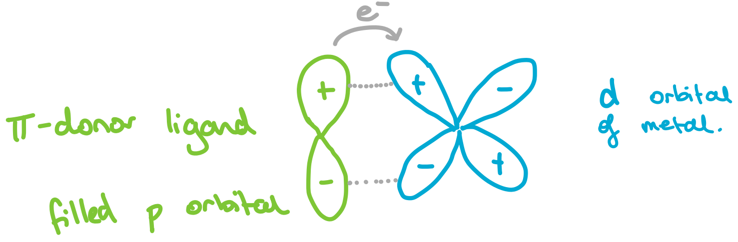
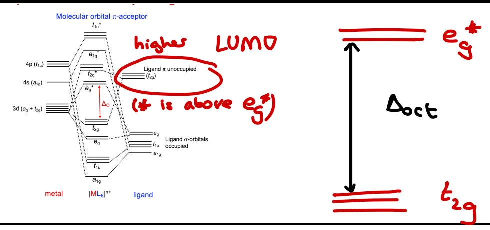
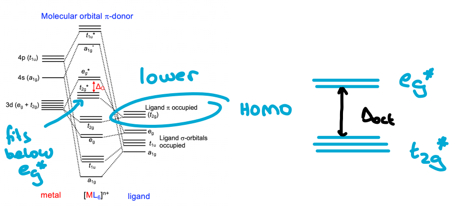
Complexes with π bonding:

The metal t_{2g} orbitals can overlap with ligand t_{2g} orbitals to form π-interactions. π-donor ligands (such as Cl, Br and I) donate electrons from their filled p orbitals to the metal and fill its empty d orbitals.



Some ligands that possess no orbitals with symmetry appropriate for π bonding, such as ammonia, are σ donors only. On the other hand, ligands with occupied *p* orbitals are potential π donors and may donate these electrons along with the σ-bonding electrons. For ligands with vacant π^* or *d* orbitals, there is a possibility of π back bonding, and the ligands may be π acceptors.

π acceptor	Strong Field Large Δ_{oct}	Have empty π orbitals Vacant antibonding orbitals LUMOs are generally antibonding	CO CN	
π donor	Weak field Small Δ_{oct}	Have filled π orbitals	Cl Br I	

Organometallic Chemistry: chemistry with carbon-metal bonds.

Coordination Compounds	Organometallic Chemistry
Includes carbon-monoxide coordination complexes	
Can be charged molecules	Generally charge-neutral
Behave like salts	Behave more like organic compounds
Often soluble in water	Often soluble in organic solvents (not water)
	Air and moisture sensitive
Often have higher melting points	Have low melting points

Organometallic complexes:

s and *p* block metals	mainly σ bonding.
d block metals	π bonding is significant

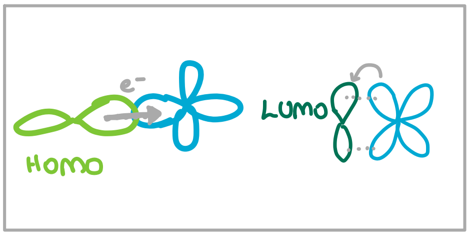
Spectrochemical Series reflects π bonding:

Halides $< OH^- < OH_2 < NH_3 < PPh_3 < CN^- < CO$

π-donor π acceptor

Dewar–Chatt–Duncanson Model:

$:\overset{\ominus}{M}-C\equiv O^{\oplus} \Longleftrightarrow M=C=O:$



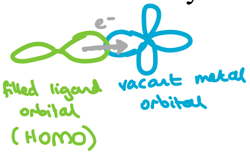
Combination of donation and back-bonding has a synergistic effect.

- Vacant π orbitals can accept residual electron density from the metal
- Consequent back-donation occurs to fill

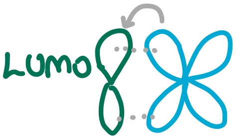
"back donation" – from filled metal orbital (since metal is in a low oxidation state)

The filled metal *d* orbital can donate electron density back to the empty π* orbital of an alkene or ligand to form a π bond.

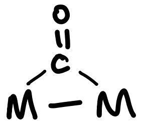
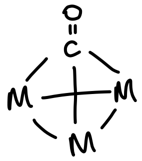
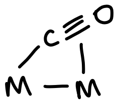
σ bonding is organic in character, from ligand HOMOs.



π back bonding from filling metal orbitals.



Bonding modes of metal carbonyl complexes:

$M-C\equiv O$ Terminal	 Bridging μ^2–CO	 μ^3–CO	

The more backdonation, the lower the wave number (in IR) and weaker the CO bond.

more metal giving e⁻ back to ligand
bridging and μ^3 COs have weaker C=O bonds; can identify these via IR spectra

↳ $C-O$ weaker

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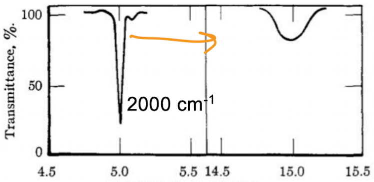
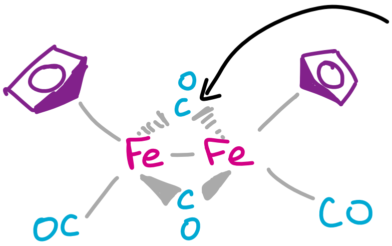


Fig. 1.—Infrared spectrum of $Cr(CO)_6$ vapor.

cm^{-1} = 10,000/microns

Example: Bridging CO and Fe-Fe bond:

lower energy bridging carbonyl



open this O to electrophilic attack.

Example. Bridging CO and Co–Co: