CHEMISTRY 3840: Inorganic Chemistry II
MIDTERM-1

Friday, February 12, 2025

INSTRUCTIONS

- This exam paper has 7 pages (including this page). Write all answers in the allotted spaces.
- The exam consists of 6 questions. You must complete all of them (unless otherwise noted).
- The exam is worth a total of 100 points. Most of these marks are for explanation/showing your work rather than for reaching the correct answer. Explain all of your answers fully, but it is not necessary to write in complete sentences (point form is acceptable).
- Remember to write your name and ID # on this page.
- This is an independent closed book exam – no material aids are permitted. Model kits are acceptable, but graphing calculators are not allowed.
- There is a 75 minute time limit.
- **Read the questions carefully**. Good luck.

WORDS RARELY SAID BY ACADEMICS:

"I turned in my grant application early."

"I have no comments."

"It's the weekend. I'll reply on Monday."

"I don't feel I really contributed, you can take my name off the author list."

"I loved the conference coffee."

"That faculty meeting was a great use of my time."

"Wow, what an insightful rejection letter."

"Can I sign up for more committees?"

"I did no work while on my beach vacation."

"I like reviewer 2."

"I'm all caught up and have nothing to do."

NAME: ANSWER KEY ID #: ____________________

Chemistry 3840
Midterm Examination #1 (February 12, 2025)

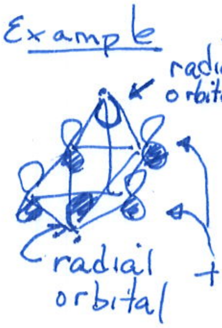
1. Fully explain ***three of the following five*** terms/concepts. Use examples. (18 points)

a) organometallic complex → metal containing compounds wherein one or more neutral or charged ligands are directly bonded to that metal and at least one of the coordinating atoms is carbon

Example:

b) tangential orbital → From a molecular orbital perspective for borohydide clusters, molecular orbitals are ~~comprised~~ comprised of tangential and radial orbitals. Radial orbitals are "sp-like" and are oriented toward the centre of the cluster. Tangential orbitals are "p-like" orbitals that lie ⊥ to the radial orbitals

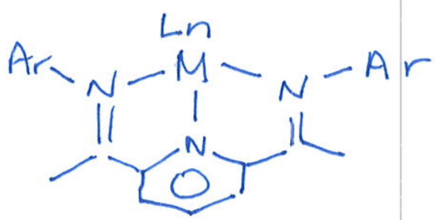
Example



c) Frustrated Lewis Pair (FLP) → The combination of a sterically hindered Lewis acid and a sterically hindered Lewis base, which because of their bulk cannot form a "normal" Lewis acid-base adduct, and hence, retain their Lewis acidity and basicity even in the presence of one another. As a consequence FLP have been shown to cooperatively activate small molecules such as H_2 and CO_2. Example: P^tBu_3 + $B(C_6F_5)_3$ $\xrightarrow{H_2}$ $[HP^tBu_3][HB(C_6F_5)_3]$

d) κ[3]-chelating ligand → chelating ligands are capable of making more than one bond to one metal centre

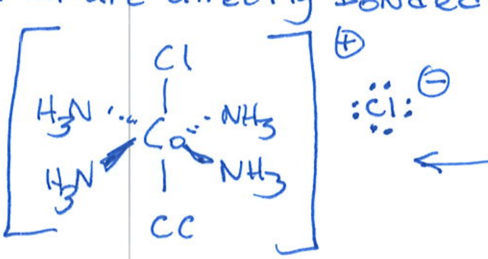
e.g.



→ κ[3] indicates a denticity of 3 (3 atoms are bonded to the metal centre). Unlike η[3], κ[3] implies that the three ligating atoms are not bonded to one another.

e) coordination sphere
↳ in a metal complex, the central metal + all ligands that are directly bonded to that metal

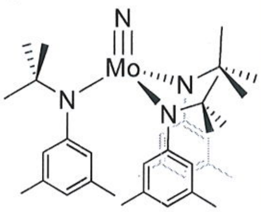
Example



all ligands + Co enclosed within the square brackets are part of the coordination sphere, while the :Cl:⁻ counterion is not

2. For ***any five*** of the following seven molecules determine:
i) the oxidation state of the metal; ii) the d-electronic configuration of the metal; iii) the electron count at the metal centre. (45 points)

a)



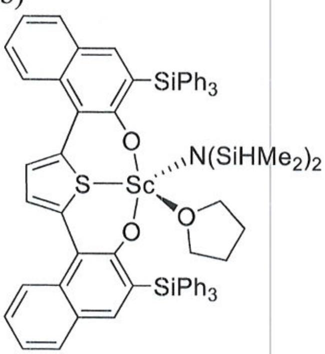
$Mo(VI) \rightarrow d^0 \rightarrow 0e^-$

$3 \times N:^{\ominus} \rightarrow 3 \times 2e^- \rightarrow 6e^-$

$:N:^{3-} \longrightarrow 6e^-$

$12e^-$

b)



$Sc(III) \rightarrow d^0 \rightarrow 0e^-$

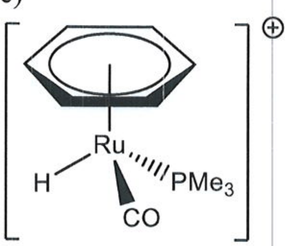
THF $\longrightarrow 2e^-$

$^{\ominus}:N(SiHMe_2)_2 \longrightarrow 2e^-$

$\longrightarrow 6e^-$

$10e^-$

c)



$Ru(II)\ d^6 \rightarrow 6e^-$

$CO \rightarrow 2e^- \rightarrow 2e^-$

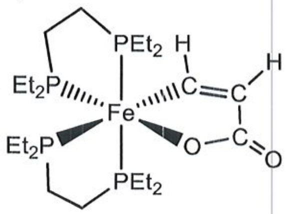
$PMe_3 \rightarrow 2e^-$

$H:^{\ominus} \longrightarrow 2e^-$

benzene $\longrightarrow 6e^-$

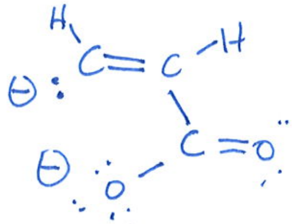
$18e^-$

d)



Fe(II) → d^6 → $6e^-$

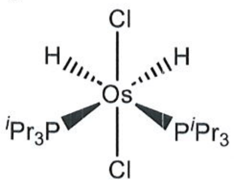
2 x $Et_2\ddot{P}$⌒$\ddot{P}Et_2$ → 2 x $4e^-$ → $8e^-$



→ $4e^-$ → $4e^-$

$18e^-$

e)



Os(IV) → d^4 → $4e^-$

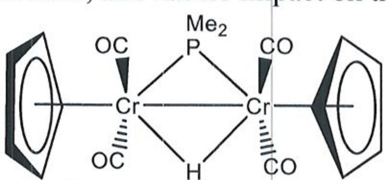
2 x H:⊖ → 2 x $2e^-$ → $4e^-$

2 x :Cl:⊖ → 2 x $2e^-$ → $4e^-$

2 x :P^iPr_3 → 2 x $2e^-$ → $4e^-$

$16e^-$

f) Note: The Cr–Cr bond counts as 1 electron for each Cr when counting electrons at the metal centres, and has no impact on the oxidation state of either metal.



→ Both Cr centres are in identical environments with the same ligands bound in the same mode to each metal

Cr(II) → d^4 → $4e^-$

Cr–Cr → $1e^-$

2x CO → 2 x $2e^-$ → $4e^-$

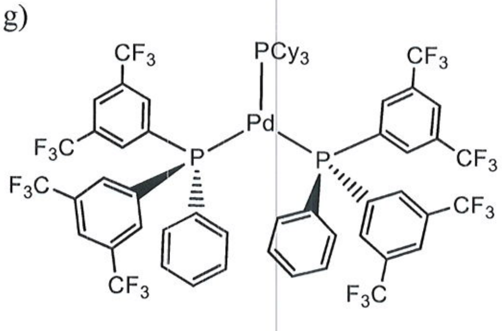
Cp⊖ → $6e^-$

$\frac{1}{2}$:$\ddot{P}Me_2$⊖ → $\frac{1}{2}$ x $4e^-$ → $2e^-$

$\frac{1}{2}$ H:⊖ → $1e^-$

$18e^-$

g)

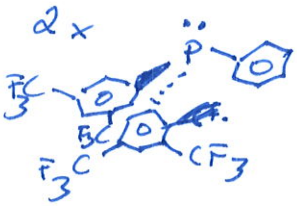


Cy = cyclohexyl

Pd(0) → d^{10} → $10e^-$

:PCy_3 → $2e^-$

2 x

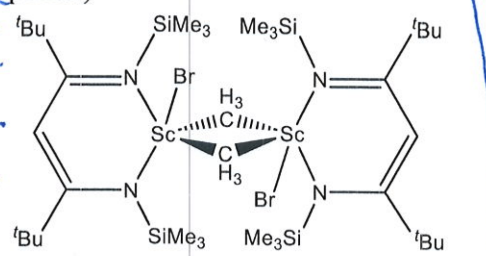


→ 2 x $2e^-$ → $4e^-$

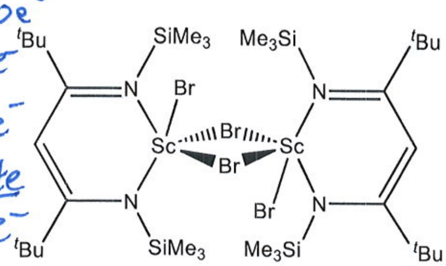
$16e^-$

3. Which of the following two complexes would you expect to be more likely for the ligand PMe_3 to coordinate to (assume that Br and CH_3 are the same size)? Justify your choice. (10 points)

Sc(III) → d^0 → 0e⁻
2 μ-$CH_3^{\ominus}$ → 2e⁻
$Br^{\ominus}$ → 2e⁻
N N$^{\ominus}$ → 4e⁻
8e⁻



Sc(III) d^0 → 0e⁻
N N$^{\ominus}$ → 4e⁻
+ Br^- → 2e⁻
2 μ-Br^- → 4e
10e⁻



→ Since $Br^{\ominus}$ and $CH_3^{\ominus}$ are the same size both compounds are identical from a steric perspective ∴ any difference in reactivity toward :PMe_3 must be solely based upon electronic differences

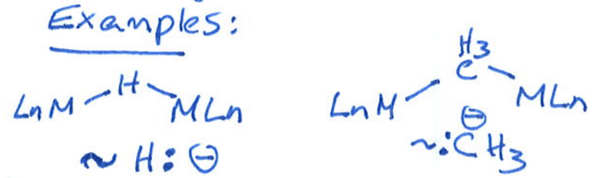
→ $^{\ominus}$:CH_3 is acting as a 3 centre 2 electron ligand when it bridges both Sc centres, while the :Br:$^{\ominus}$ is a 3 centre 4e⁻ ligand. Hence the e⁻ count for the Sc centres in the right compound is different (higher) than the one on the left.

↳ Since the complex on the right is more e⁻ rich (less e⁻ deficient) it is expected to be less likely that PMe_3 will coordinate to those Sc centres than the more e⁻ deficient Sc centres in the complex on the left (10e⁻ vs 8e⁻)

4. Explain, using examples, the difference between a monoanionic, 2-electon bridging ligand and a monoanionic, 4-electron bridging ligand. (8 points)

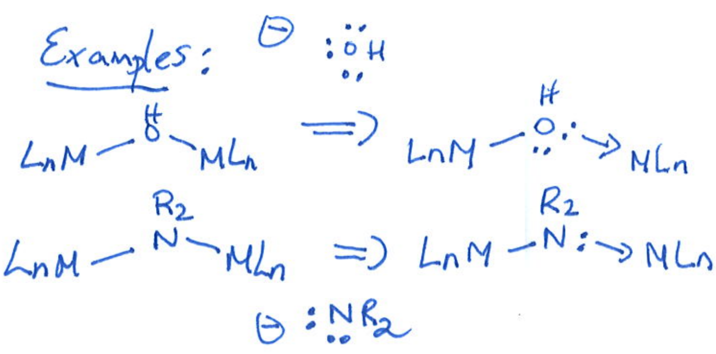
Monoanionic 2e⁻ bridging ligand → donates a total of 2e⁻ to all of the metals which the ligand bridges
→ a net charge of −1 on that ligand
→ in the case where 2 metals are bridged an electron deficient 3 centre 2 electron bonding mode describes the M–L–M interaction.

Examples:



Monoanionic 4e⁻ bridging ligand
→ donates a total of 4e⁻ to all of the metals which the ligand bridges
→ a net charge of −1 on that ligand
→ Common when a monoanionic ligand that bears more than one lone pair bridges 2 metals

Examples:



5. Use Wade's rules to classify $CB_{11}H_{12}^-$ as *nido*, *closo* or *arachno*. Show your work. (9 points)

11 BH = ~~2x~~ 11 × 2e⁻ ⟶ 22e⁻

1 CH ⟶ 2e⁻

C e⁻ ⟶ 1e⁻

⊖ ⟶ 1e⁻

26e⁻.

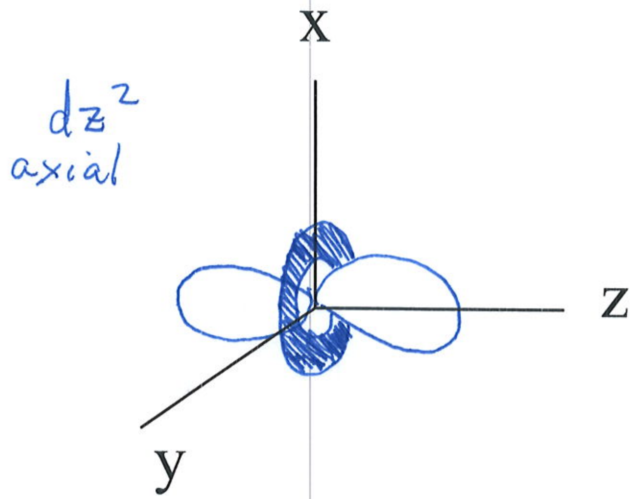
$\frac{26e}{2}$ = 13 electron pairs for skeletal bonding

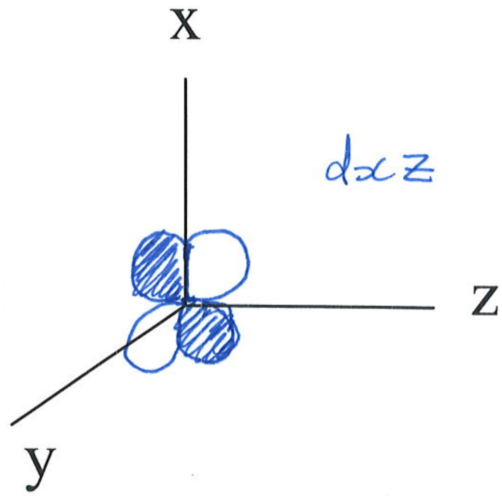
12 cage atoms (1 C, 11 B)

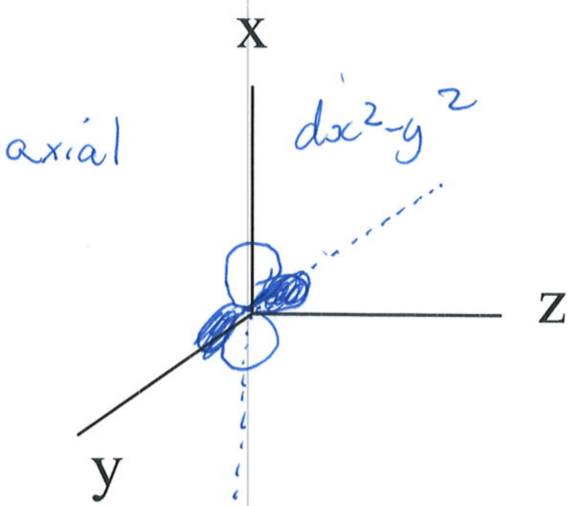
∴ n + 1 electron pairs for skeletal bonding

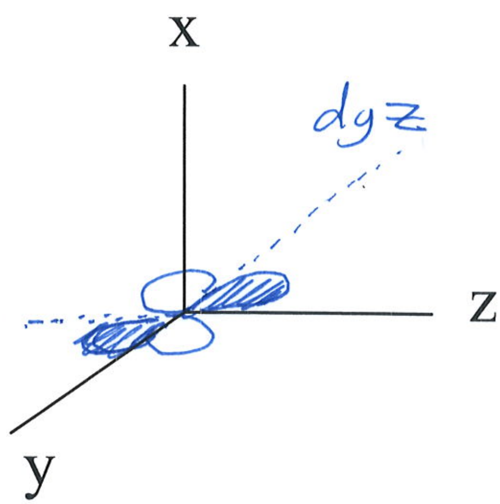
∴ Closo

6. Draw and label the d-orbitals. Use the provided axes. Be sure to place signs on all lobes, label each orbital as gerade or ungerade. (10 points).









→ all 5 d-orbitals are gerade.