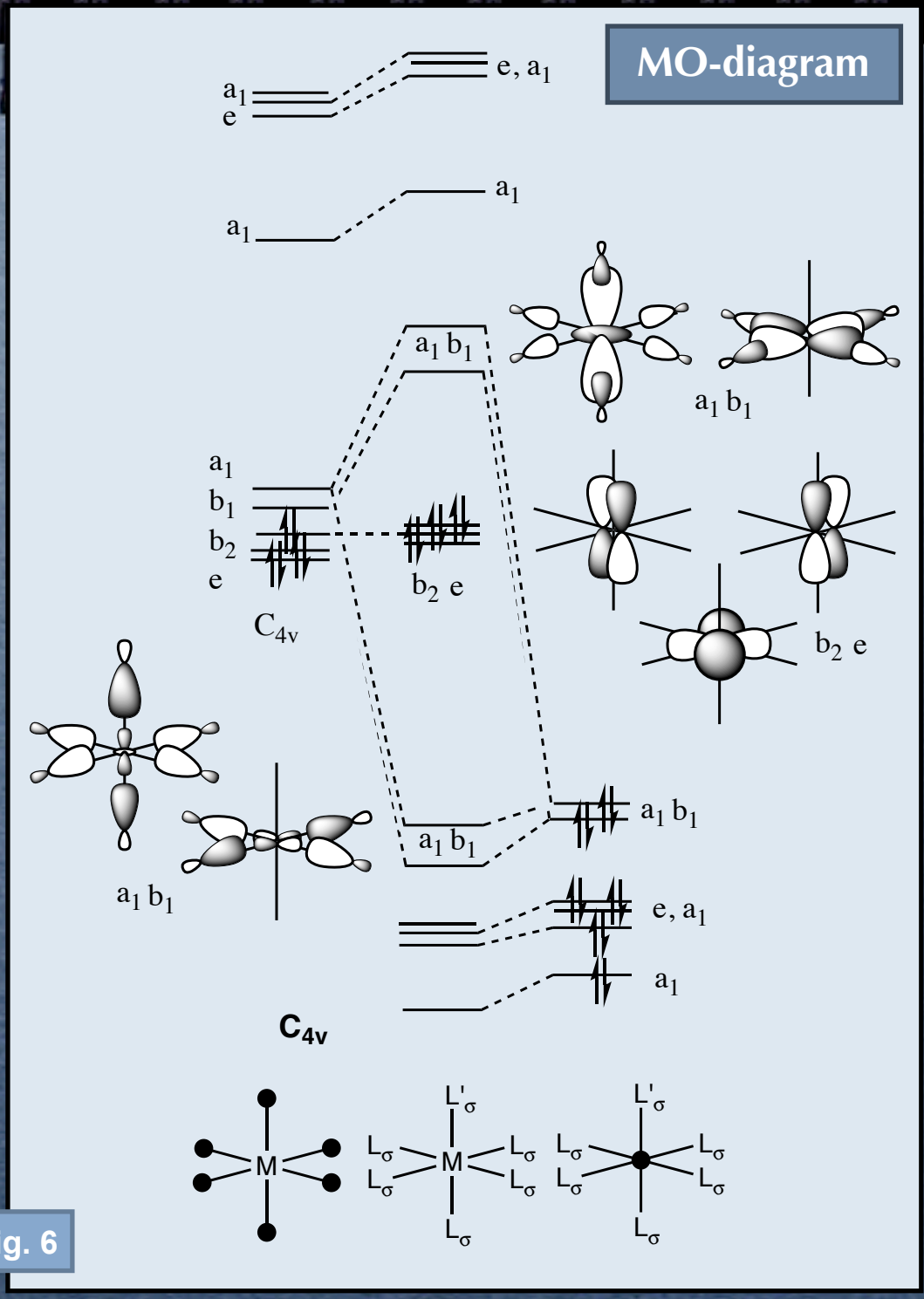
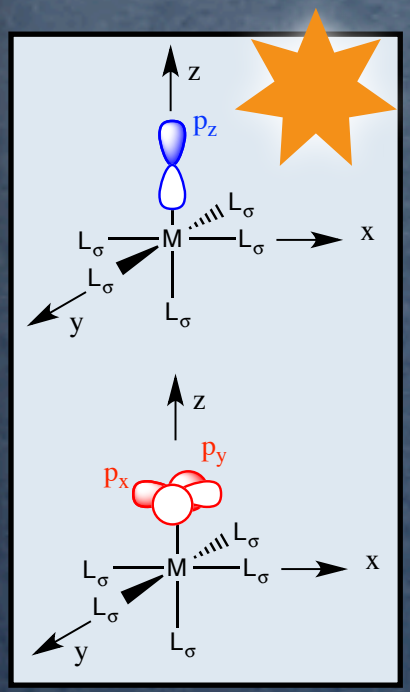


Fig. 6

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



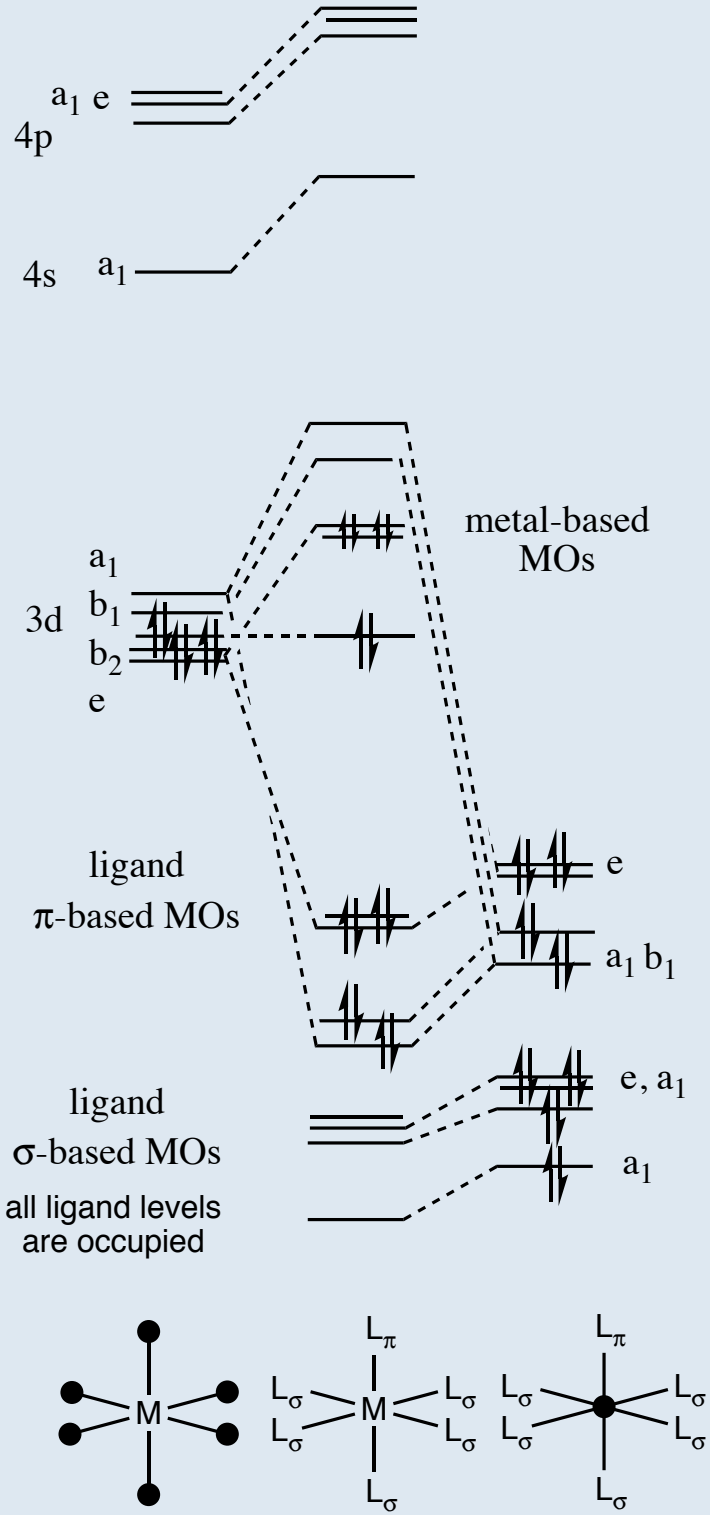
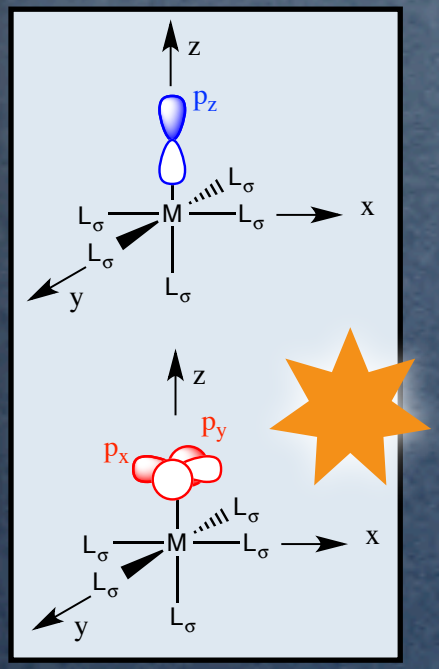


Fig. 7

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



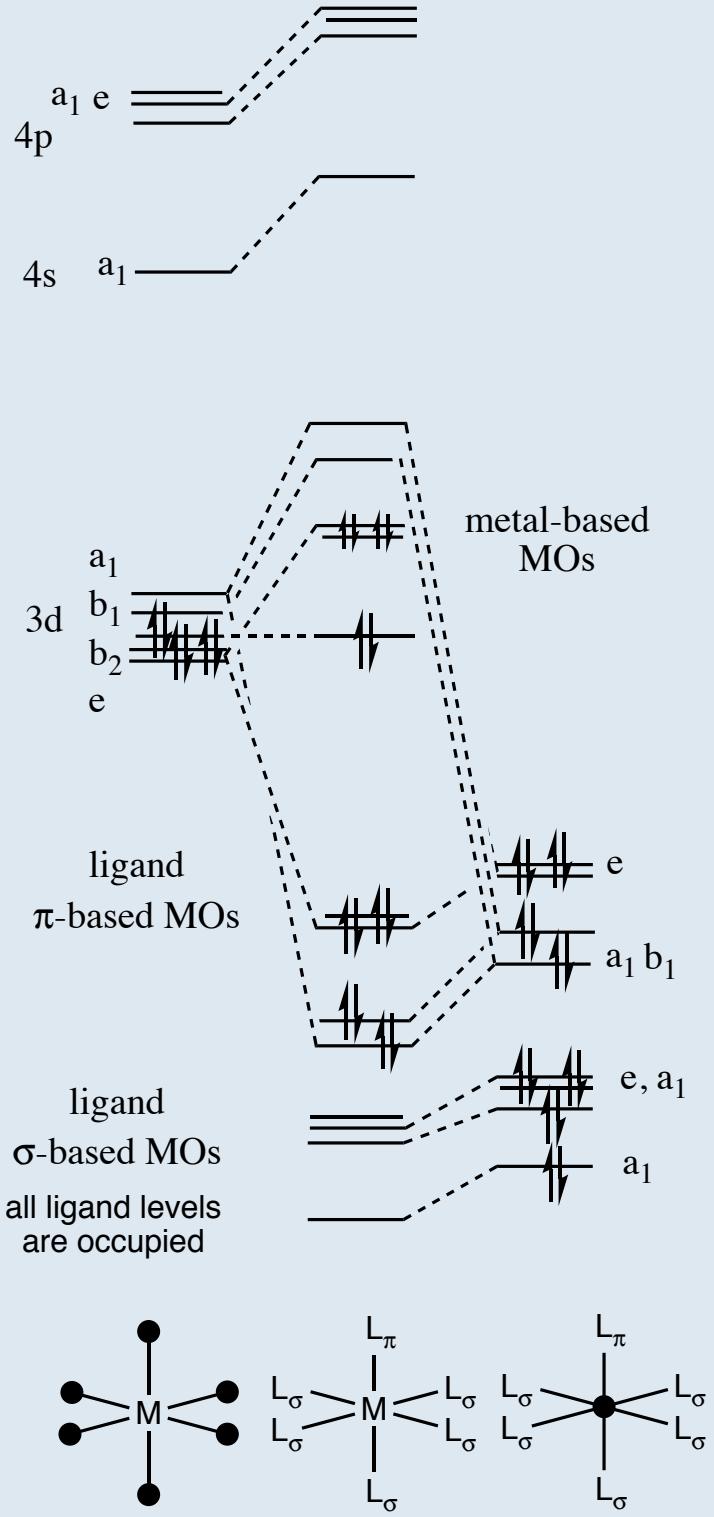


Fig. 7

π-Donor Ligand

- **where to position the FOs?**
  - CI is electronegative FOs lie below TM orbitals
  - pAOs non-bonding -> slightly above σ-donor FOs
- **(p_x,p_y,p_z) degenerate in CI**
  - p_z effects σ-donor framework slightly
  - p_x,p_y slightly above

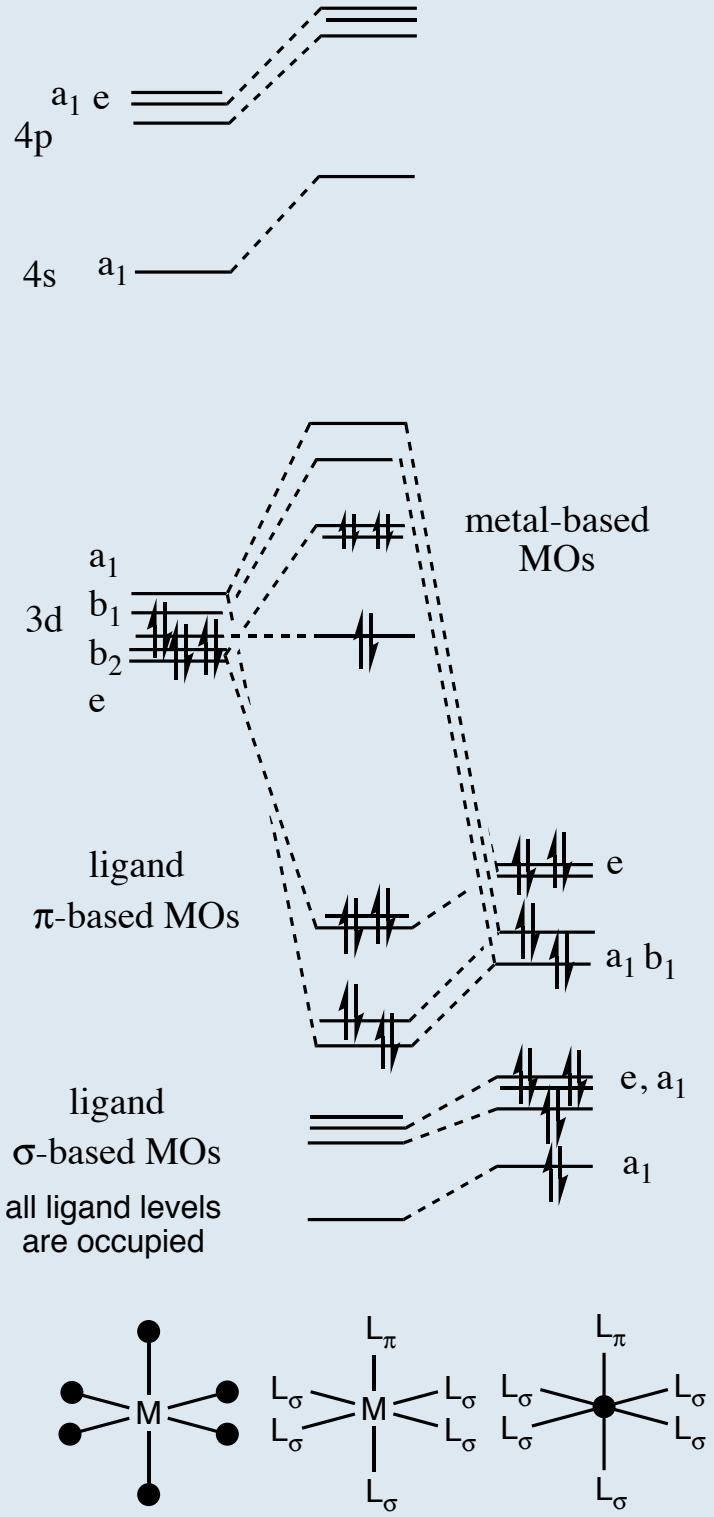


Fig. 7

π-Donor Ligand

- **new π-donor orbitals:**
  - form a bonding/antibonding pair
- **interaction**
  - π-orbitals higher energy
  - smaller Δε 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

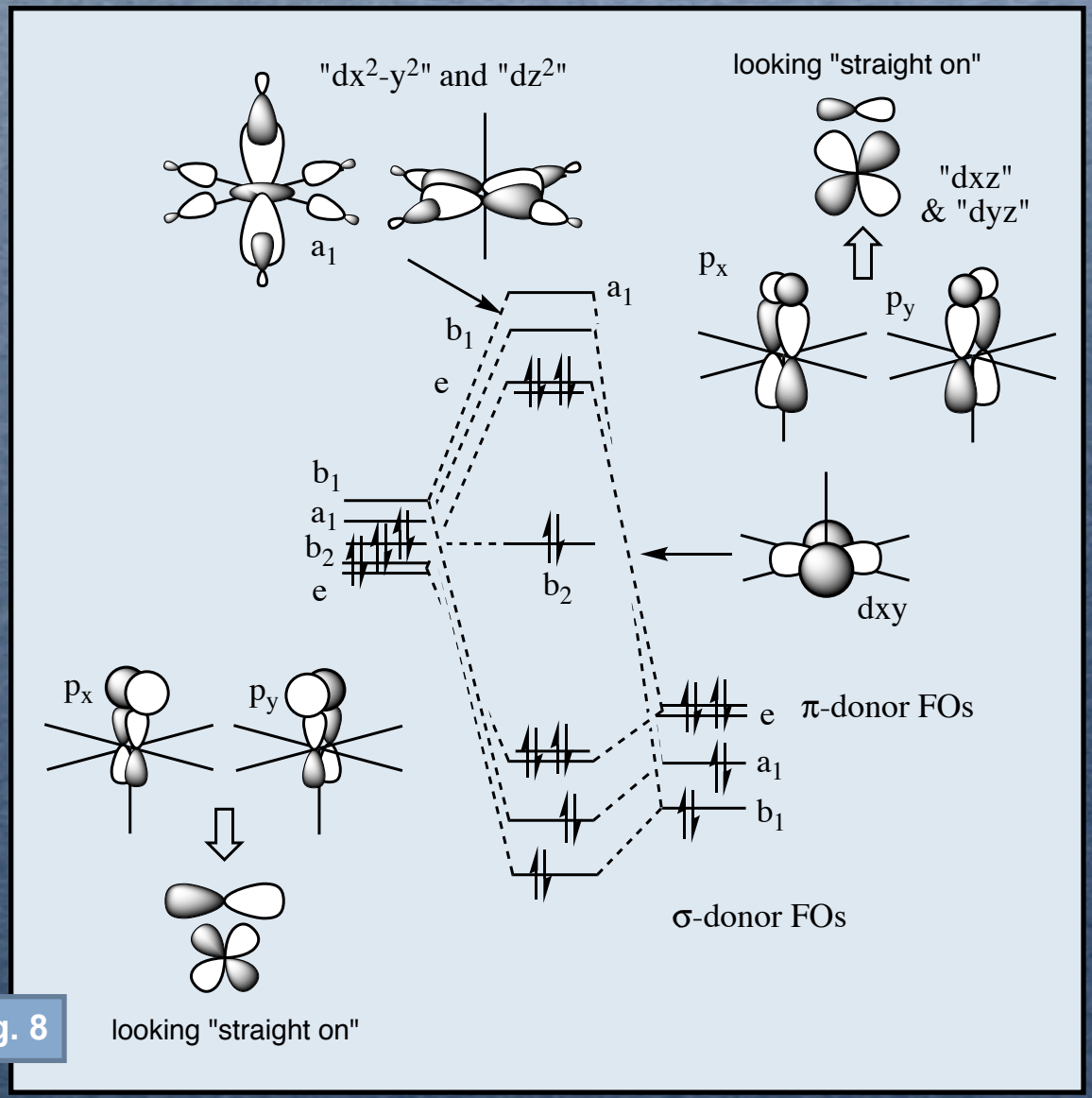


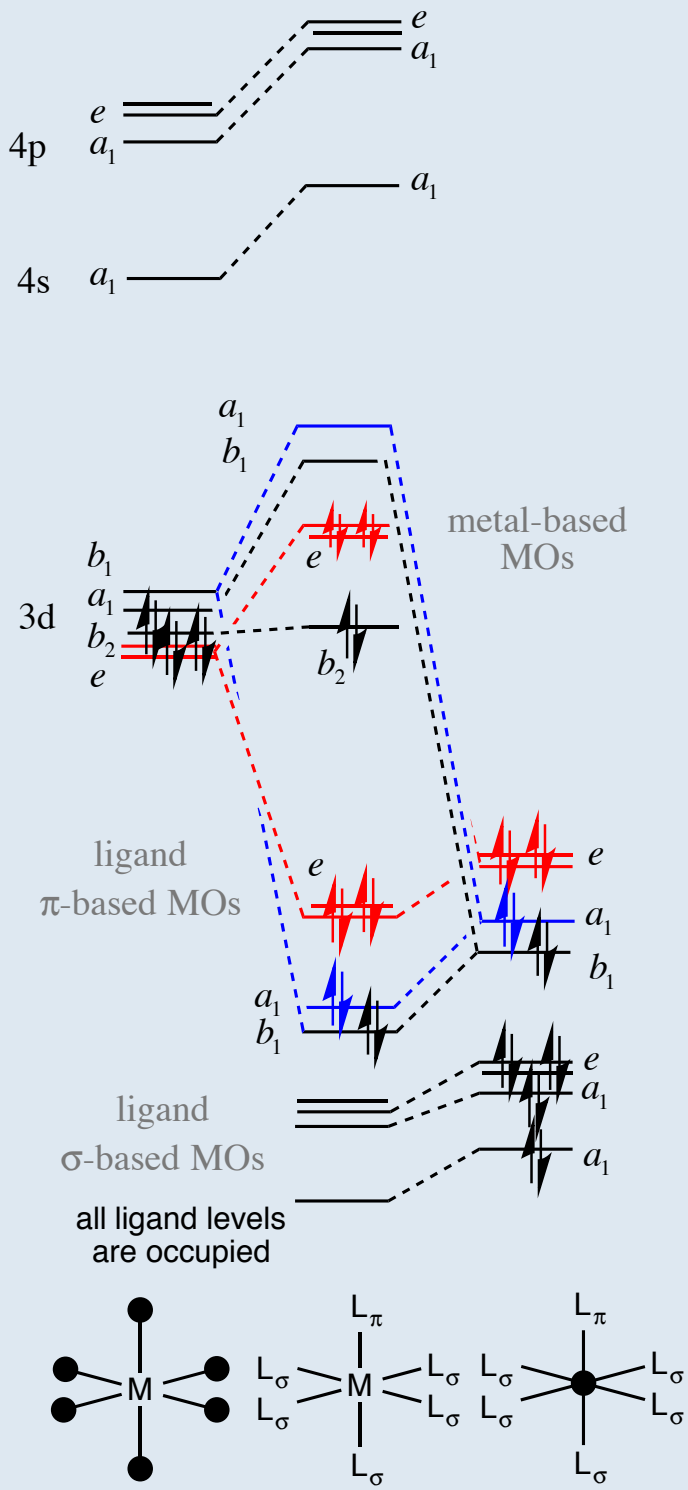
Fig. 8

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 b_2 are "t_{2g}"
  - a_1 and b_1 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 destablisation of "e" orbitals due to an antibonding interaction with π-FOs**

Important!

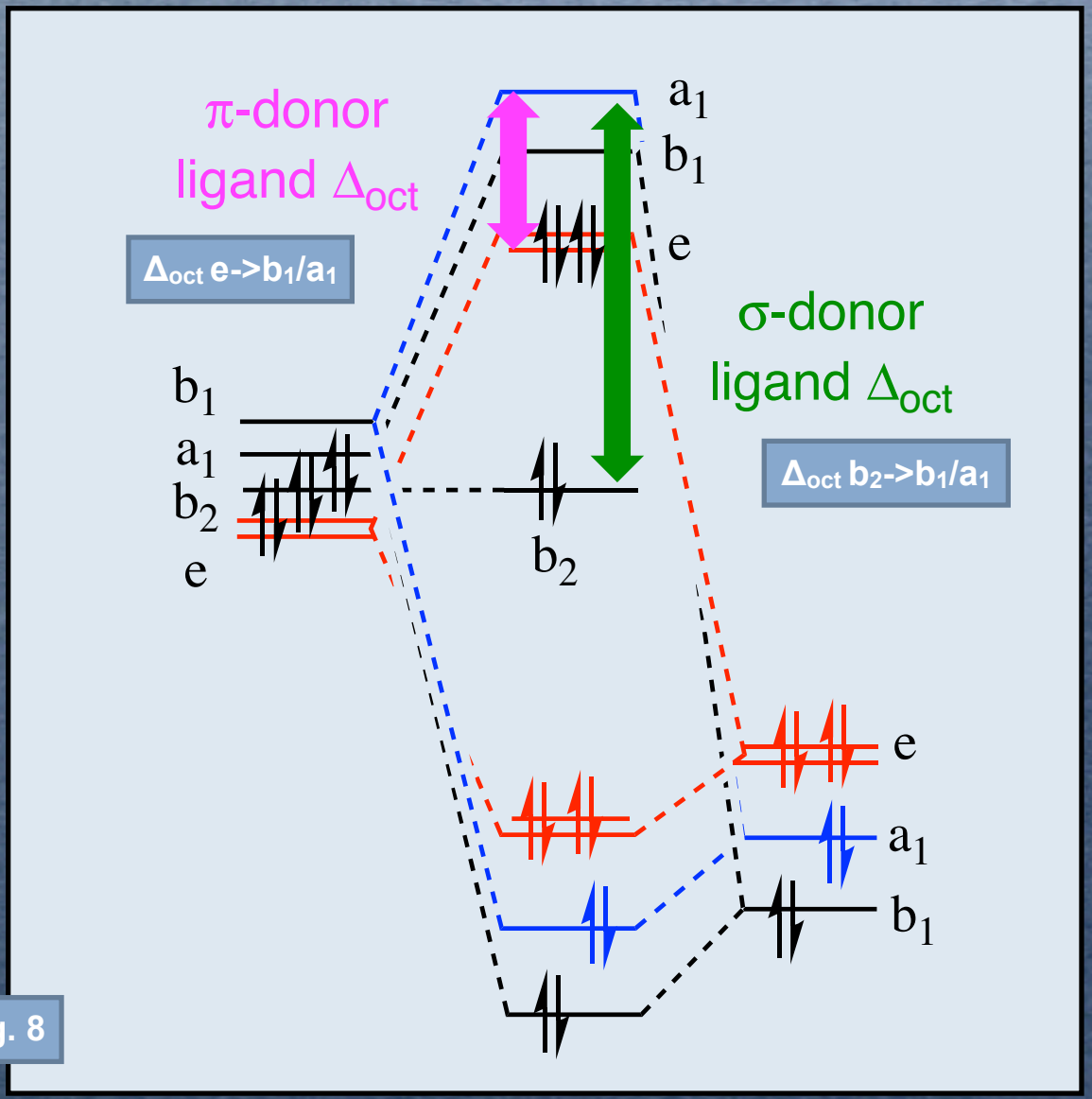


Fig. 8

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 dz^2 dx^2-y^2
  - stabilisation of the dAOs with lobes directed between the axes, ie dxy dxz dyz
- **Δ_{oct} measures splitting of e_g and t_{2g}**

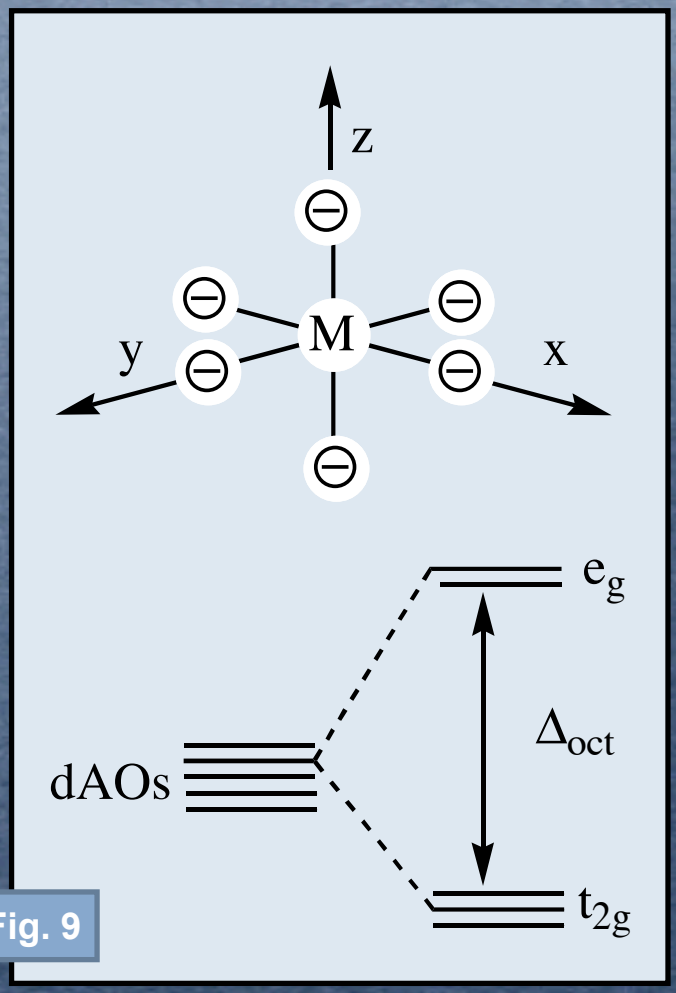


Fig. 9

Spectrochemical Series

- **O^{2-}**
  - **has a large charge => should generate a large Δ_{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

Fig. 10

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

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

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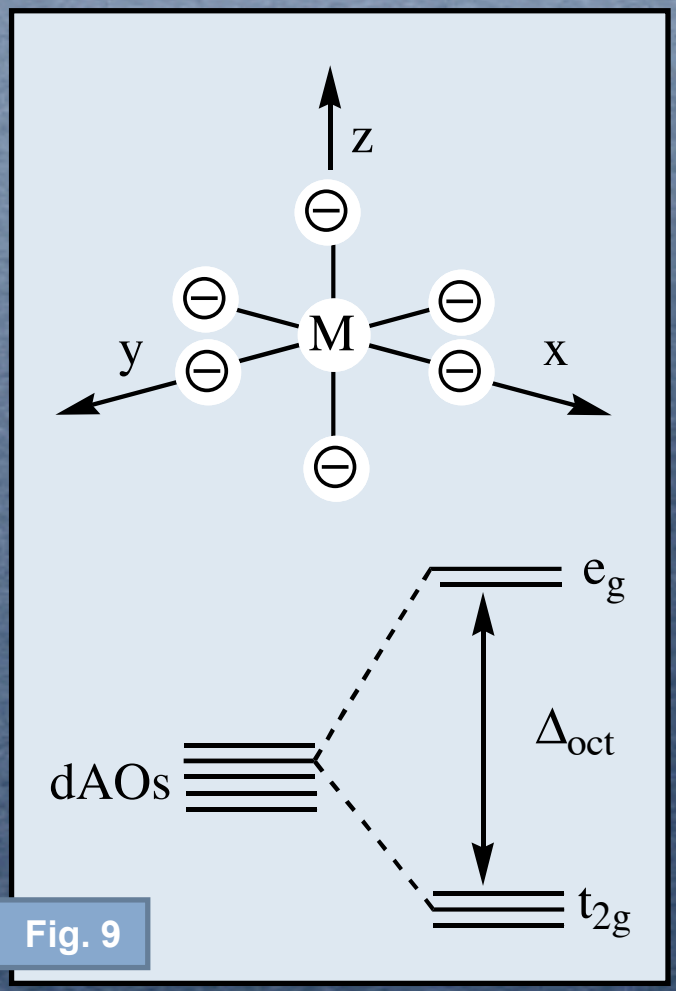

Fig. 9

Images from http://www.gemstone.org/gem-by-gem/english/

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}

$$I^- < Br^- < Cl^- < F^-$$
$$< OH^- < O^{2-} < H_2O$$
$$< NH_3 < NO_2^- < CH_3^-$$
$$< C_6H_5^- < CN^- < CO$$

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BUT:

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

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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)

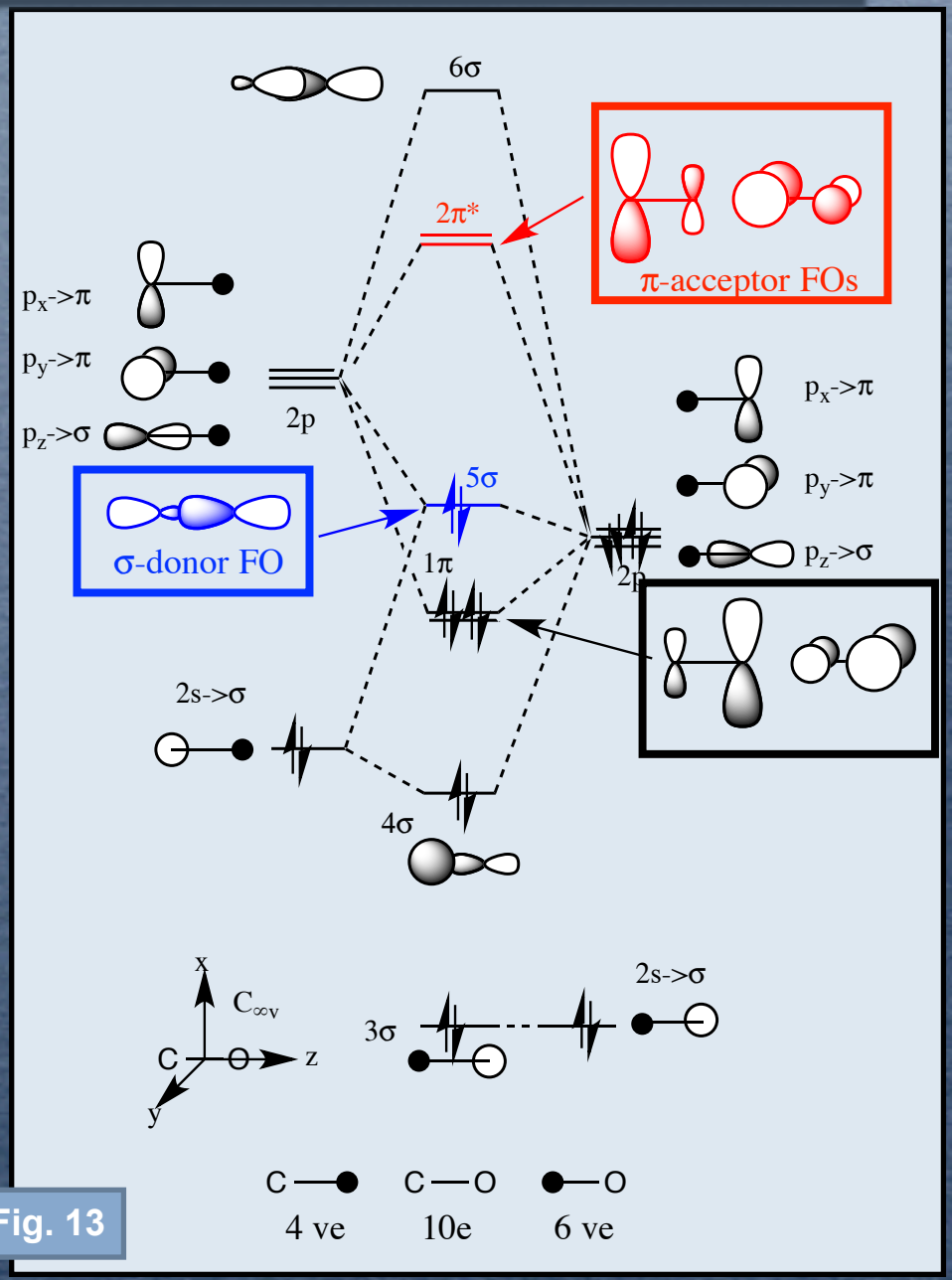


Fig. 13

π-Acceptor Ligand

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

σ-bonding orbitals

contribute to σ-frame work

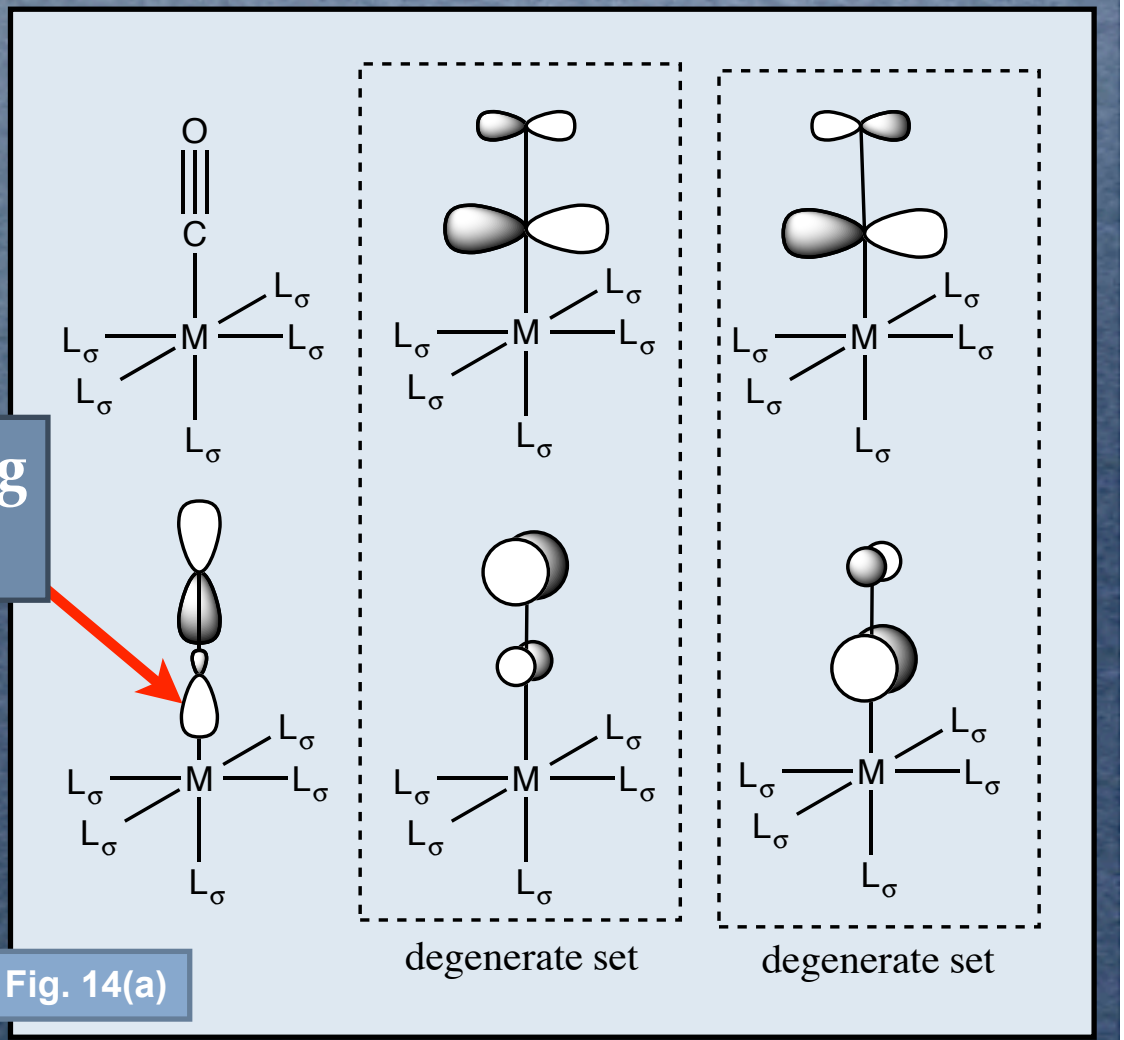


Fig. 14(a)

π-Acceptor Ligands

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

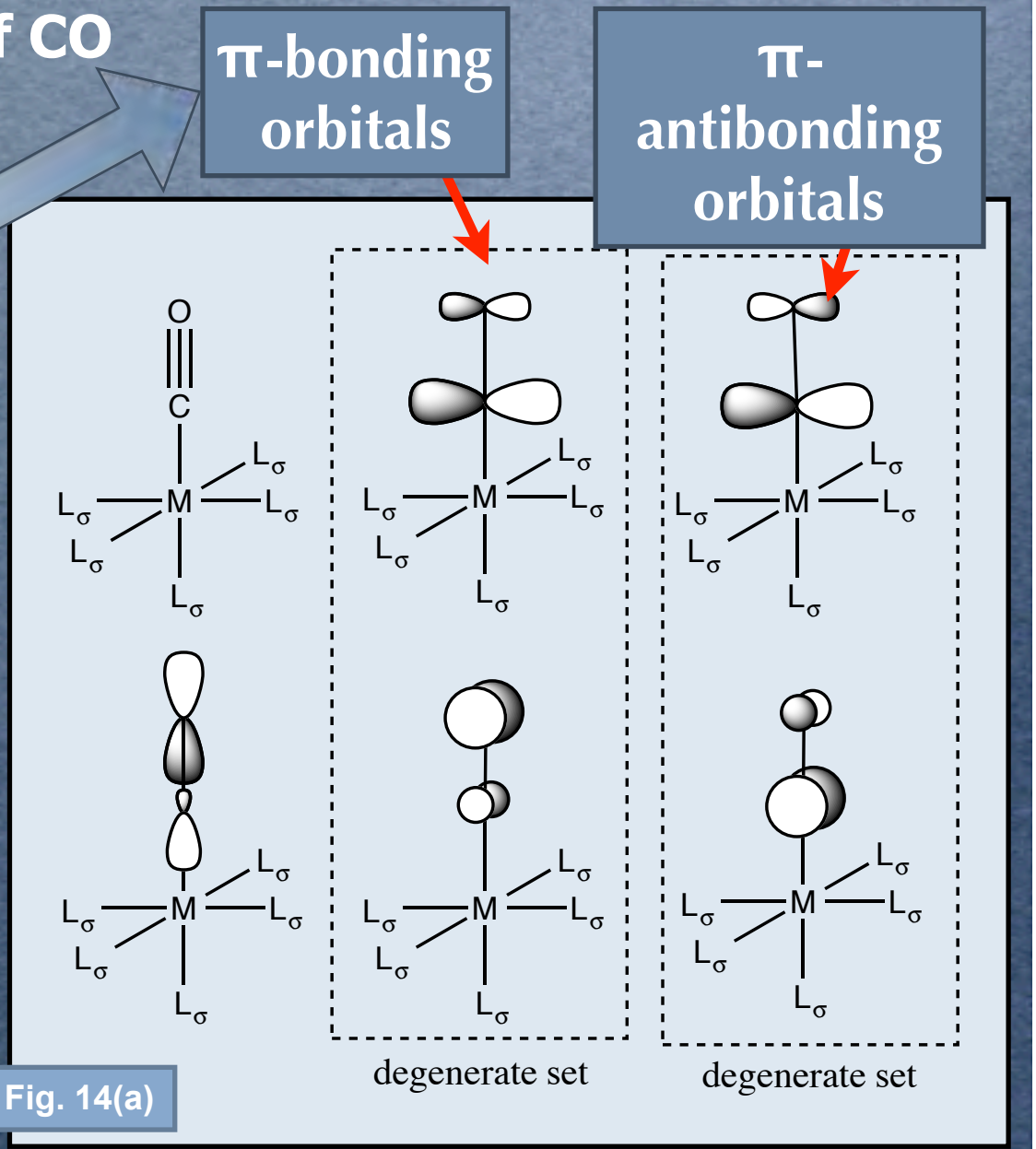


Fig. 14(a)

Symmetry Labels

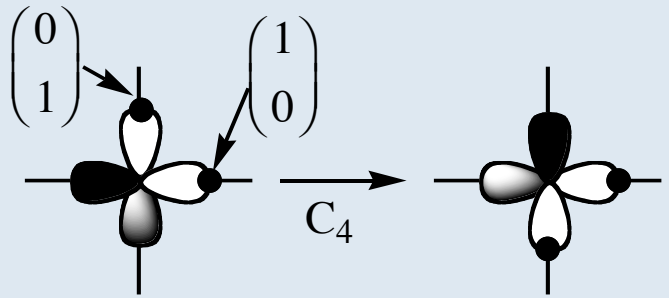
π-orbitals

- 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



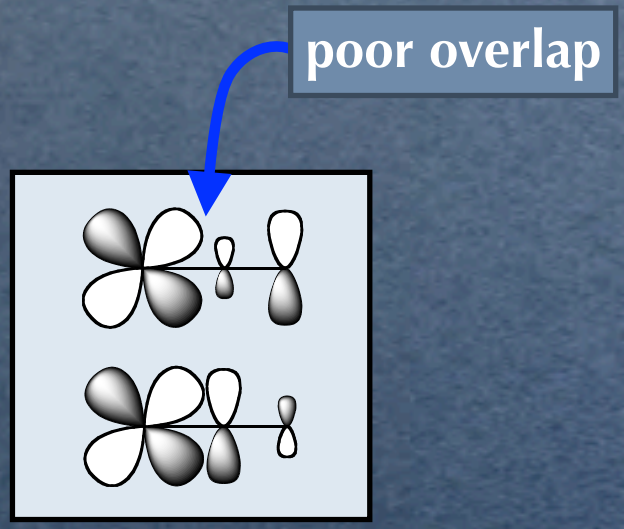
$$C_4 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \rightarrow \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$$

take the trace =0+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



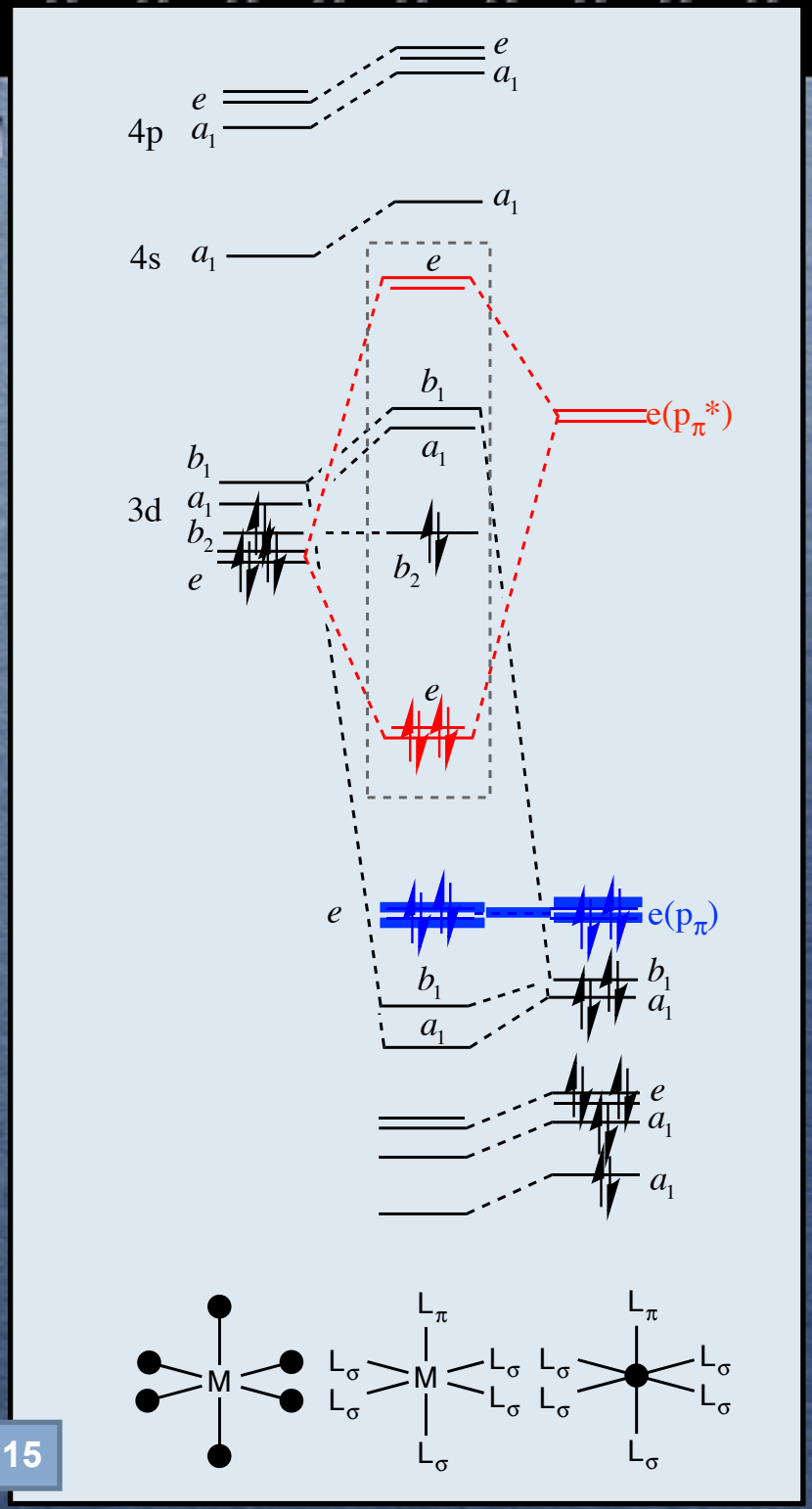
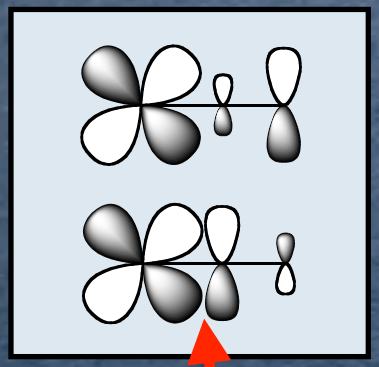


Fig. 15

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

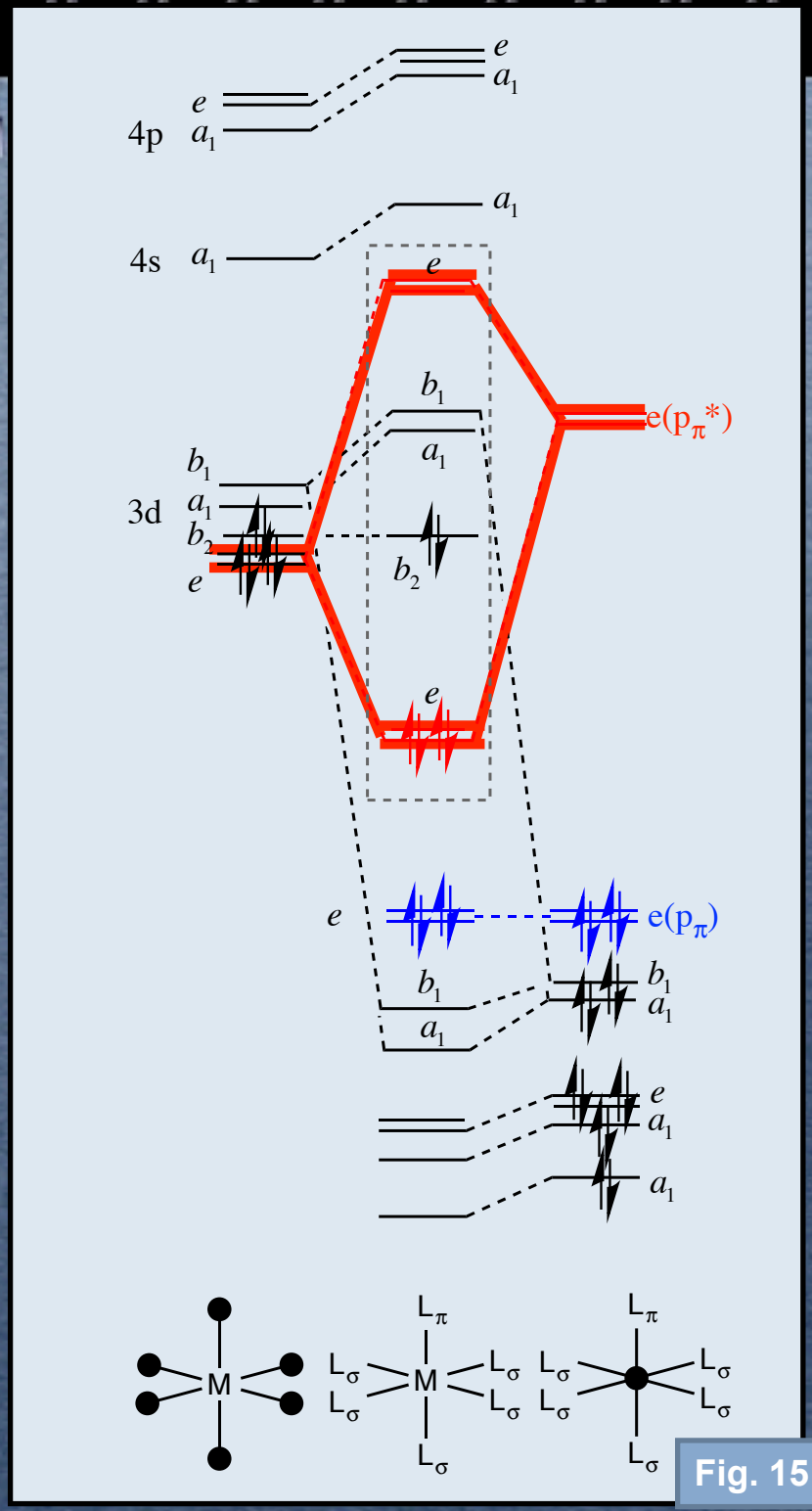


Fig. 15

The Important MOs

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

Important!

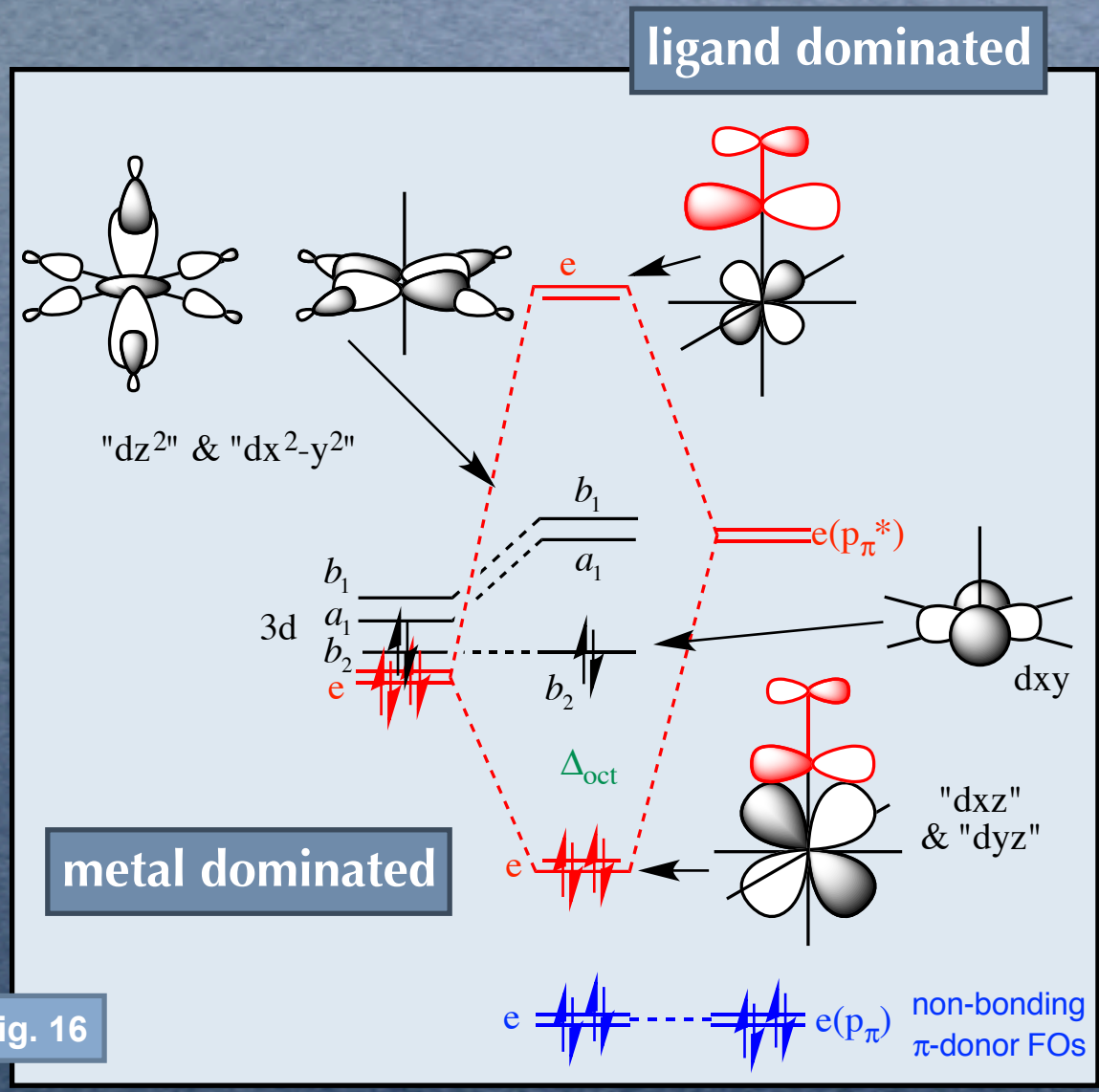


Fig. 16

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!

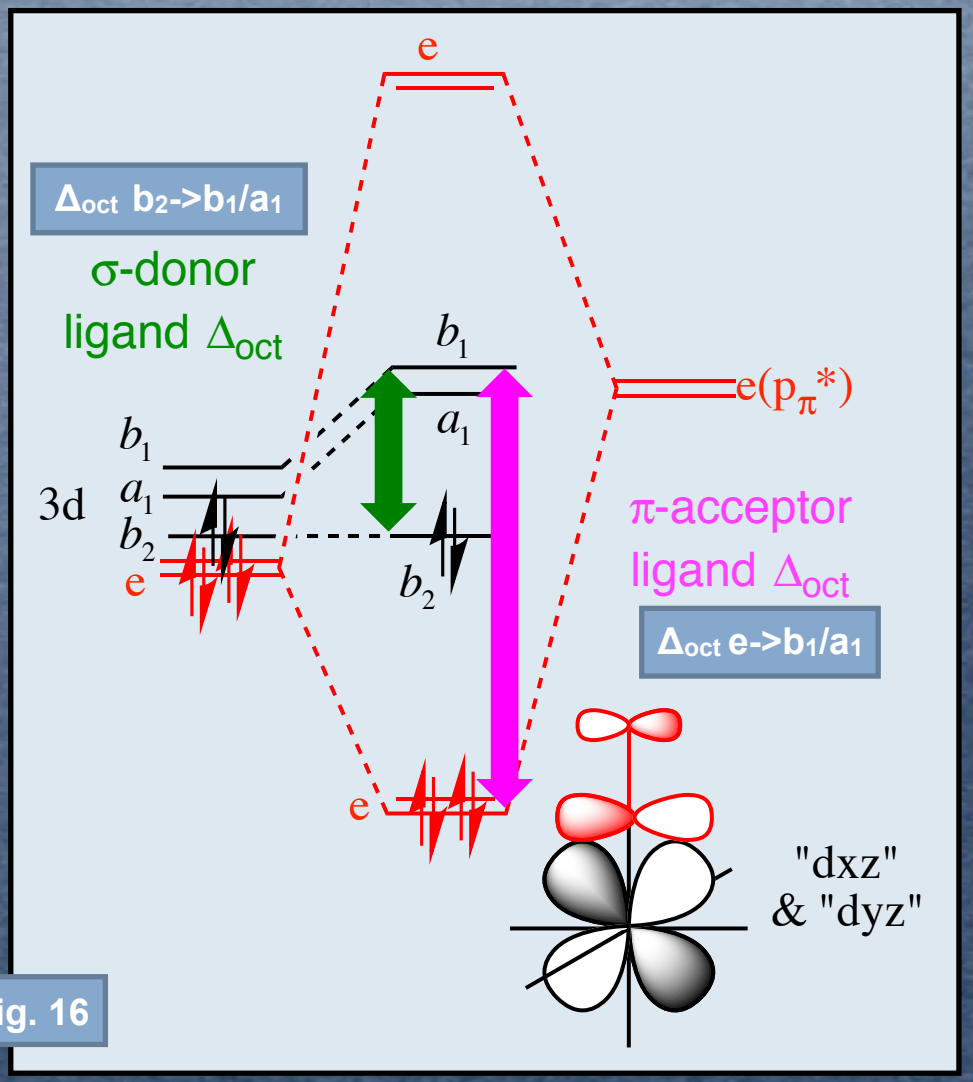


Fig. 16

Summary for Δ_{oct}

σ-donor ligands

$I^- < Br^- < Cl^- < NO_3^- < F^- < OH^- < O^{2-} < H_2O < NH_3 < en < NO_2^- < CH_3^- < C_6H_5^- < PPh_3 < CN^- < CO$

π-donor ligands

π*-acceptor ligands

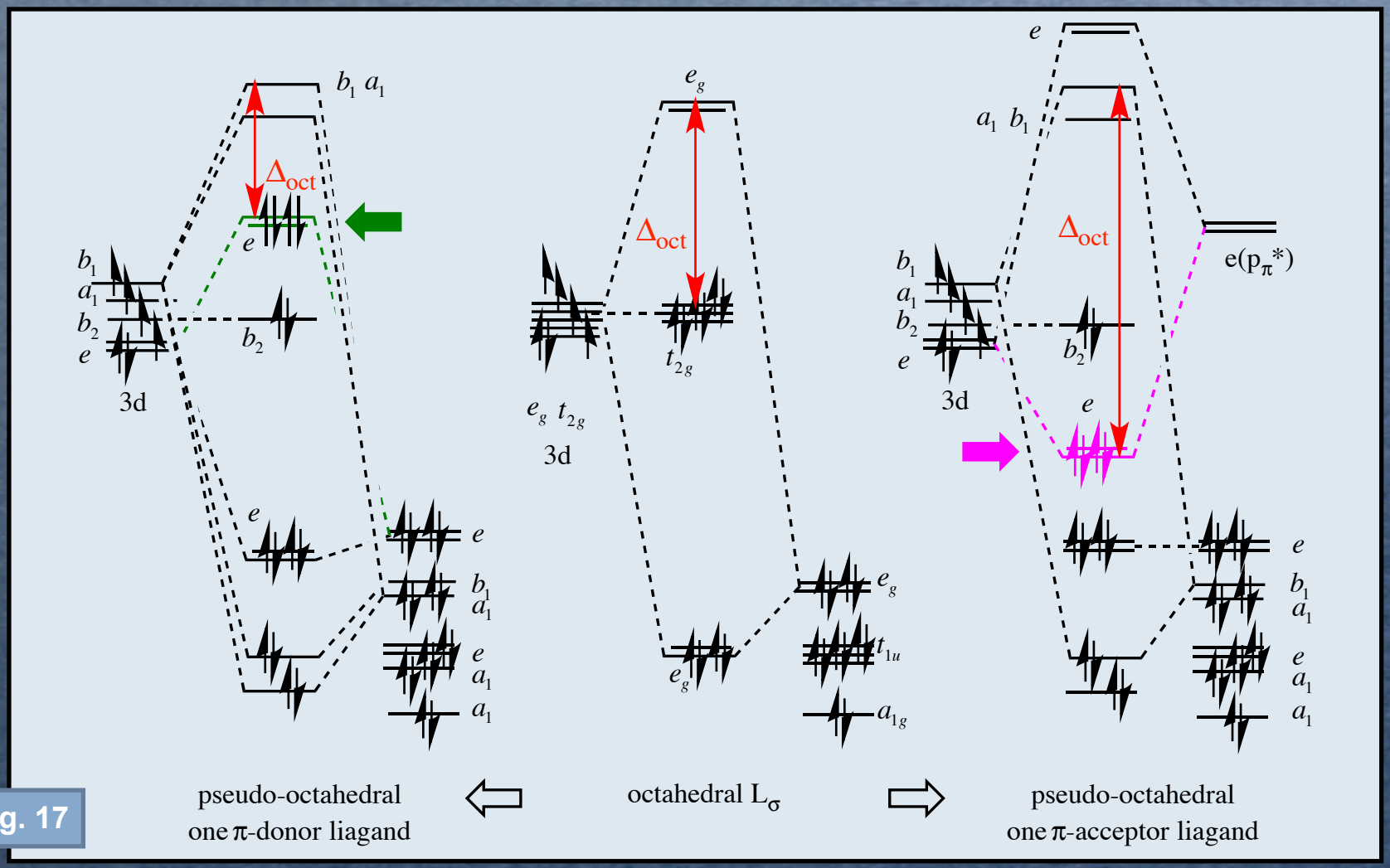


Fig. 17

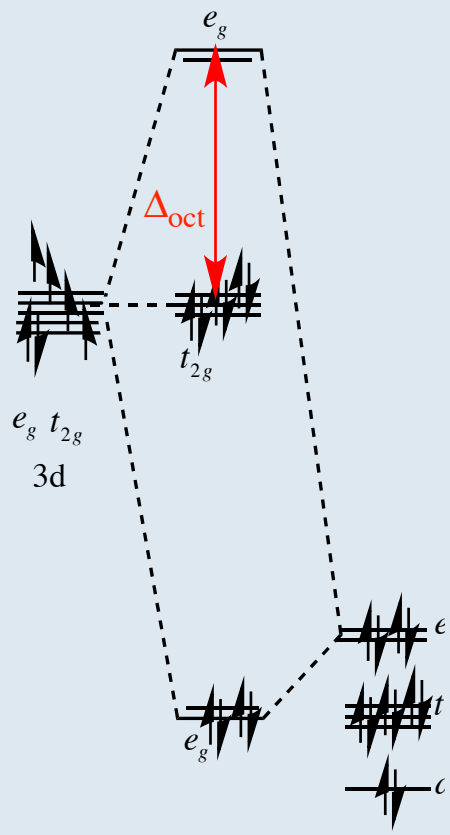
Summary for Δ_{oct}

σ-donor ligands

$I^- < Br^- < Cl^- < NO_3^- < F^- < OH^- < O^{2-} < H_2O < NH_3 < en < NO_2^- < CH_3^- < C_6H_5^- < PPh_3 < CN^- < CO$

π-donor ligands

π*-acceptor ligands



σ-donor "reference"

Fig. 17

Summary for Δ_{oct}

σ-donor ligands

$I^- < Br^- < Cl^- < NO_3^- < F^- < OH^- < O^{2-} < H_2O < NH_3 < en < NO_2^- < CH_3^- < C_6H_5^- < PPh_3 < CN^- < CO$

π-donor ligands

π*-acceptor ligands

π-donor
dAO dominate
antibonding e MO
up ↑↑↑
Δ_{oct} smaller

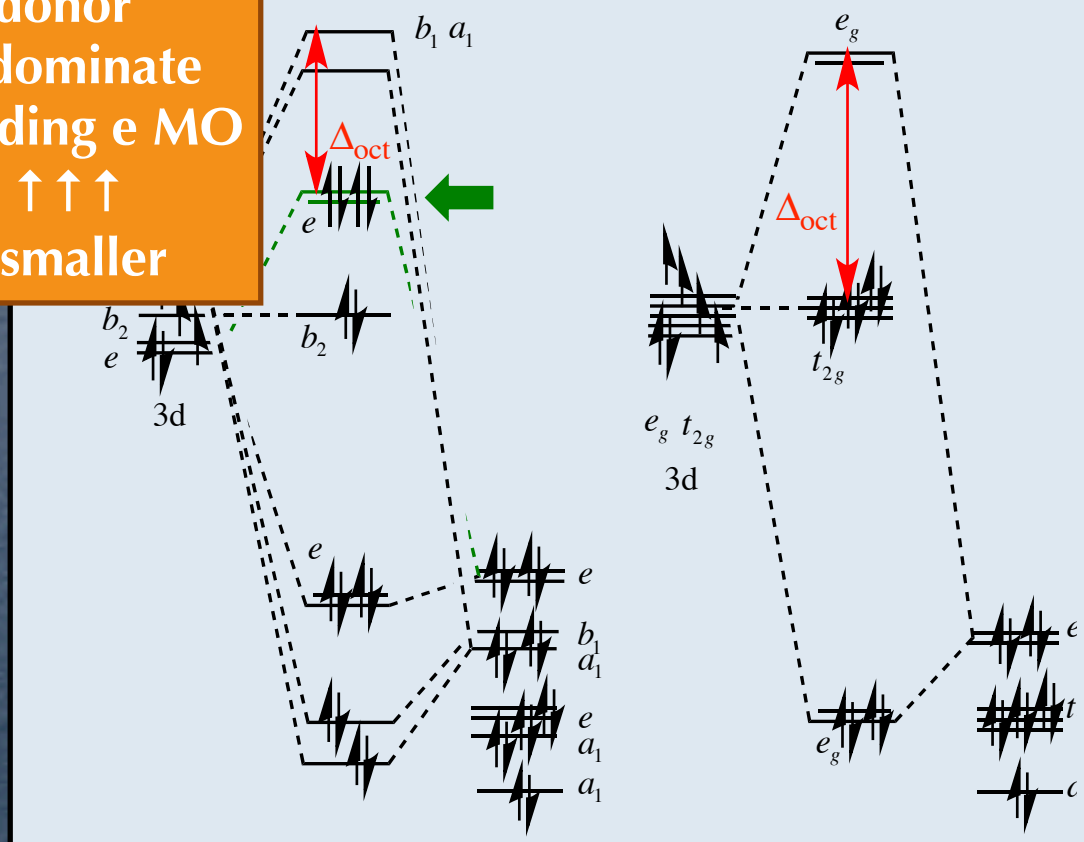


Fig. 17

Summary for Δ_{oct}

σ-donor ligands

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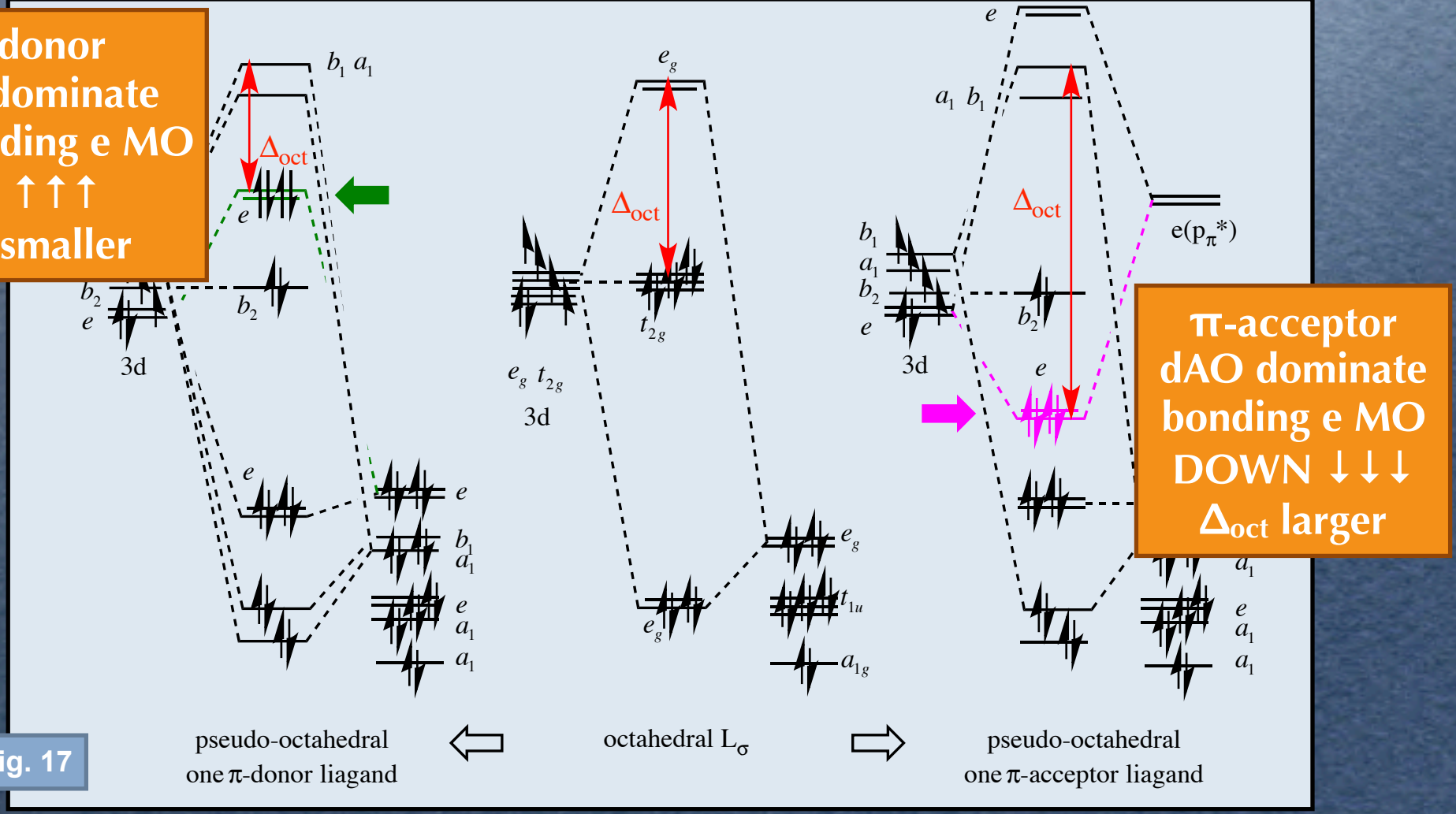
π-donor ligands

π*-acceptor ligands

π-donor dAO dominate antibonding e MO up ↑↑↑ Δ_{oct} smaller



π-acceptor dAO dominate bonding e MO DOWN ↓↓↓ Δ_{oct} larger

Fig. 17

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 spectrochemcial 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!!