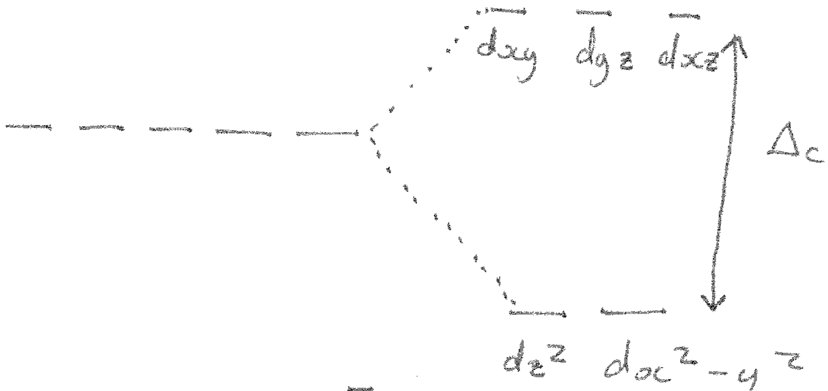
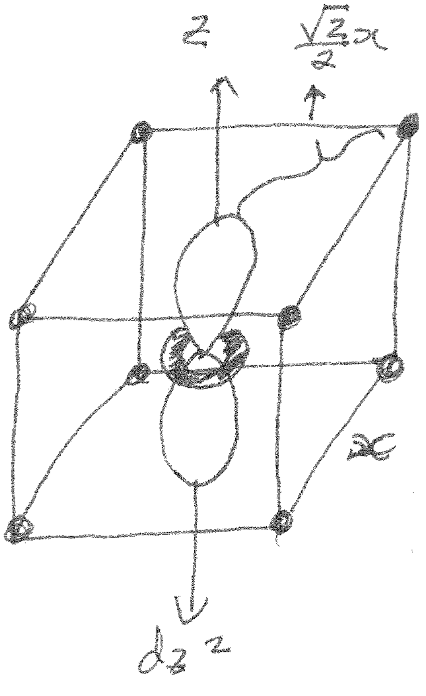
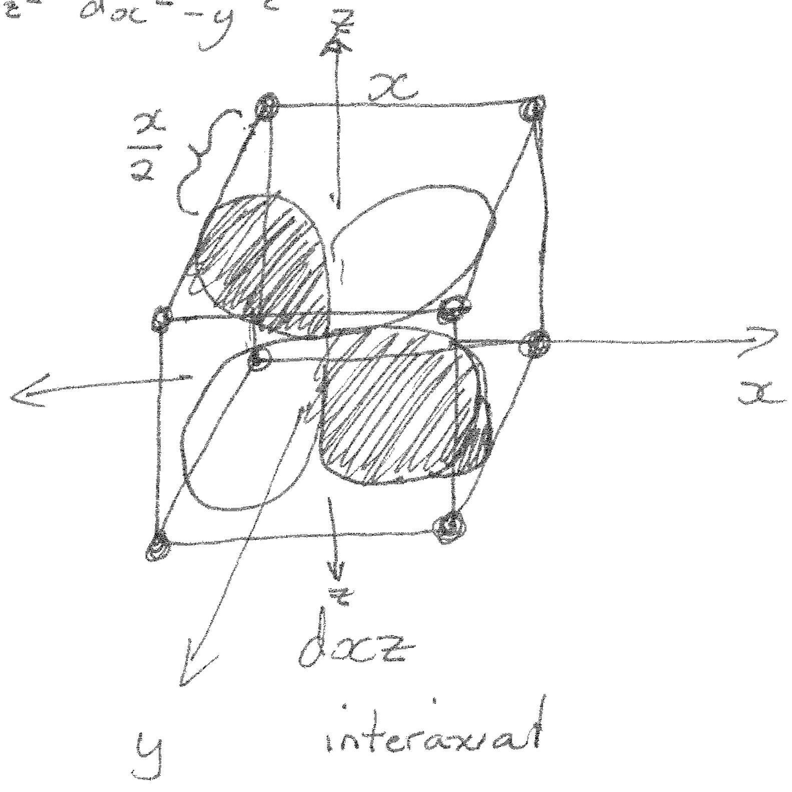
# Chemistry 3840
## Assignment # 2 Answer Key

1. Unlike an octahedral complex wherein all of the ligands lie upon the axes, a complex with cubic geometry has all ligands off-axes (similar to a tetrahedron). As a consequence the interaxial ~~ligands~~ orbitals ($d_{xy}$, $d_{xz}$, $d_{xy}$) more closely approach the ligands $\left(\frac{x}{2}\right)$ than the ~~inter~~axial orbitals ($d_{z^2}$, $d_{x^2-y^2}$) do $\left(\frac{\sqrt{2}\,x}{2}\right)$. Since CFT represents ligands as point negative charges which repel the $e^-$ in the d-orbitals the interaxial orbitals would be expected to be higher in energy than the axial orbitals.





axial



interaxial

# Assignment #2 Answer Key

2) Coordination Isomers: $[Co(NH_3)_6][Cr(CN)_6]$

$+$

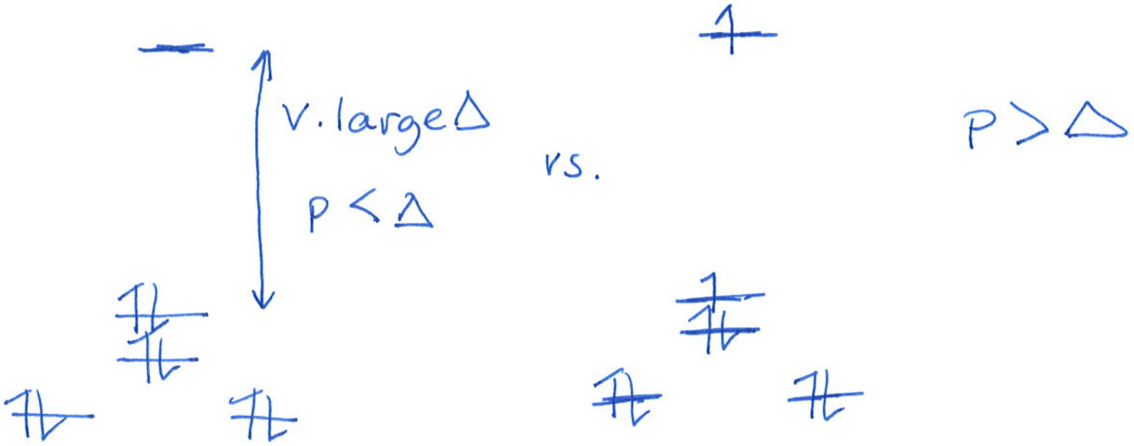
$[Cr(NH_3)_6][Co(CN)_6]$

Linkage Isomers: $[NBu_4][Pt(\underline{S}CN)_3(PEt_3)]$

$+$

$[NBu_4][Pt(\underline{N}CS)_3(PEt_3)]$

3)



diamagnetic
square planar
d8

paramagnetic
square planar
d8

→ Since Δ is typically very large in square planar complexes, it would be unusal for $e^-$ pairing energy (P) to be greater than Δ, which would be necessary to have a paramagnetic square planar $d^8$ complex.

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4. $$\tau_5 = \frac{\beta - \alpha}{60^\circ} = \frac{168.76^\circ - 138.49^\circ}{60^\circ} = \frac{30.27^\circ}{60^\circ} = 0.5045$$

∴ almost halfway between square pyramidal and trigonal bipyramidal geometry.

5. $[Ni(CO)_4]$ vs $Na[Co(CO)_4]$

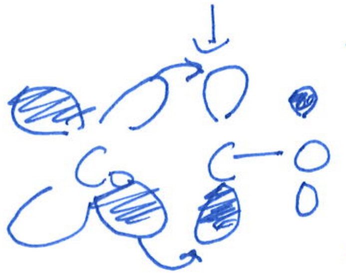
| | |
|---|---|
| $Ni(0), d^{10} \rightarrow 10e^-$ | $Co(-1), d^{10} \rightarrow 10e^-$ |
| $4 \times CO = 4 \times 2e^- \rightarrow 8e^-$ | $4 \times CO \rightarrow 4 \times 2e^- \rightarrow 8e^-$ |
| $18e^-$ | $18e^-$ |

→ Both complexes are $18e^-$, and both metals are $d^{10}$

→ Ni is in 0 oxidation state, while Co is in −1 oxidation state.

↳ ∴ Co is expected to be more efficient at π-back bonding

σ-donation



π-backbonding

} population of this M.O. by π-backbonding strengthens M–C bond but weakens C–O bond, reducing C–O IR stretching frequency.

→ $[Ni(CO)_4]$ will have a higher IR carbonyl stretching frequency because Ni backbonds
↳ relative to $Na[Co(CO)_4]$ ←
less, and correspondingly, the C–O bond are stronger.

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6a) $\underbrace{[Fe(CN)_6]^{3-}}$ ← larger CFSE

→ all ligands are π-acceptors and therefore "strong field" ligands } ∴ low spin

→ $:\overset{\ominus}{C}\equiv \dot{N}:$ is monoanionic.

∴ Fe(III) $d^5$

$$CFSE = 5\left(\frac{-2}{5}\Delta_o\right) + 2P$$

$$\boxed{CFSE = -2\Delta_o + 2P}$$

---

$[Fe(H_2O)_6]^{3+}$

→ $H_2O$ is not a π acceptor ligand or "strong field" ligand.

→ Fe is first row metal ∴ small $\Delta_o$ } ∴ high spin

$$CFSE = 3\left(\frac{-2}{5}\Delta_o\right) + 2\left(\frac{3}{5}\Delta_o\right)$$

$$= \frac{-6}{5}\Delta_o + \frac{6}{5}\Delta_o$$

$$\boxed{CFSE = 0\Delta_o}$$

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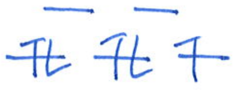
6b) Both $[Fe(CN)_6]^{3-}$ and $[Ru(CN)_6]^{3-}$ have only π acceptor (strong field) ligands and are thereby low spin $d^5$



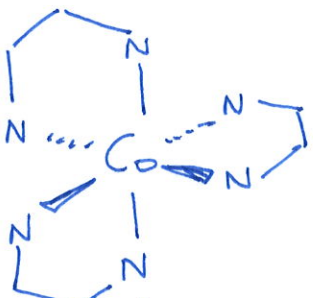
$$CFSE = 5\left(\frac{-2}{5}\right)\Delta_o + 2P \ \boxed{= -2\Delta_o + 2P}$$

↓ for both complexes

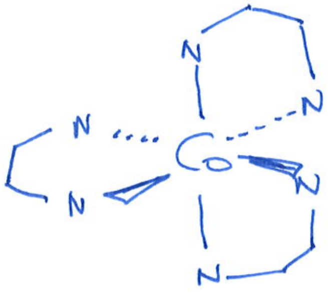
→ $[Ru(CN)_6]^{3-}$ will have a larger $\Delta_o$ because Ru is lower in group 8 than Fe. Larger $\Delta_o$ means a larger CFSE.

# Assignment #2 Answer Key

7a)



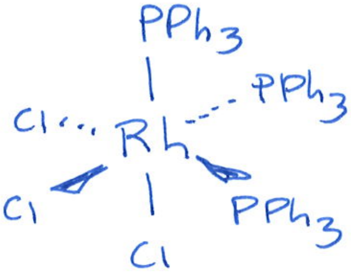
Λ



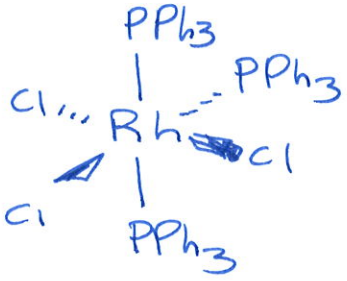
Δ

→ No preference

b)



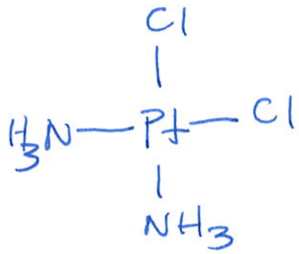
fac



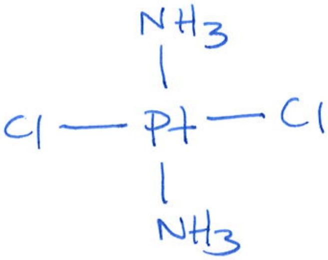
mer

→ No preference

c)



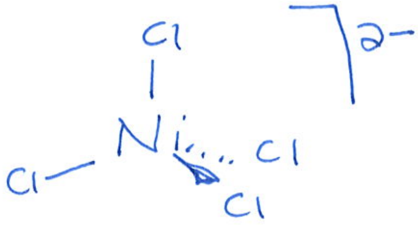
cis



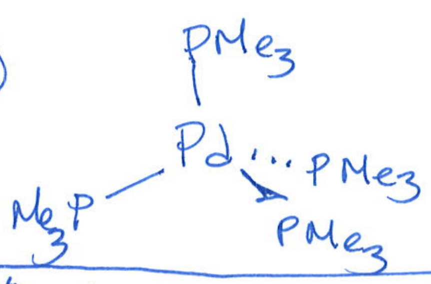
trans

→ No preference.

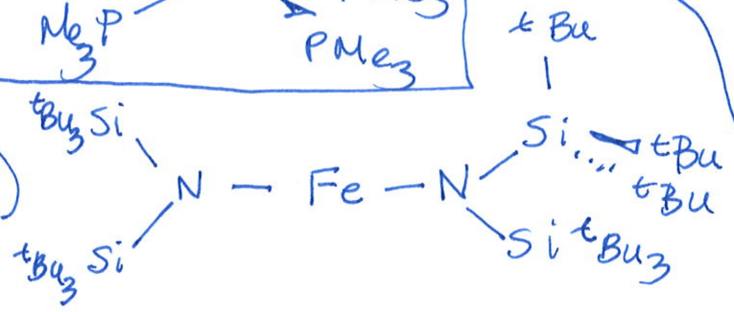
d)



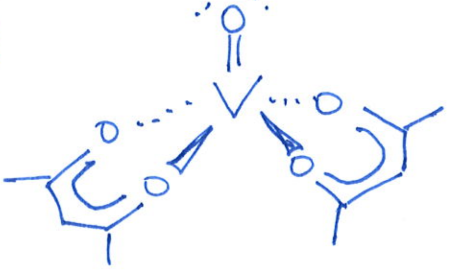
e)



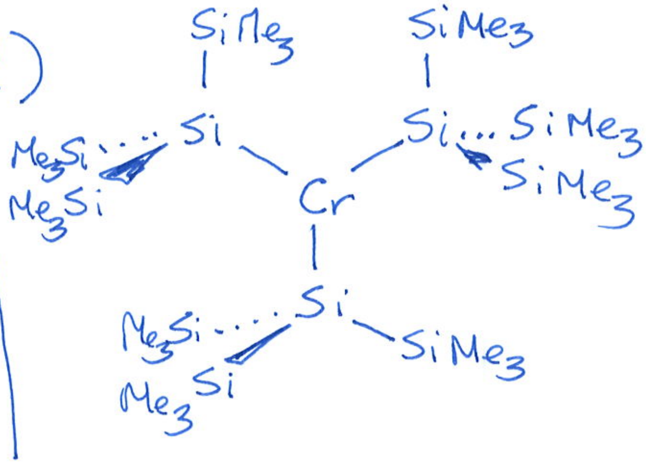
f)



g)



h)



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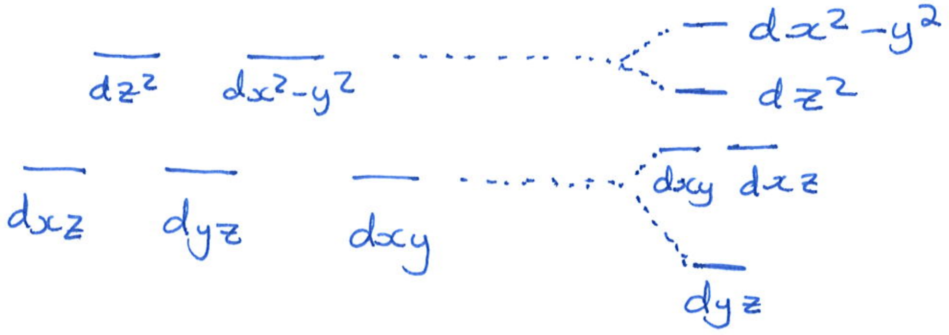
8. Compression along the $x$-axis (and corresponding elongation in the $y/z$ plane) will increase the energy of orbitals that have $x$-character and decrease those with $y$ and $z$ character.



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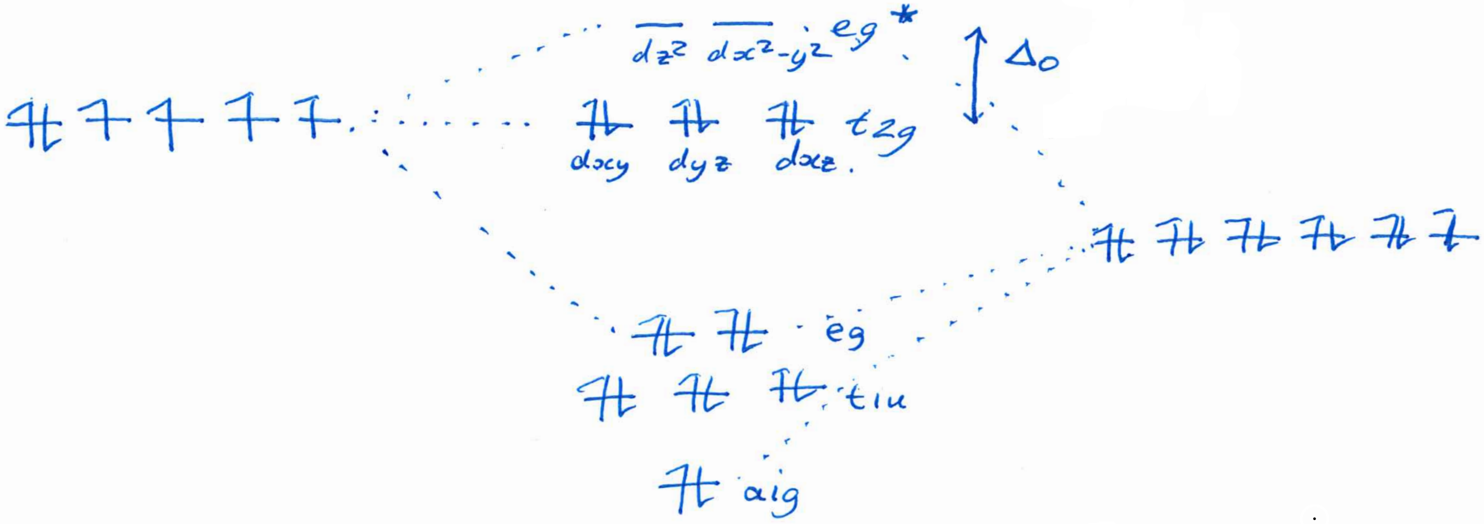
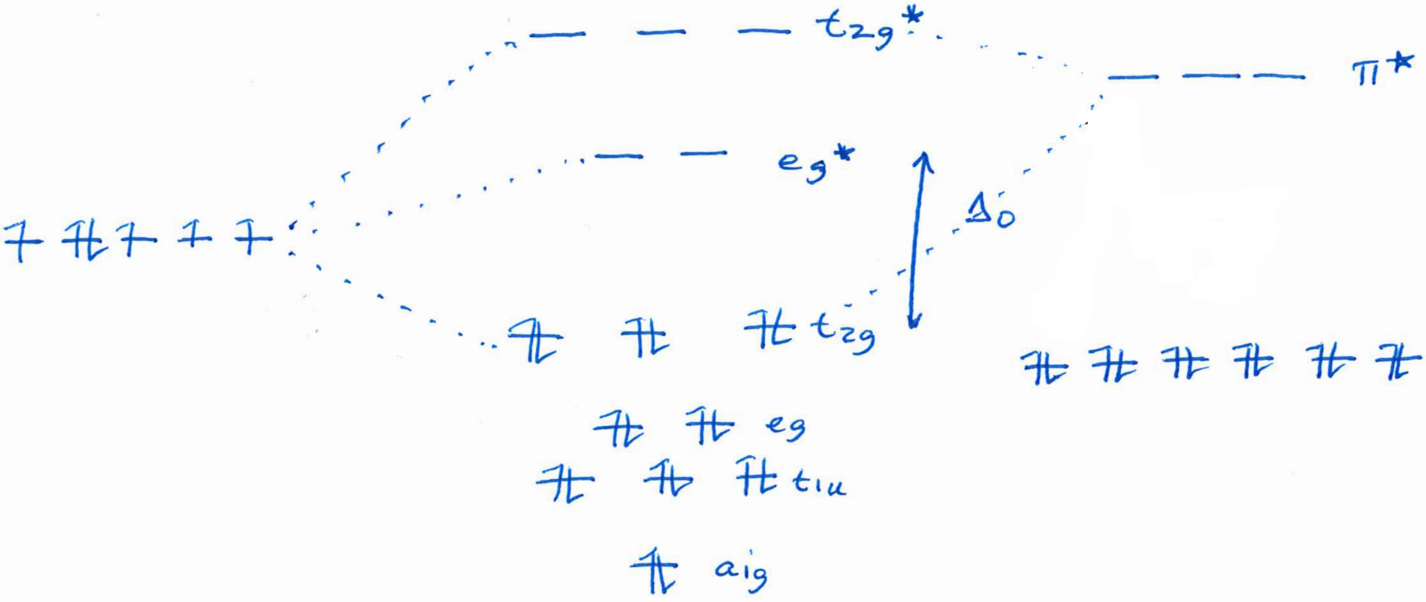
9 With no π-acceptor ligands (only σ donor ligands) the $t_{2g}$ orbitals are nonbonding:
e.g $d^6$ metal



→ but π-acceptor ligands render the $t_{2g}$ orbitals bonding, lowering their energy: and increasing $\Delta_o$
e.g. $Mo(CO)_6$



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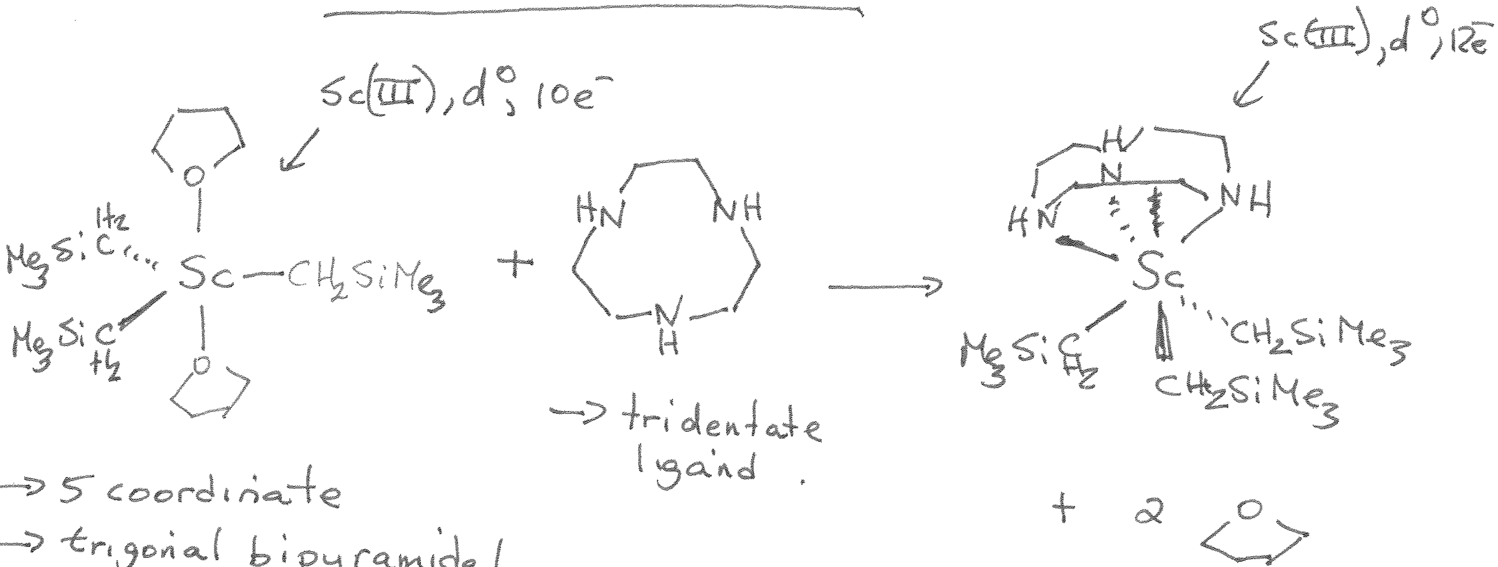
10.



→ 5 coordinate

→ trigonal bipyramidal with large ligands in equatorial sites

→ 6 coordinate

→ octahedral

→ tacN is a facially capping ligand.

→ THF is a neutral monodentate ligand whereas tacn is a tridentate neutral ligand. Seeing as THF is a stable molecule a straightforward substitution reaction would be expected. The chelate effect would favour the product because tacn will chelate to the metal in a $\kappa^3$ fashion.

→ Since the product is more sterically (6 coordinate vs 5) and electronically ($12e^-$ vs $10e^-$) saturated, it would be expected to be more stable than starting material.