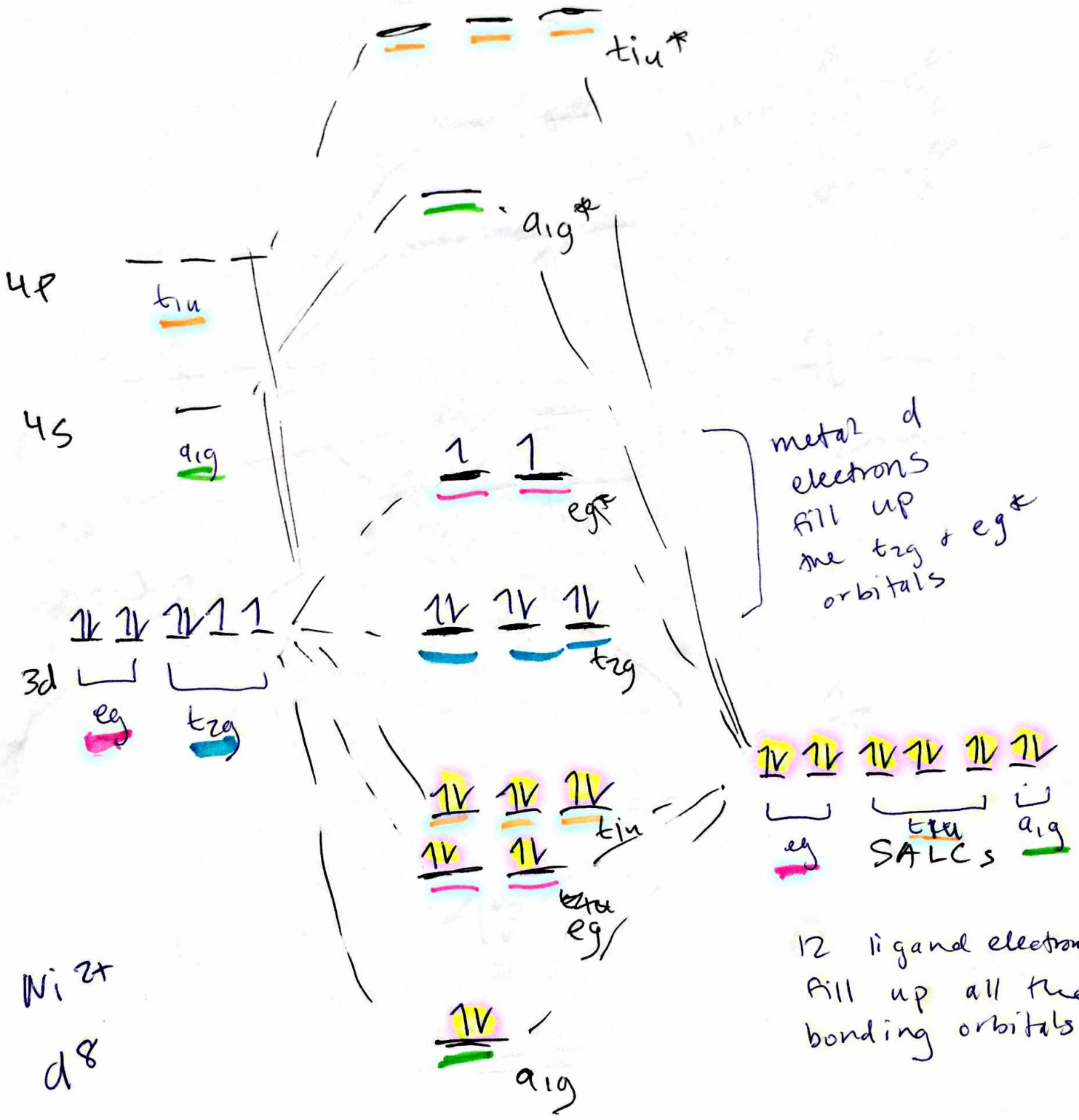
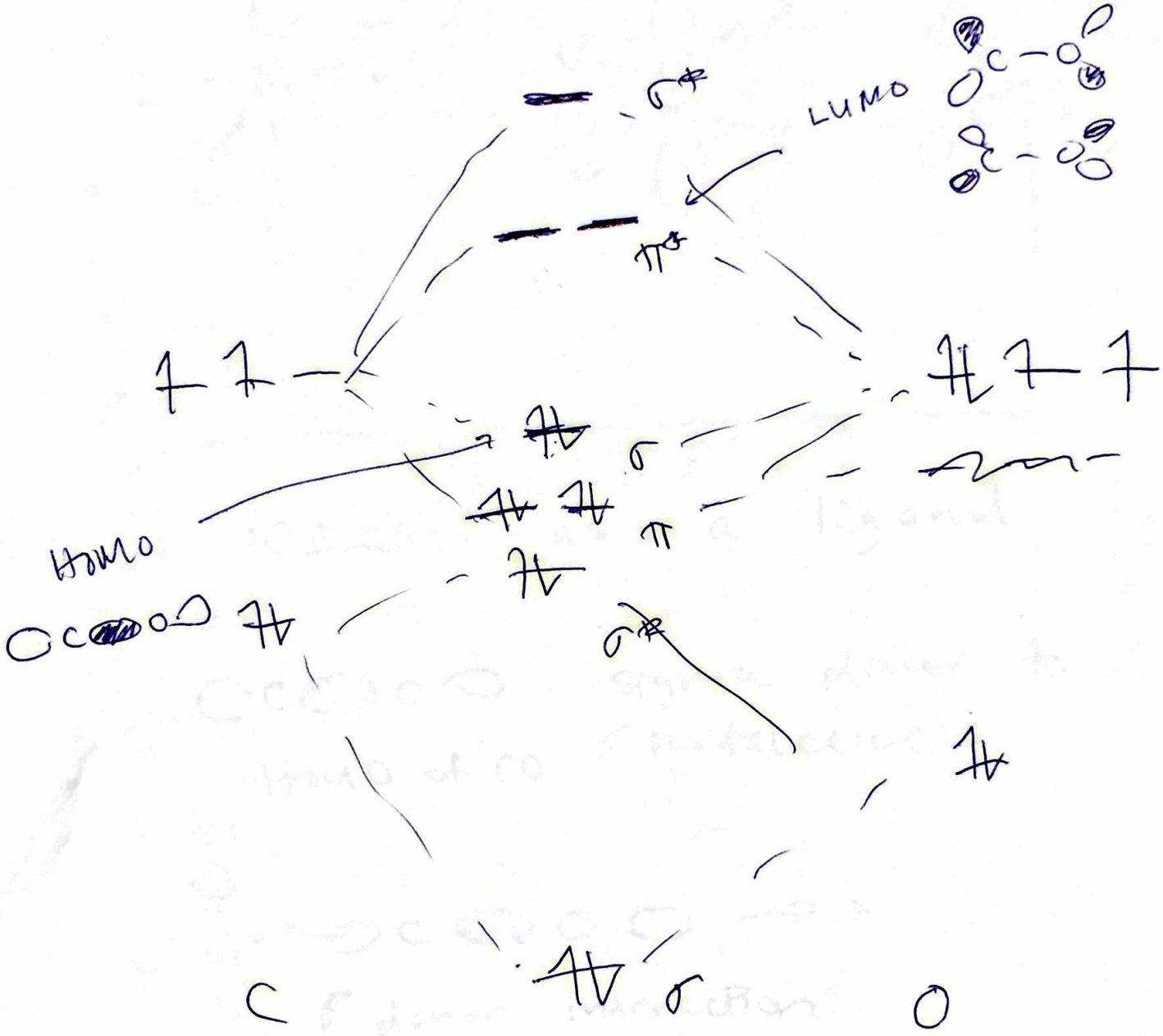
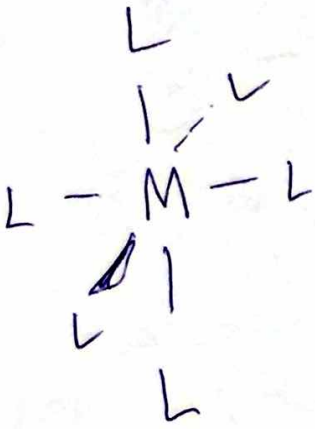
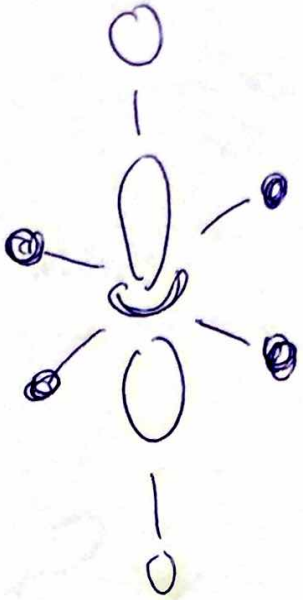
Lecture 15 CH431 10/18/16

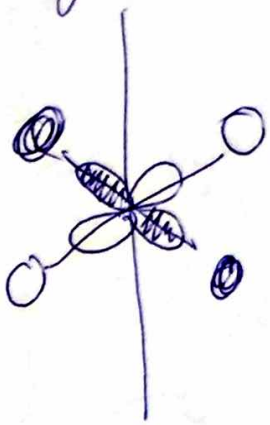



LUMO
HOMO
π*
σ*
π
σ





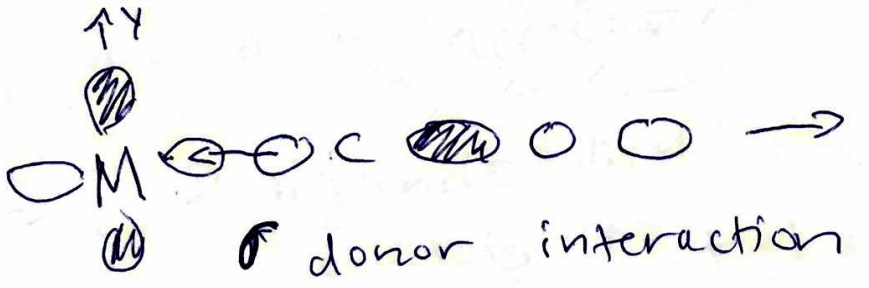
sigma interactions only



:C≡O: as a ligand

sigma donor to metal center

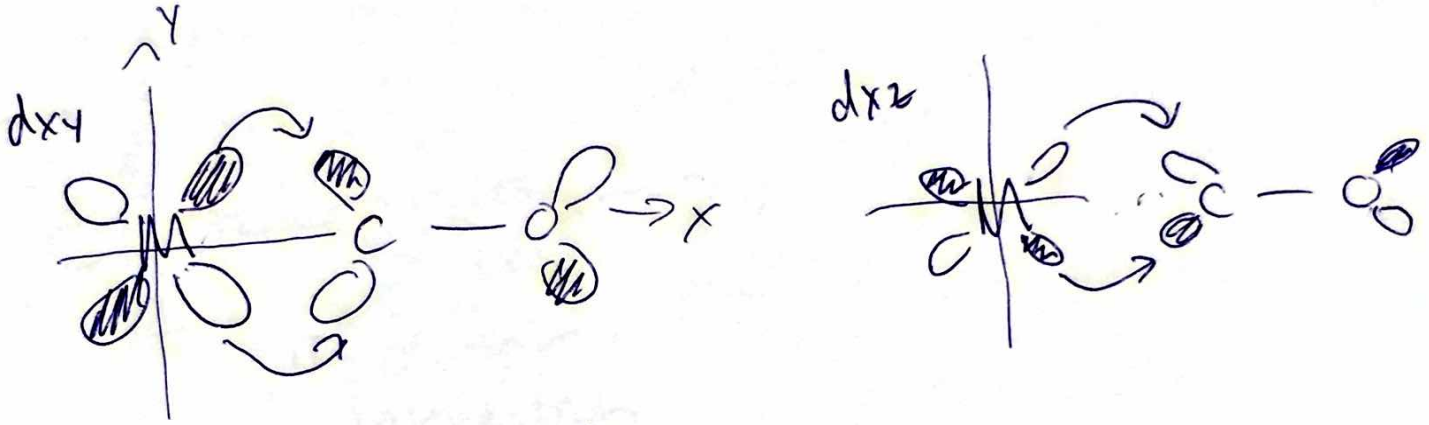
HOMO of CO



$d_{x^2-y^2}$

π^* orbitals of CO : LUMOS

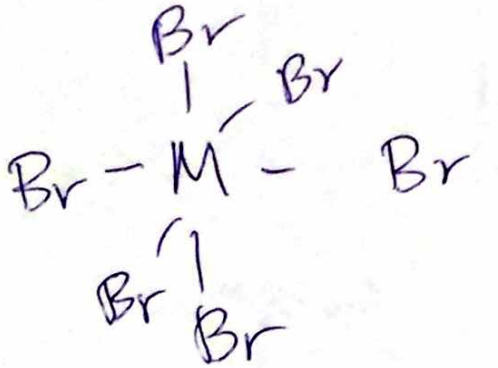
π^* from p_x orbitals π^* from p_y orbitals

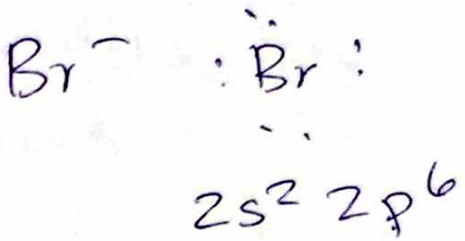


Metal "back bonds" into empty π^* orbitals of $C \equiv O$ ⟷ π back bonding

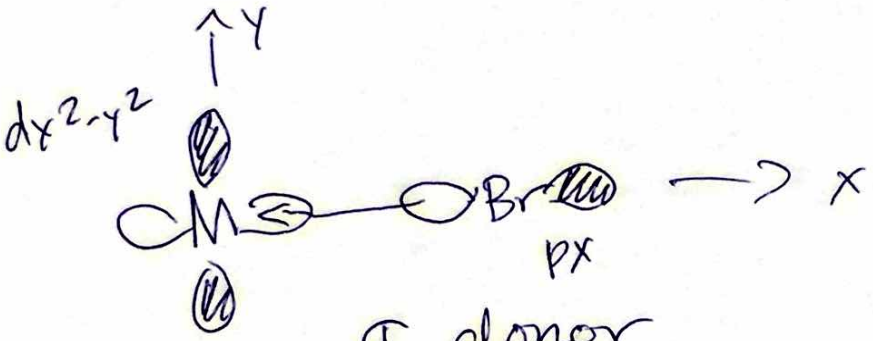
→ CO is known as a π acceptor

→ ligands that have empty π^* orbitals that have the right symmetry to accept electrons from metal t_{2g} orbitals

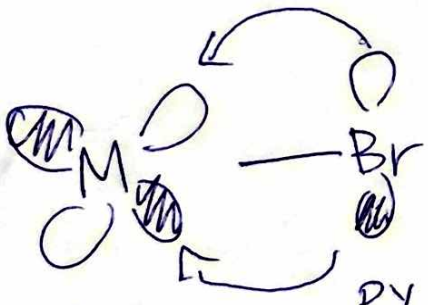




σ interaction

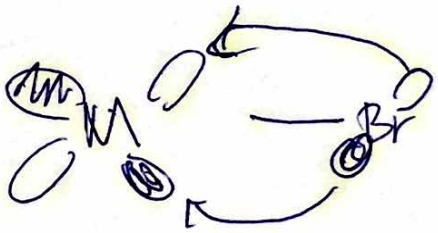


σ donor interaction



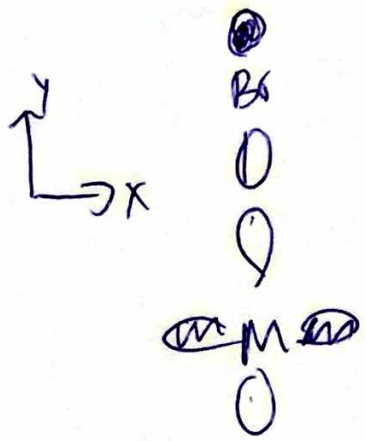
π donor

(py is filled with electrons)



π donor

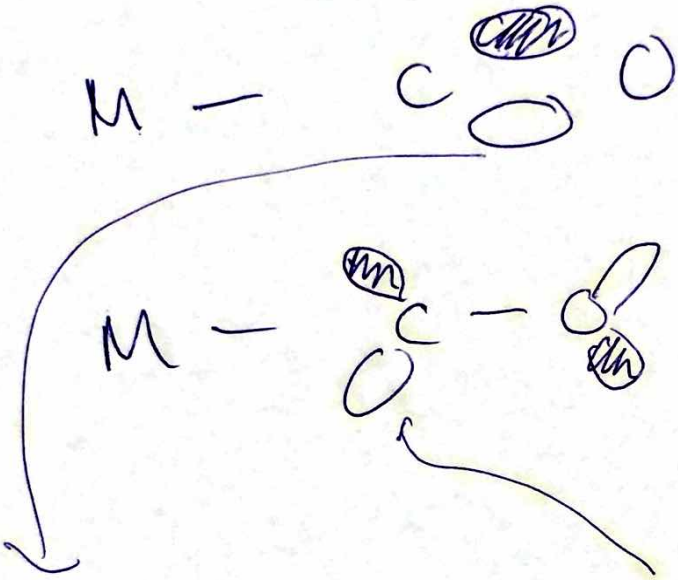
π donor ligands: have lots of lone pairs, typically p_x, p_y, or p_z interaction w/ metal center



in this case, Py of Br is sigma donor, other two orbitals are the π donors

π donation does not happen w/ π bonding orbitals in CO

→ they're not geometrically / sterically available



M — C ≡ O ✗ no π donor

M — C — O ✓ yes π acceptor

electron density in between C & O only, no density out side of C–O bond, so no overlap with metal d orbitals

π^* orbitals have electron density pointed away from CO bond and towards metal center, can overlap w/ metal d orbitals