CHEM 20200 (Inorganic Chemistry II) Problem Sets

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April 21, 2021
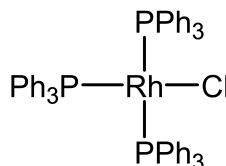
Contents

1 Electronic Phenomena

4/7: 1. For each complex, provide the (i) oxidation state, (ii) d^n configuration, and (iii) NVE (number of valence electrons, or electron count) at the metal. Provide this information for both metals and provide the number of M−M bonds in the bimetallic cases.
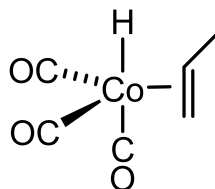
1)

Answer.

  (i) Rh^+ (each phosphine is L-type; the chlorine is X-type).

 (ii) Rh^+ is d^8.

(iii) Each phosphine is a 2-electron donor, and the chlorine is a 1-electron donor. Thus, the ligands donate $3 \cdot 2 + 1 \cdot 1 = 7$ electrons in total. This combined with the above results yields $7 + 9 = 16$ as the electron count.
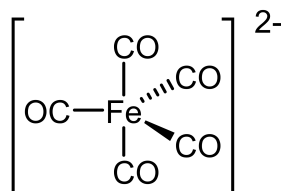
□

2)

Answer.

  (i) Co^+ (each carbonyl is L-type; the hydride is X-type; the propene is L-type).

 (ii) Co^+ is d^8.

(iii) Each carbonyl is a 2-electron donor, the hydrogen is a 1-electron donor, and propene is a 2-electron donor. Thus, the ligands donate $3 \cdot 2 + 1 \cdot 1 + 1 \cdot 2 = 9$ electrons in total. This combined with the above result yields $9 + 9 = 18$ as the electron count.
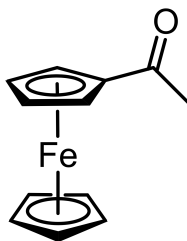
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3)

Answer.

  (i) Fe^{2-} (each carbonyl is L-type; the charge is 2−).

 (ii) Fe^{2-} is d^{10}.

(iii) Each carbonyl is a 2-electron donor. Thus, the ligands donate $5 \cdot 2 = 10$ electrons in total. This combined with the above results yields $10 + 8 - (-2) = 20$ as the electron count.
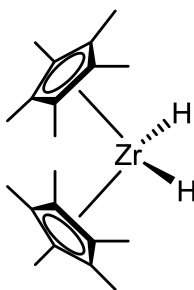
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4)

Answer.

(i) Fe^{2+} (both ligands are X-type).

(ii) Fe^{2+} is d^6.

(iii) Both ligands are 5-electron donors. Thus, the ligands donate $2 \cdot 5 = 10$ electrons in total. This combined with the above results yields $10 + 8 = 18$ as the electron count.
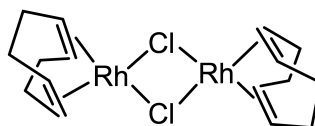
$\square$

5)

Answer.

(i) Zr^{4+} (all ligands are X-type).

(ii) Zr^{4+} is d^0.

(iii) Both pentamethylcyclopentadienyl (Cp^*) groups are 5-electron donors, and both hydrogens are 1-electron donors. Thus, the ligands donate $2 \cdot 5 + 2 \cdot 1 = 12$ electrons in total. This combined with the above results yields $12 + 4 = 16$ as the electron count.

$\square$

6)

Answer.

(i) Both metals are Rh^+ (both cycloocta-1,5-dienyl (COD) groups are L_2-type; both bridging chlorines are LX-type [they can be thought of as bonding covalently to one rhodium and datively to the other, so when the bonds are cleaved, each chlorine steals one covalent electron from a rhodium and reclaims its two dative electrons]).

(ii) Rh^+ is d^8.

(iii) Both COD groups are 4-electron donors, and both bridging chlorines are 3-electron donors. Thus, the ligands donate $2 \cdot 4 + 2 \cdot 3 = 14$ electrons in total. This combined with the above results yields $\frac{14 + 2 \cdot 9}{2} = 16$ as the electron count at each rhodium. It follows that there should be $\frac{36 - 2 \cdot 16}{2} = 2$ $Rh-Rh$ bonds.
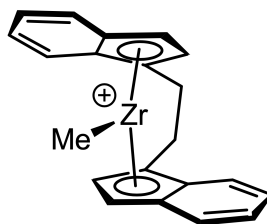
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7)
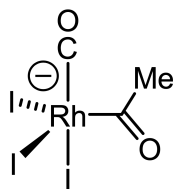
Answer.

 (i) Rh^{3+} (the carbonyl is L-type; each iodide is X-type; the other ligand is X-type; the charge is $1-$).

 (ii) Rh^{3+} is d^6.

 (iii) The carbonyl is a 2-electron donor, each iodide is a 1-electron donor, and the other ligand is a 1-electron donor. Thus, the ligands donate $1 \cdot 2 + 3 \cdot 1 + 1 \cdot 1 = 6$ electrons in total. This combined with the above results yields $6 + 9 - (-1) = 16$ as the electron count.

☐

8)

Answer.

 (i) Zr^{4+} (the methyl is X-type; the other ligand is X_2-type; the charge is $1+$).

 (ii) Zr^{4+} is d^0.

 (iii) The methyl is a 1-electron donor, and the other ligand is a 10-electron donor. Thus, the ligands donate $1 \cdot 1 + 1 \cdot 10 = 11$ electrons in total. This combined with the above results yields $11 + 4 - 1 = 14$ as the electron count.

☐

9)

Answer.

 (i) W^0 (each carbonyl is L-type; both phosphines are L-type; the other ligand is L-type).

 (ii) W^0 is d^6.

 (iii) Each carbonyl is a 2-electron donor, both phosphines are 2-electron donors, and the other ligand is a 2-electron donor. Thus, the ligands donate $3 \cdot 2 + 2 \cdot 2 + 1 \cdot 2 = 12$ electrons in total. This combined with the above results yields $12 + 6 = 18$ as the electron count.
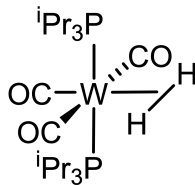
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10)
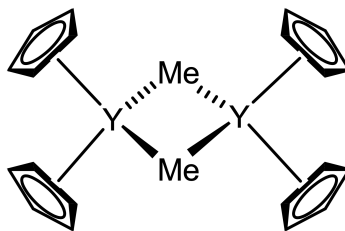
Answer.

(i) Y^{3+} (each Cp is X-type; each bridging methyl is LX-type).

(ii) Y^{3+} is d^0.

(iii) Each Cp is a 5-electron donor, and each methyl is a 3-electron donor. Thus, the ligands donate $4 \cdot 5 + 2 \cdot 3 = 26$ electrons in total. This combined with the above results yields $\frac{26+2\cdot3}{2} = 16$ as the electron count at each yttrium. It follows that there should be $\frac{36-2\cdot16}{2} = 2$ $Y-Y$ bonds.

□

11)

Answer.

(i) Fe^0 (both carbonyls are L-type; the other ligand is X-type; the charge is $1-$).

(ii) Fe^0 is d^8.

(iii) Both carbonyls are 2-electron donors, and the methylcyclopentadienyl group is a 5-electron donor. Thus, the ligands donate $2 \cdot 2 + 1 \cdot 5 = 9$ electrons in total. This combined with the above results yields $9 + 8 - (-1) = 18$ as the electron count.
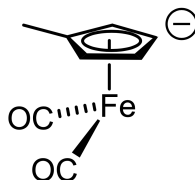
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12)
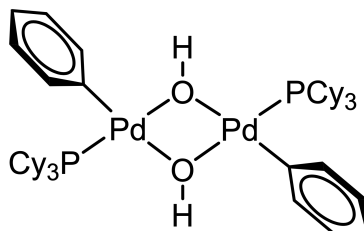
Answer.

(i) Pd^{2+} (both benzenes are X-type; both phosphines are L-type; both bridging hydroxides are LX-type).

(ii) Pd^{2+} is d^8.

(iii) Both benzenes are 1-electron donors, both phosphines are 2-electron donors, and both bridging hydroxides are 3-electron donors. Thus, the ligands donate $2 \cdot 1 + 2 \cdot 2 + 2 \cdot 3 = 12$ electrons in total. This combined with the above results yields $\frac{12+2\cdot10}{2} = 16$ as the electron count at each palladium. It follows that there should be $\frac{36-2\cdot16}{2} = 2$ $Pd-Pd$ bonds.

□

13)

Answer.

  (i) Re^+ (the [linear] nitrosyl group is L-type but takes on a positive charge during bond cleavage; the methyl group is X-type; the phosphine is L-type; the Cp^* group is X-type).

 (ii) Re^+ is d^6.

(iii) The nitrosyl group is a 3-electron donor (assuming it bonds linearly), the methyl group is a 1-electron donor, the phosphine is a 2-electron donor, and the Cp^* is a 5-electron donor. Thus, the ligands donate $1 \cdot 3 + 1 \cdot 1 + 1 \cdot 2 + 1 \cdot 5 = 11$ electrons in total. This combined with the above results yields $11 + 7 = 18$ as the electron count.

$\square$

14)
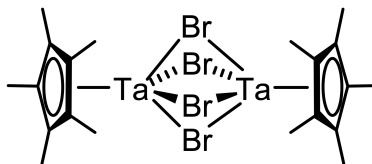
Answer.

  (i) Ta^{3+} (both Cp^* groups are L-type; each bridging bromine is LX-type).

 (ii) Ta^{3+} is d^2.

(iii) Both Cp^* groups are 5-electron donors, and each bridging bromine is a 3-electron donor. Thus, the ligands donate $2 \cdot 5 + 4 \cdot 3 = 22$ electrons in total. This combined with the above results yields $\frac{22 + 2 \cdot 5}{2} = 16$ as the electron count at each tantalum. It follows that there should be $\frac{36 - 2 \cdot 16}{2} = 2$ Ta–Ta bonds.

$\square$

15)
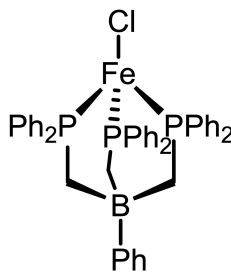
Answer.

  (i) Fe^{2+} (the chloride is X-type; the other ligand is L_3-type but carries a negative formal charge).

 (ii) Fe^{2+} is d^6.

(iii) The chlorine is a 1-electron donor, and the other ligand is a 5-electron donor (3 dative bonds minus a single negative formal charge on the boron). Thus, the ligands donate $1 \cdot 1 + 1 \cdot 5 = 6$ electrons in total. This combined with the above results yields $6 + 8 = 14$ as the electron count.
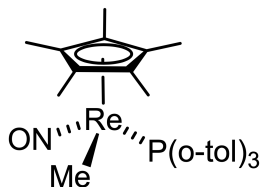
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16)
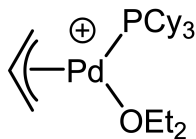
Answer.

  (i) Pd^0 (the phosphine is L-type; the ether is L-type; the other ligand is L-type but takes on a positive charge during bond cleavage; the charge is 1+).

 (ii) Pd^0 is d^{10}.

(iii) The phosphine is a 2-electron donor, the ether is a 2-electron donor, and the other ligand is a 3-electron donor. Thus, the ligands donate $1 \cdot 2 + 1 \cdot 2 + 1 \cdot 3 = 7$ electrons in total. This combined with the above result yields $7 + 10 - 1 = 16$ as the electron count.

$\square$

17)
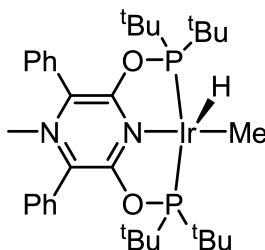
Answer.

  (i) Ir^{2+} (the methyl is X-type; the hydride is X-type; the other ligand is L_3-type).

 (ii) Ir^{2+} is d^7.

(iii) The methyl group is a 1-electron donor, the hydrogen is a 1-electron donor, and the other ligand is a 7-electron donor (3 dative bonds plus a single positive formal charge on the leftmost nitrogen in the above picture). Thus, the ligands donate $1 \cdot 1 + 1 \cdot 1 + 1 \cdot 7 = 9$ electrons in total. This combined with the above result yields $9 + 9 = 18$ as the electron count.

$\square$

18)
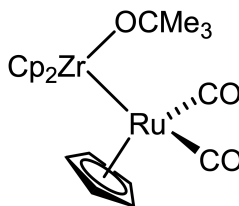
Answer.

  (i) Zr^{3+} (the *t*-butoxide is X-type; both Cp groups are X-type; the Zr–Ru bond makes no contribution), and Ru^+ (both carbonyls are L-type; the Cp is X-type; the Zr–Ru bond makes no contribution).

 (ii) Zr^{3+} is d^1, and Ru^+ is d^7.

(iii) For the zirconium atom, the *t*-butoxide group is a 1-electron donor, both Cp groups are 5-electron donors, and the Zr−Ru bond is a 1-electron donor. Thus, the ligands donate $1 \cdot 1 + 2 \cdot 5 + 1 \cdot 1 = 12$ electrons in total to the zirconium atom. This combined with the above results yields $12 + 4 = 16$ as the electron count for the zirconium atom. For the ruthenium atom, both carbonyls are 2-electron donors, the Cp group is a 5-electron donor, and the Zr−Ru bond is a 1-electron donor. Thus, the ligands donate $2 \cdot 2 + 1 \cdot 5 + 1 \cdot 1 = 10$ electrons in total. This combined with the above results yields $10 + 8 = 18$ as the electron count for the ruthenium atom. It follows that there should be $\frac{36 - (16 + 18)}{2} = 1$ extra Zr−Ru bond beyond what is shown in the above picture (2 in total).

□

19)

Answer.

(i) Pt^{2+} (the bromine is X-type; the other ligand is L_2X-type).

(ii) Pt^{2+} is d^8.

(iii) The bromine is a 1-electron donor, and the other ligand is a 5-electron donor (2 dative bonds plus 1 covalent bond). Thus, the ligands donate $1 \cdot 1 + 1 \cdot 5 = 6$ electrons in total. This combined with the above result yields $6 + 10 = 16$ as the electron count.
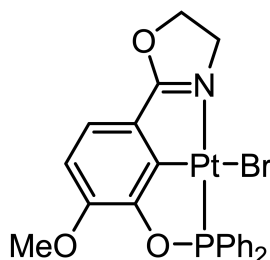
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20)
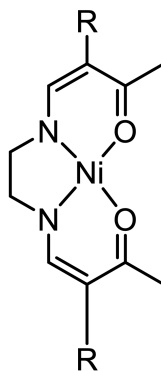
Answer.

(i) Ni^{2+} (the ligand is L_2X_2-type).

(ii) Ni^{2+} is d^8.

(iii) The ligand is a 6-electron donor (2 dative bonds plus 2 covalent bonds). This combined with the above result yields $6 + 10 = 16$ as the electron count.

□

2. For the following pairs of complexes from problem 1, pick and justify based on the trend.

   a) Which complex is more basic and which is more acidic between 2 and 5 (Co and Zr)?

   Answer. 5 is more acidic because it wants to gain two electrons to get to 18 to be more stable, whereas 2 already has 18 electrons, and thus is more basic relatively.   □

   b) Which complex is more likely to be reduced or oxidized between 4 and 15 (both Fe)?

   Answer. 4 is more likely to be oxidized, and 15 is more likely to be reduced. 4 already has 18 electrons, so it won't want any more. 15 is at 14 electrons, so it would surely stabilize it to gain a few more.   □

   c) Which complex is more likely to have its $M-C$ bond hydrolyze between 8 and 12 (Zr and Pd)?

   Answer. 8 is more likely to have its $M-C$ bond hydrolyze. In 12, benzene, because it is so stable, is not a great leaving group and the square planar ge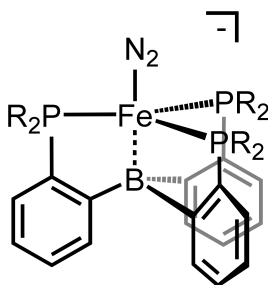ometry at each metal center is extra stable because of the 16 electron rule (or 18 electrons depending on $Pd-Pd$ bonding). However, in 8, the $M-CH_3$ bond is highly unstable due to the electron count of 14.   □

3. Consider the following complex.

   a) Assign an oxidation state, d count, overall electron count, and "L/X/Z" formalism.

   Answer. The oxidation state is Fe^0 since all ligands form dative bonds.
   The d count is d^8.
   With respect to the overall electron count, N_2 is a 2-electron donor and the bottom ligand is a 6-electron donor. Thus, the electron count is $(2+6) + (8) - (-1) = 17$.
   The nitrogen is L-type, and the other ligand is L_3Z-type (assuming that there is a single $Fe-B$ bond).   □

   b) Draw 3 different resonance structures for both the $Fe-N_2$ interaction and the $Fe-B$ interactions in this compound (a total of 6) and explain how the oxidation state, d count, and "L/X/Z" formalism changes as a function of resonance structure.

   Answer. $Fe - \overset{\oplus}{N} \equiv N\textbf{:}$ will be our base Lewis structure of this type. This is an L-type ligand.

   $Fe = \overset{\oplus}{N} = \overset{\ominus}{\overset{\cdot\cdot}{N}}$ exhibits no changes in oxidation state, d count, or type[1].

   $Fe \equiv \overset{\oplus}{N} - \overset{2\ominus}{\overset{\cdot\cdot}{N}\textbf{:}}$ exhibits no changes in oxidation state, d count, or type.

   $Fe \quad B$ will be our base Lewis structure of this type. This is not any type of ligand as no bond is present.

   $Fe - \overset{\ominus}{B}$ exhibits no changes in oxidation state or d count. This is a Z-type ligand.

   $Fe = \overset{2\ominus}{B}$ exhibits no changes in oxidation state, d count, or type (still Z-type).   □

   [1]As per Sophie's explanation in office hours, there are not actually more electrons in the $M-C$ double bond in this resonance structure; rather, it simply shows up spectroscopically as shorter, so we denote this still 2-electron bond as having bond order 2. We have a similar case for the other resonance structures.

c) How might the valence of the species differ from the oxidation state in the resonance structure depicted in the chem draw above?

Answer. For the reason discussed in Footnote 1, the valence would not change in any of the $Fe-N$ resonance structures. However, depending on the nature and extent of the $Fe-B$ bonding, it could well increase when bonding first occurs (although, again, it will not likely change within the bonded resonance structures). ☐

4. For the following ligands, draw all possible resonance structures with formal charges, indicate the number of electrons donated to a generic metal complex, and assign the ligand to its appropriate "L/X/Z" formulation.

a) PR_3.

Answer. Structure:

$$M - P - R$$

(with R above and below P)
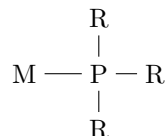
2-electron donor.
L-type ligand. ☐

b) CO.

Answer. Resonance structures:

$$M - C \equiv O:^{\oplus} \longleftrightarrow M = C = O: \longleftrightarrow M \equiv C - \ddot{O}:^{\ominus}$$
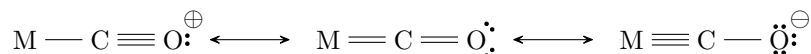
2-electron donor.
L-type ligand. ☐

c) NO.

Answer. Resonance structures:

$$\left[M - N^{\oplus} \equiv O: \right]^{+} \longleftrightarrow \left[M = N^{\oplus} = O: \right]^{+} \longleftrightarrow \left[M \equiv N^{\oplus} - \ddot{O}:^{\ominus} \right]^{+}$$

$$M \diagdown \overset{\ddot{N}}{\diagup} \diagdown O:$$
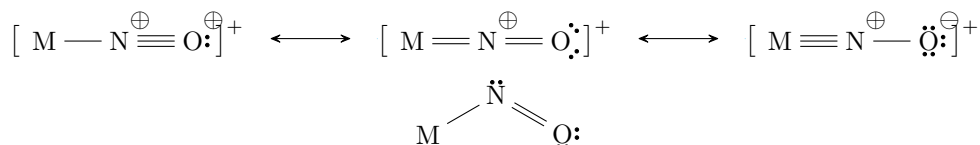
The top set of resonance structures are 3-electron-donating L-type ligands. The bottom structure is a 1-electron-donating X-type ligand. ☐

d) C_3H_5.

Answer. Resonance structures:

$$\text{(allyl resonance structures bound to M)} \longleftrightarrow$$

3-electron donor.
LX-type ligand. ☐

e) "NR."

Answer. Resonance structures:

2-electron donor.

X_2-type ligand. □

5. Predict the spin state, μ_{eff}, and χT values for the following ions in the indicated geometry.

a) Tetrahedral Mn(II).

Answer. High spin d^5 (tetrahedral has small orbital splitting). Thus,

$$\mu_{\text{eff}} = 2\sqrt{\frac{5}{2}\left(\frac{5}{2}+1\right)} \qquad\qquad \chi T = \frac{2^2}{8}\left(\frac{5}{2}\left(\frac{5}{2}+1\right)\right)$$

$$= \sqrt{35} \qquad\qquad\qquad\qquad = \frac{35}{8}$$

□

b) Octahedral Ir(III).

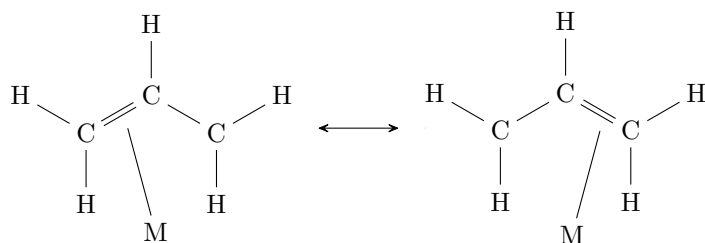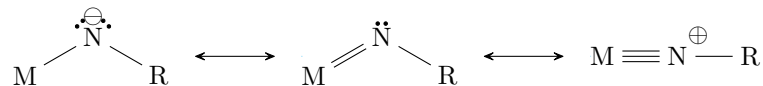*Answer.* Low spin d^6 (high oxidation state implies large Δ, so low spin). Thus,

$$\mu_{\text{eff}} = 2\sqrt{0(0+1)} \qquad\qquad \chi T = \frac{2^2}{8}(0(0+1))$$

$$= 0 \qquad\qquad\qquad\qquad = 0$$

□

c) Octahedral Ru(III).

Answer. Low spin d^5 (high oxidation state implies large Δ, so low spin). Thus,

$$\mu_{\text{eff}} = 2\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)} \qquad\qquad \chi T = \frac{2^2}{8}\left(\frac{1}{2}\left(\frac{1}{2}+1\right)\right)$$

$$= \sqrt{3} \qquad\qquad\qquad\qquad = \frac{3}{8}$$

□

d) Square planar Co(II).

Answer. Low spin d^7 (square planar has large orbital splitting). Thus,

$$\mu_{\text{eff}} = 2\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)} \qquad\qquad \chi T = \frac{2^2}{8}\left(\frac{1}{2}\left(\frac{1}{2}+1\right)\right)$$

$$= \sqrt{3} \qquad\qquad\qquad\qquad = \frac{3}{8}$$

□

e) Square planar Pt(II).

Answer. Low spin d^8 (square planar has large orbital splitting). Thus,

$$\mu_{\text{eff}} = 2\sqrt{0(0+1)} \qquad\qquad \chi T = \frac{2^2}{8}(0(0+1))$$
$$= 0 \qquad\qquad\qquad\qquad = 0$$

$\square$

f) Octahedral Ni(II).

Answer. High spin d^8 (low oxidation state implies small Δ, so high spin). Thus,

$$\mu_{\text{eff}} = 2\sqrt{1(1+1)} \qquad\qquad \chi T = \frac{2^2}{8}(1(1+1))$$
$$= 2\sqrt{2} \qquad\qquad\qquad\qquad = 1$$

$\square$

g) Tetrahedral Cr(II).

Answer. High spin d^4 (tetrahedral has small orbital splitting). Thus,

$$\mu_{\text{eff}} = 2\sqrt{2(2+1)} \qquad\qquad \chi T = \frac{2^2}{8}(2(2+1))$$
$$= 2\sqrt{6} \qquad\qquad\qquad\qquad = 3$$

$\square$

6. Predict the relative radii between the two ions listed (i.e., same, larger, or smaller) assuming an octahedral field, and rationalize your choice.

a) Low spin Fe(II) or high spin Fe(II).

Answer. High spin Fe(II) has a larger radius than low spin Fe(II) because the e_g orbitals are antibonding, so having more antibonding electrons both pushes the bounds of the atom (increasing the atomic radius) and weakens bonds (increasing the covalent radius). $\square$

b) Mn(II) or Mn(III).

Answer. Mn(II) has a larger radius than Mn(III) because having more electrons means more intra-orbital repulsions, all of which push the bounds of the atom. $\square$

c) Low spin Ti(II) or high spin Ti(II).

Answer. The radius is the same (low spin equals high spin for d^2 complexes). $\square$

d) Zr(IV) or Zr(III).

Answer. Zr(III) has a larger radius than Zr(IV) for the same reasons listed in part (b). $\square$

7. The isolobal analogy is frequently used to help relate seemingly disparate fragments. Utilize this analogy to compare the bonding in terminal nitride (N) and alkylidyne (CR) complexes.

Answer. Since we have $M \equiv N\mathbf{:}$ and $M \equiv \ddot{C} - R$ for how the two ligands bond, we can assume based on the fact that the two ligands are isoelectronic and isolobal (simply replace a lone pair in the nitride with the bond in the alkylidyne, or vice versa) that they have similar bonding, stability, and chemical properties. $\square$

8. Read Green (1995). Based on this paper, answer the following questions.

   a) In your own words, explain the reasons why the author considers a different form of bond classification necessary.

      Answer. The ionic method relies heavily on the calculation of the metal center's oxidation state and coordination number. However, while these two quantities suitably treated the known inorganic compounds of the early twentieth century (i.e., ones that were easily described as ionic), they play less nicely with the oft covalently bonded complexes of today. As such, Green (1995) created the covalent bond classification method to solve issues arising from these two quantities.

      In brief, the problems with the oxidation state stem from the fact that calculations of it are debatable for some bonds, and they flat-out neglect homopolar bonds. The problems with coordination number mainly surround the fact that it can treat very similar compounds quite differently (for example, $Mo(CO)_6$, $Mo(\eta\text{-}C_6H_6)(CO)_3$, and $Mo(\eta\text{-}C_6H_6)_2$ have coordination numbers of 6, 9, and 12, respectively).   □

   b) Is it more common to have a MoL_2X_4 compound or MoL_4X_2 compound?

      Answer. It is more common to have a MoL_2X_4 compound than a MoL_4X_2 compound, as can be read from Figure 1 on Green (1995, p. 128).   □

   c) What are the differences in the ligand bonding orbitals for L-, X-, and Z-type ligands?

      Answer. L-type: Two electrons are donated from a ligand-based orbital to an empty orbital on the metal center via the formation of a single dative bond.

      X-type: One electron is donated from a singly occupied ligand-based orbital to the metal center via the formation of a single covalent bond that also requires one electron from the metal center.

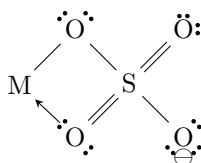   Z-type: An empty ligand orbital accepts an electron pair from the metal via the formation of a single bond.   □

   d) Draw L_2, LX, and X_2 forms of a sulfate ion bound to a generic metal M.

      Answer.
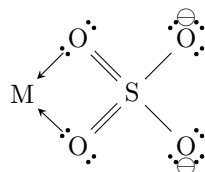
      (a) L_2 form.   (b) LX form.   (c) X_2 form.
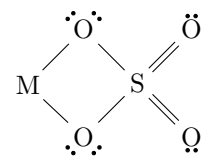
      Figure 1: Different ways sulfate can bind to a metal center.

                                                                                                                      □

   e) What does valency/valence number mean and how does that differ from oxidation state? What type of complex has a different valence number and oxidation state? Similarly, what does ligand bond number mean and how does this differ from coordination number? Give an example of a ligand where coordination number and ligand bond number differ.

      Answer. **Valency**: The number of X-functions on the ligands, where an X-function is a singly occupied orbital on the ligand which requires one electron from the metal center to form a two-electron covalent bond. *Also known as* **valence number**, **V.N.**

      Oxidation state: The number of electrons that the metal center gains or loses when all bonds are homolytically and ionically cleaved. *Also known as* **O.S.**

      Unlike the O.S., the V.N. includes homopolar (e.g., $M-M$) bonds and cannot, by definition, be negative.

Ligand bond number: The sum of the number of X-functions and the number of L-functions on the ligands, where an X-function is defined as above and an L-function is a single ligand orbital occupied by two electrons, both of which are donated to an empty orbital on the metal center during bonding. *Also known as* **L.B.N.**

Coordination number: The number of other atoms bonded to the metal center. *Also known as* **C.N.**

The L.B.N. and C.N. differ when the metal ligand bonding is more complex. For example, one place where the two differ is in any coordination complex with a double bonded ligand (that's two X-functions but only one ligand). □

f) What does two ligands being in the same ligand domain mean? How does this relate to the isolobal analogy from question 7?

Answer. It means that they have similar steric and electronic properties. Although ligands in the same domain may not be isolobal (or isoelectronic) and have *that* kind of close similarity, they do share more than a passing resemblance. □

2   Intro to Reactions and Ligands

4/19:   1. For the following pairs of complexes, predict which should exchange more rapidly and justify your answer.

  a) $[Cr(CN)_6]^{4-}$ or $[Cr(CN)_6]^{3-}$.
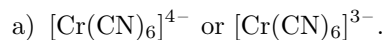
  Answer. $[Cr(CN)_6]^{4-}$ should exchange more rapidly. This is due to the lesser magnitude oxidation state on the chromium.   □

  b) $[Cr(H_2O)_6]^{3+}$ or $[Ni(H_2O)_6]^{2+}$.
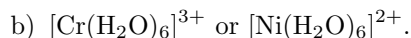
  Answer. $[Ni(H_2O)_6]^{2+}$ should exchange more rapidly. This is because the nickel's d^8 configuration will be more labile than the chromium's d^3 configuration, despite the nickel's smaller size. The instability of the d^8 configuration comes from its partially filled antibonding orbitals, and the stability of the d^3 configuration comes from its half-filled t_{2g} set.   □

  c) $[Co(NH_3)_6]^{3+}$ or $[Co(NH_3)_6]^{2+}$.
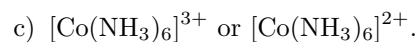
  Answer. $[Co(NH_3)_6]^{2+}$ should exchange more rapidly. This is due to the lesser magnitude oxidation state on the cobalt.   □

  d) $[Cu(NH_3)_4]^{2+}$ or $[Cu(en)_2]^{2+}$.
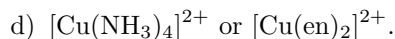
  Answer. $[Cu(NH_3)_4]^{2+}$ should exchange more rapidly. This is due to the chelate effect, which $[Cu(en)_2]^{2+}$ has but $[Cu(NH_3)_4]^{3+}$ doesn't. Indeed, even though the copper in $[Cu(NH_3)_4]^{3+}$ has a higher oxidation state, the extra stability from both entropic considerations and, to a lesser extent, effective concentration in the chelate effect slows the exchange rate of $[Cu(en)_2]^{2+}$ even more.   □

  e) $[PtCl_3NH_3]^-$ or $[Pt(CN)_3NH_3]^-$.
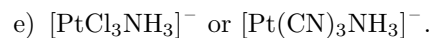
  Answer. $[Pt(CN)_3NH_3]^-$ should exchange more rapidly. This is because CN^- is a stronger trans-directing ligand than Cl^-, so the NH_3 opposite it should exchange much more rapidly.   □

  2. Consider two generic ML_6 and ML_4 complexes.

  a) If you had to guess at a mechanism for the substitution of a ligand L' in these complexes, which would be dissociative and which would be associative?

  Answer. ML_6 ligand substitution would probably be dissociative, and ML_4 ligand substitution would probably be associative. This is because there is greater steric clashing in ML_6 which makes it more favorable for a ligand to dissociate, and sterics hinder a ligand L' from attacking ML_6 to a greater extent than ML_4.   □

  b) In the substitution reaction of the ML_6 complex with L', you do detailed kinetic studies that suggest that the rate has a first order dependence on $[ML_6]$ and $[L']$. Is this consistent with your answer from part (a)? What dependence should be observed for associative/dissociative mechanisms?

  Answer. A first order dependence on $[ML_6]$ and $[L']$ suggests an associative mechanism. This is not consistent with my answer from part (a). Indeed, if a dissociative mechanism for ML_6 ligand substitution were present, we would expect to see pseudo-first order conditions in $[ML_6]$, alone, upon swamping the reaction with $[L']$.   □

  3. In the electron transfer reaction between $[Co(NH_3)_5X]^{2+}$ and $[Cr(H_2O)_5]^{2+}$, the rate of the reaction depends strongly on the X^- ligand. When $X = Cl^-$, the rate is $60\,000$ and when $X = H_2O$ (note that the complex is 3+ in this case) a rate of 0.5 is observed. Rationalize this difference in rate.

Answer. As ligand size and charge increase, so does reaction rate. Ligand size helps because the extra diffusion of the electron cloud literally extends electron density further between the compounds and doesn't necessitate that they exist so close together. Charge also helps because of its electrostatic influence (it's easier to transfer an electron if there are more electrons at play to assist in the process). □

4. In class we discussed the Creutz-Taube ion, which is a classic example of a mixed-valence complex. The degree of mixed-valency will be directly proportional to the rate of inter-valence charge transfer.

   a) Mixed valency is more difficult to engender in first row complexes. For instance, the Fe-analogue of the Creutz-Taube ion $[(NH_3)_5Fe-pyz-Fe(NH_3)_5]^{5+}$ is charge localized. Why might this be the case in this Fe example?

      Answer. Although iron and ruthenium share a group (and thus an electron configuration and many properties), the iron ion is significantly smaller than the ruthenium ion. Thus, its less diffuse electron cloud hinders its ability to delocalize charge, meaning that it is both more reticent to give up and accept an electron. Additionally, since it can have a high spin configuration, there is more nuclear rearrangement to undergo during each transfer. □

   b) Predict which of the following pairs will be most delocalized (fastest IVCT) and least delocalized (slowest IVCT) for the following Creutz-Taube ion analogues (all ligands are the same as in part (a)).

      i. $[Cr_2]^{5+}$ or $[Cr_2]^{7+}$.

         Answer. $[Cr_2]^{7+}$ will be more delocalized. Despite the higher magnitude oxidation state, these chromiums have at most 3 d-electrons, whereas the other pair can go up to 4. For the others, going up to 4 d-electrons means having either an $e_g{}^*$ electron or forcing spin pairing; either outcome would increase the nuclear reorganization needed between each transition and decrease the IVCT. □
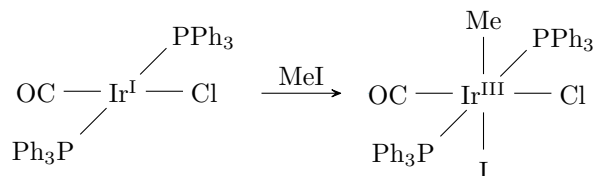
      ii. $[Co_2]^{5+}$ or $[Fe_2]^{5+}$ (all ions are low-spin).

         Answer. $[Fe_2]^{5+}$ will be more delocalized. Even though it has fewer electrons than $[Co_2]^{5+}$, it has a larger radius, so it can more easily share them. □

5. Predict the reactivity of $Ir(CO)(Cl)(PPh_3)_2$ with the following reagents.

   a) MeI.
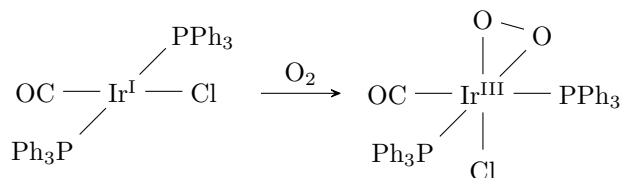
      Answer. This reaction will proceed as follows (S_N2 mechanism).

   b) O_2.

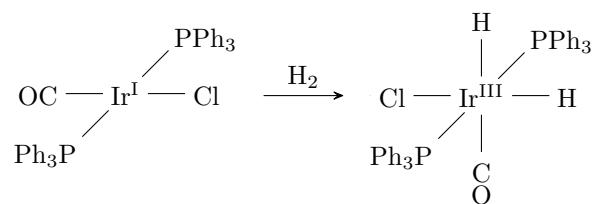   *Answer.* This reaction will proceed as follows (concerted mechanism).

c) H_2.

    Answer. This reaction will proceed as follows (concerted mechanism).

                              □

6. Metal alkyl species have historically been difficult to isolate.

   a) Why?

      Answer. Alkyl species are often very stable, so it's hard to get them to react in such a way that you can separate them from whatever else they're mixed up in. Additionally, some of the first alkyls to be identified were highly reactive, e.g., the extremely flammable $ZnEt_2$ (isolated by reacting zinc metal with two equivalents of ethyl iodide) and the reactive Grignard reagents. □

   b) Name three alkyl (or aryl, etc.) groups that should be stable.

      Answer. Alkyl groups without β-hydrogens are generally more stable. Two examples of these are fluoroalkyls and the methyl group. However, some alkyl groups have stable β-hydrogens for other reasons, such as ring strain. One example of such a group is norbornyl. □

   c) In class, I said that metallacycles are more stable than other alkyls. Why? Would you expect a larger or smaller metallacycle to be more stable?

      Answer. Metallacycles are less reactive because their β-hydrogens are less reactive due to ring strain. As such, a smaller metallacycle would probably be more stable with respect to β-hydride elimination because it is less likely to bend into a favorable position. Additionally, the ideal size for metallacycle stability is a 5- or 6-membered ring, which is fairly small. □

7. Metal olefin complexes can react via insertion, electrophilic attack, and nucleophilic attack. For each of these transformations, indicate the change in electron count, coordination number, and oxidation state on the metal center.

   Answer. Insertion: e^- count decreases by 2, C.N. decreases by 2, and O.S. does not change.

   Electrophilic attack: e^- count decreases by 1, C.N. decreases by 1, and O.S. increases by 2.

   Nucleophilic attack: e^- count does not change, C.N. decreases by 1, and O.S. does not change.   □

8. Transition metal carbene complexes have been known for many years, but there are two distinct types: Fischer Carbenes and Schrock type Alkylidenes. Differentiate these ligand types using diagrams and resonance structures. How should their reactivity change?

   Answer.

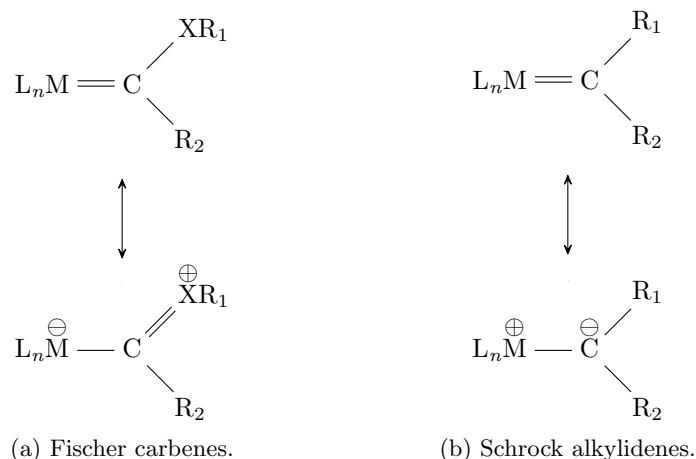(a) Fischer carbenes.   (b) Schrock alkylidenes.

Figure 2: Carbene regime resonance structures.

   Fischer carbenes are electrophilic at the carbon, and Schrock alkylidenes are nucleophilic at the carbon. This notably implies that Fischer carbenes more readily participate in cyclopropanation.   □

9. Rank the following complexes, from highest to lowest, in terms of their CO stretching frequency and rationalize: $Pt(CO)_4{}^{2+}$, $Ni(CO)_4{}^{2+}$, $PtCl_2(CO)_2$, $Fe(CO)_5{}^{2-}$, $Re(CO)_4{}^{3-}$, and $Mo(CO)_6$.

Answer.

$$Ni(CO)_4{}^{2+} > Pt(CO)_4{}^{2+} > PtCl_2(CO)_2 > Mo(CO)_6 > Fe(CO)_5{}^{2-} > Re(CO)_4{}^{3-}$$
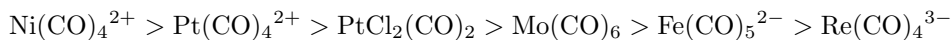
ν_{CO} increases as backbonding decreases. As such, to rank the complexes by their CO stretching frequency, it will suffice to rank them by the strength of their backbonding. Note that backbonding decreases as d count increases, and as we move up and to the right in the transition metals on the periodic table. $L \longrightarrow M$ σ donation can also increase metal backbonding.

We will show that every compound in the list exhibits less backbonding than the one after it.

To begin, the only difference between $Ni(CO)_4{}^{2+}$ and $Pt(CO)_4{}^{2+}$ is the position of the metal center in Group 10. Since Ni is a first row TM and Pt is a third row TM, the Ni center will backbond more weakly than Pt center.

The only difference between $Pt(CO)_4{}^{2+}$ and $PtCl_2(CO)_2$ is the exchange of two carbonyl ligands for chlorides. Since chlorides are stronger σ donors, they will make their Pt center slightly more electron rich, causing it to engage in slightly more backbonding.

To compare $PtCl_2(CO)_2$ and $Mo(CO)_6$, we will focus on the large differences in the metal center and neglect the smaller ones in the ligands. Indeed, although Pt is a third row TM and Mo is second row, platinum both has a higher oxidation state and comes later in the periodic table (i.e., has a higher electronegativity). Both of these factors decrease its relative backbonding.
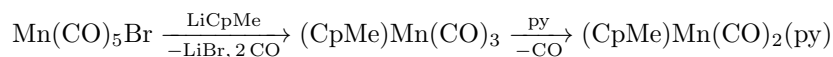
There are a number of differences between $Mo(CO)_6$ and $Fe(CO)_5{}^{2-}$. To begin with, Mo is lower and earlier in the periodic table than Fe. However, molybdenum also has a relatively higher oxidation state and more ligands to which it can backbond. As such, it backbonds less to each ligand overall.

Lastly, we must discuss $Fe(CO)_5{}^{2-}$ and $Re(CO)_4{}^{3-}$. Both have identical d counts, but Fe comes later in the periodic table, is higher in the periodic table, has a higher oxidation state, and has more ligands than Re. As such, the iron center most certainly backbonds less strongly than the rhenium center. $\square$

10. Provide synthetic routes to the following compounds from the specified starting material. Show all coproducts and provide balanced reactions for each step in your synthesis.

a) $(CpMe)Mn(CO)_2(py)$ from $Mn(CO)_5Br$.

Answer.

$$Mn(CO)_5Br \xrightarrow[-LiBr, \, 2\,CO]{LiCpMe} (CpMe)Mn(CO)_3 \xrightarrow[-CO]{py} (CpMe)Mn(CO)_2(py)$$

$\square$

b) $Cp_2Zr(CO)_2$ from $ZrCl_4$.

Answer.

$$ZrCl_4 \xrightarrow[-2\,LiCl]{2\,LiCp} Cp_2ZrCl_2 \xrightarrow[-2\,KCl]{2\,KC_8} Cp_2Zr \xrightarrow{2\,CO} Cp_2Zr(CO)_2$$

$\square$
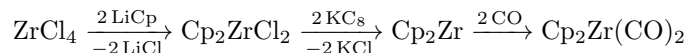
c) $[(C_5H_4Pr)CpFe]^+[PF_6]^-$ from $FeCl_2$.

Answer.

$$FeCl_2 \xrightarrow[-LiCl]{LiCp} CpFeCl \xrightarrow[-LiCl]{LiC_5H_4Pr} (C_5H_4Pr)CpFe \xrightarrow[-Ag^0]{AgPF_6} [(C_5H_4Pr)CpFe]^+[PF_6]^-$$

$\square$
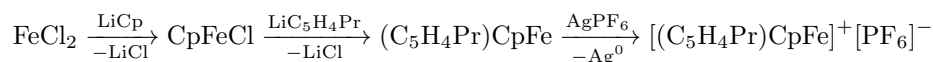
d) $PhMn(CO)_5$ from $Mn_2(CO)_{10}$.

Answer.

$$\frac{1}{2}\, Mn_2(CO)_{10} \xrightarrow{\frac{1}{2}Br_2} Mn(CO)_5Br \xrightarrow[-LiBr]{LiPh} PhMn(CO)_5$$

□
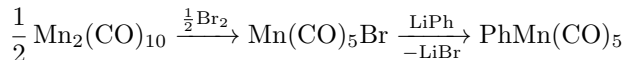
e) $CpMo(CO)_2(PPh_3)\{C(=O)Bu\}$ from $Mo(CO)_6$.

$$Mo(CO)_6 \xrightarrow[-2\,CO]{Br_2} Mo(CO)_4Br_2 \xrightarrow[-LiBr,\,CO]{LiCp} CpMo(CO)_3Br \xrightarrow[-BEt_3,\,LiBr]{LiBHEt_3} CpMo(CO)_3H$$

$$\xrightarrow{\qquad} CpMo(CO)_2\{C(=O)Bu\} \xrightarrow{PPh_3} CpMo(CO)_2(PPh_3)\{C(=O)Bu\}$$
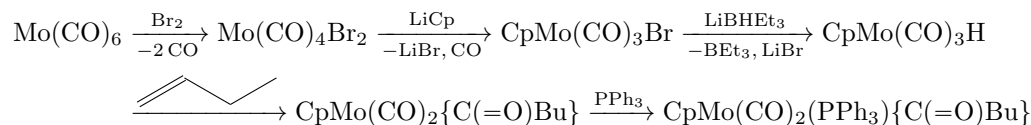
f) $[Cp^*Ta(\mu_2\text{-}Br)_2]_2$ from $TaBr_5$.

Answer.

$$2\,TaBr_5 \xrightarrow[-2\,LiBr]{2\,LiCp^*} 2\,CpTaBr_4 \xrightarrow[-4\,KBr]{4\,KC_8} 2\,CpTaBr_2 \longrightarrow [Cp^*Ta(\mu_2\text{-}Br)_2]_2$$

□
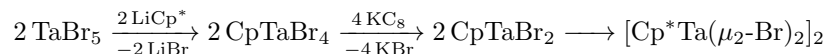
g) $(PPh_3)_2NiClNO$ from $NiCl_2$.

Answer.

$$NiCl_2 \xrightarrow[-Cl]{KC_8} NiCl \xrightarrow{NO^-} NiClNO \xrightarrow{2\,PPh_3} (PPh_3)_2NiClNO$$
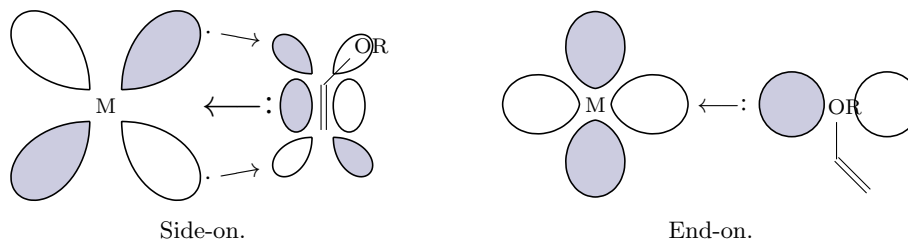
□

11. Vinyl ethers can bind to metals in an "end-on" or "side-on" manner, as shown below.

Side-on.   End-on.

a) Describe the key bonding interactions in each case. Please be specific about which orbitals are involved and illustrate your description with clear diagrams.

Answer.

Side-on.   End-on.

In the side-on manner, there is σ donation and π acceptance (the metal d_{xy} orbital is involved). In the end-on case, there is only σ donation (the metal $d_{x^2-y^2}$ orbital is involved). □

b) What properties of the L_nM unit will favor the end-on binding mode? Which properties will favor the side-on mode?
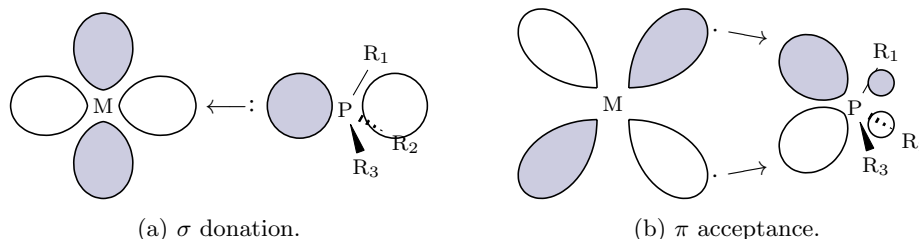
Answer. If the metal center is electron rich and soft, the side-on mode will be favored as it gives the metal center the chance to delocalize its electron density through M $\longrightarrow$ L π backbonding. If it is electron poor and hard, the end-on mode will be favored due to the dative nature of the bond from the ether and the hardness of the oxygen atom. □

12. Equilibrium constants for the reaction $Co(CO)Br_2L_2 \longrightarrow CoBr_2L_2 + CO$ are given below. All values of K were measured at the same temperature.

L	K
PEt_3	1
PEt_2Ph	2.5
$PEtPh_2$	24.2

a) Depict the orbital interactions between a phosphine ligand and a metal center.

Answer.

(a) σ donation.

(b) π acceptance.

□

b) Account for this trend in equilibrium constants.

Answer. Phenyl groups are more electron rich than ethyl groups. As such, their donation to the metal center both makes it easier for cobalt to dissociate a carbonyl and helps stabilize the unstable $15\,e^-$ product. □

c) Of these three phosphines, which will give the cobalt complex with the lowest energy carbonyl stretch in the infrared spectrum? Explain briefly.

Answer. $PEtPh_2$ because its inductive donation effects are the greatest. The extra electron density that it donates to the cobalt center will increase cobalt's backbonding to the carbonyl ligand, lowering ν_{CO}. □

13. This question is meant to guide you through through Prof. Jack Halpern's classic kinetic study of Vaska's complex $IrCl(CO)(PPh_3)_2$ and its Br and I analogues for the oxidative addition of H_2, O_2, and CH_3I (Chock & Halpern, 1966).

a) Provide three-dimensional drawings for the three $IrX(CO)(PPh_3)_2$ complexes studied for CH_3I and H_2 reactivity. Classify each ligand as σ/π and as donor/acceptor.
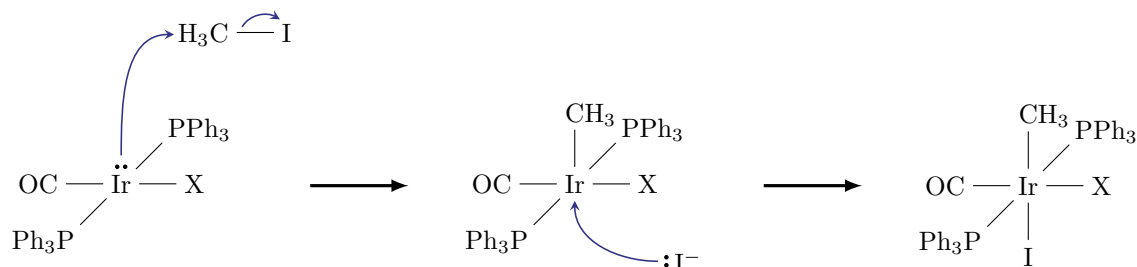
Answer.
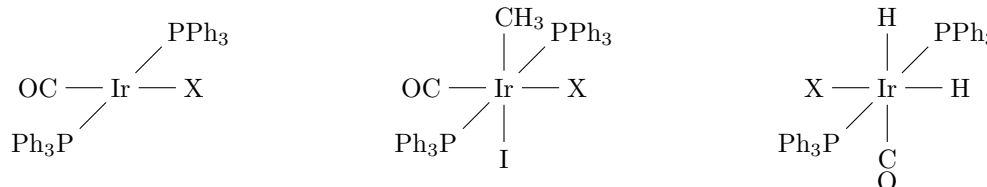
Every X is a σ, π-donor. H and CH_3 are pure σ-donors. CO and PPh_3 are σ-donors/π-acceptors.

□

b) Draw a general mechanism for the oxidative addition of CH_3I to $IrX(CO)(PPh_3)_2$. Explain each step in your own words and label species as a nucleophile or an electrophile as appropriate.

Answer.

The first step is S_N2, with Vaska's complex acting as the incoming nucleophile for the backside attack of methyl iodide. As a result of this step, the methyl group of methyl iodide bonds to Vaska's complex and the electrons that had been bonding the iodine to the methyl group get pushed back on to the electrophilic iodine, which then leaves. Newly saturated with electrons, the iodide ion engages in another backside attack, this time on Vaska's complex *trans* to where the methyl added at the open octahedral coordination site. □

c) Rank these complexes in increasing order of electron density on the metal. Explain your ranking and support it with experimental data.

Answer.
$$IrI(CO)(PPh_3)_2 < IrBr(CO)(PPh_3)_2 < IrCl(CO)(PPh_3)_2$$
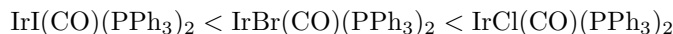
For the three forms of Vaska's complex (one with each halogen save fluorine), we have $\nu_{CO} = 1950, 1955, 1975\,\text{cm}^{-1}$ for $X = Cl, Br, I$, respectively. This implies that π backbonding follows the order $Cl > Br > I$. It follows that the order of electron density is the same, as shown above. □

d) Which $IrX(CO)(PPh_3)_2$ complex reacts with CH_3I the fastest?

Answer. $IrCl(CO)(PPh_3)_2$ reacts with CH_3I the fastest. □

e) Give a general mechanism for the oxidative addition of H_2 to $IrX(CO)(PPh_3)_2$ and explain each step in your own words. Consider our discussion in lecture when drawing the transition state.

Answer.
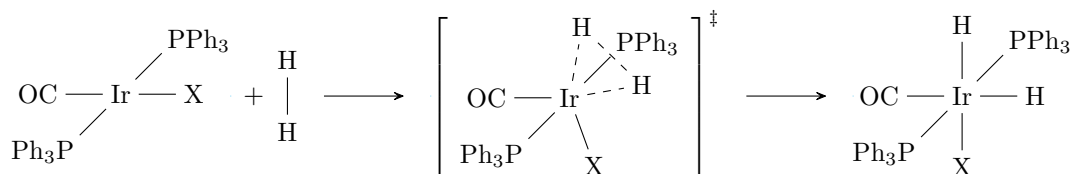
This is a concerted oxidative addition. We know that it is concerted because the rate law is first order in both reactants. In the one step, the H_2 molecule approaches the iridium center, pushing one of the ligands out of the way and forming a transition state where each hydrogen begins to bond with the iridium and the $H-H$ bond itself begins to break. □

f) Which complex reacts with H_2 the fastest? Considering the transition state you drew above, speculate as to why this is the case.

Answer. $IrI(CO)(PPh_3)_2$ reacts with H_2 the fastest. This could be because iodine is the best σ-donor, meaning that iridium has more electron density with which it can attack H_2. □

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Chock, P. B., & Halpern, J. (1966). Kinetics of the addition of hydrogen, oxygen, and methyl iodide to some square-planar iridium(I) complexes. *Journal of the American Chemical Society, 88*(15), 3511–3514. https://doi.org/10.1021/ja00967a009

Green, M. L. H. (1995). A new approach to the formal classification of covalent compounds of the elements. *Journal of Organometallic Chemistry, 500*(1-2), 127–148. https://doi.org/10.1016/0022-328X(95)00508-N