Assignment #1 Solutions, continued:

7. (a) Assume e_σ is identical for L and L', then using positions 1, 2, 6, 11, and 12,

d_{z^2} 2.75 e_σ

d_{xy} $d_{x^2-y^2}$ 18/16 e_σ

d_{xz} d_{yz} 0

(b) L' axial (position 1)

d_{z^2} 2.75 e_σ

d_{xy} $d_{x^2-y^2}$ 18/16 e_σ

d_{xz} d_{yz} $-e_\pi$

L' equatorial (position 2)

d_{z^2} 2.75 e_σ

$d_{x^2-y^2}$ 18/16 e_σ

d_{xy} 18/16 e_σ - e_π

d_{yz} 0

d_{xz} $-e_\pi$

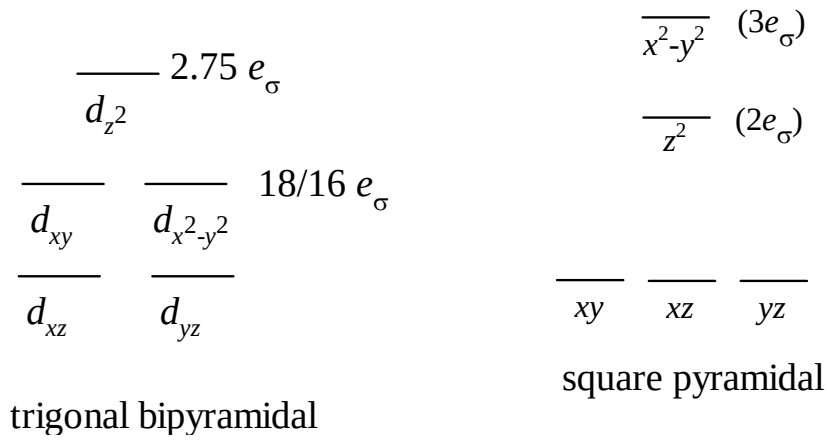
(c) Whether the π-acceptor ligand sits in an axial or equatorial spot may depend on metal *d*-electron count and electron pairing issues.

d^1 no preference (stabilised by e_π in both cases)

$d^{2, 3, 4, 5, 6}$ prefer axial (assume low spin in all cases, d^2 and d^6 only more stable due to electron pairing effects)

rest - no preference

8. For σ-only (assuming only "high spin):



Based only on these diagrams (*i.e.*, ignoring sterics, which ALWAYS favour trigonal bipyramidal), the following destabilisations (in units of e_σ) occur:

*d*e⁻ count	tbp	sq. pyr.	geometric preference
1, 2	0	0	none (therefore, tbp by sterics)
3	1.125	0	sq. pyr.
4	2.25	2	sq. pyr.
5, 6, 7	5	5	tbp (by sterics)
8	6.125	5	sq. pyr.
9	7.25	7	sq. pyr
10	10	10	tbp (by sterics)

for π-acceptors:

$\overline{d_{z^2}}$ 2.75 e_σ

$\overline{d_{xy}}$ $\overline{d_{x^2-y^2}}$ 1.125 e_σ - 1.5e_π

$\overline{d_{xz}}$ $\overline{d_{yz}}$ -3.5e_π

trigonal bipyramidal

$\overline{x^2-y^2}$ (3e_σ)

$\overline{z^2}$ (2e_σ)

$\overline{xz}$ $\overline{yz}$ (-3e_π)

$\overline{xy}$ (-4e_π)

sq.pyr., π-acceptor

*d*e⁻ count	tbp	sq. pyr.	geometric preference
1	-3.5e_π	-4e_π	sq. pyr.
2	-7e_π	-7e_π	tbp (by sterics)
3	1.125e_σ - 8.5e_π	-10e_π	sq. pyr.
4	2.25e_σ - 10e_π	2e_σ - 10e_π	sq. pyr.
5	5e_σ - 13.5e_π	5e_σ - 10e_π	tbp
6	5e_σ - 17e_π	5e_σ - 14e_π	tbp
7	5e_σ - 17e_π	5e_σ - 17e_π	tbp (by sterics)
8	6.125e_σ - 18.5e_π	5e_σ - 20e_π	sq. pyr.
9	7.25e_σ - 20e_π	7e_σ - 20e_π	sq. pyr
10	10e_σ - 20e_π	10e_σ - 20e_π	tbp (by sterics)

23. Remember, the hint is to double-up positions 11 and 12.

(a), (c)

$\overline{d_{z^2}}$ 3.5e_σ

$\overline{d_{xy}}$ $\overline{d_{x^2-y^2}}$ 2.25e_σ

$\overline{xz}$ $\overline{yz}$ 0

σ-only

——— 3.5e_σ

$\overline{d_{xy}}$ $\overline{d_{x^2-y^2}}$ 2.25e_σ - 3e_π

$\overline{xz}$ $\overline{yz}$ -5e_π

with π-acceptor

(b) In the point group D_{6h}, d_{z^2} (A_{1g}), $d_{x^2-y^2}$ & d_{xy} (E_{2g}), d_{xz} & d_{yz} (E_{1g})

(d) the following electron counts will give potential J-T effects (due to degenerate orbitals being unevenly filled):

high spin: d^1, d^3, d^6, d^8

low spin: d^1, d^3, d^5, d^7