

CHEM 20200 (Inorganic Chemistry II) Problem Sets

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May 22, 2021

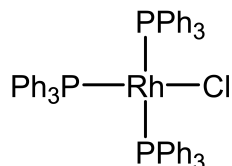
Contents

1	Electronic Phenomena	1
2	Intro to Reactions and Ligands	14
3	Intro to Catalysis	22
4	More Catalytic Processes	25
5	Even More Catalytic Processes	31
	References	39

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)

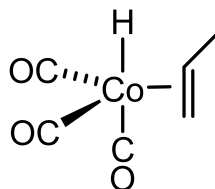


Answer.

- (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)

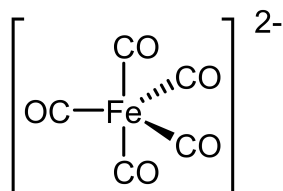


Answer.

- (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.

□

3)

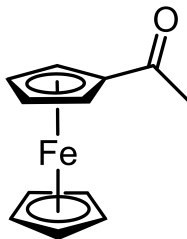


Answer.

- (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.

□

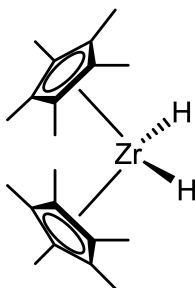
4)

*Answer.*

- (i) Fe^{2+} (both ligands are L_2X -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.

□

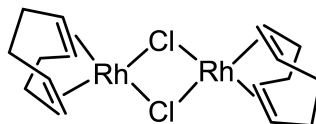
5)

*Answer.*

- (i) Zr^{4+} (both pentamethylcyclopentadienyl (Cp^*) groups are L_2X -type; both hydrides are X-type).
- (ii) Zr^{4+} is d^0 .
- (iii) Both 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.

□

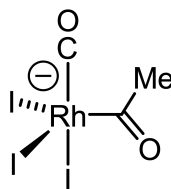
6)

*Answer.*

- (i) Both metals are Rh^+ (both cycloocta-1,5-dienyl (COD) groups are L_2 -type; both bridging chlorines ($\mu\text{-Cl}$) 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 $\mu\text{-Cl}$ ligands 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. Since this is a $16e^-$ square planar complex, there will be no Rh-Rh bonds even though the rhodiums have the electrons to form them.

□

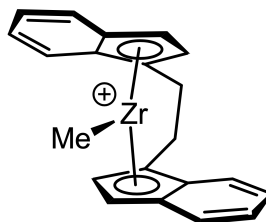
7)

*Answer.*

- (i) Rh^{3+} (the carbonyl is L-type; each iodide is X-type; the acyl 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.

□

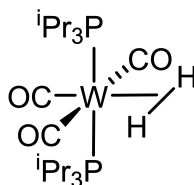
8)

*Answer.*

- (i) Zr^{4+} (the methyl is X-type; the other ligand is L_4X_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.

□

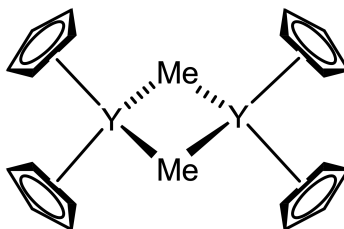
9)

*Answer.*

- (i) W^0 (every 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 H_2 adduct 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.

□

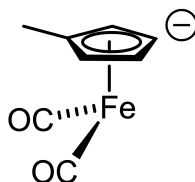
10)

*Answer.*

- (i) Y^{3+} (each cyclopentadienyl (Cp) group is L_2X -type; both bridging methyl (μ -Me) groups are LX-type).
- (ii) Y^{3+} is d^0 .
- (iii) Each Cp is a 5-electron donor, and both μ -Me groups are 3-electron donors. Thus, the ligands donate $4 \cdot 5 + 2 \cdot 3 = 26$ electrons in total. This combined with the above results yields $\frac{26+2 \cdot 3}{2} = 16$ as the electron count at each yttrium. Since neither yttrium has extra d electrons, there will be no Y–Y bonds.

□

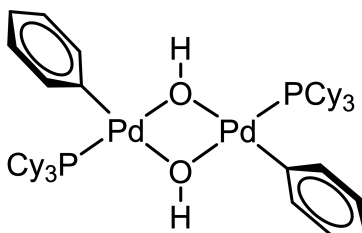
11)

*Answer.*

- (i) Fe^0 (both carbonyls are L-type; the methylcyclopentadienyl (CpMe) group is L_2X -type; the charge is $1-$).
- (ii) Fe^0 is d^8 .
- (iii) Both carbonyls are 2-electron donors, and the CpMe 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.

□

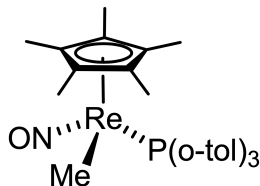
12)

*Answer.*

- (i) Pd^{2+} (both phenyl groups are X-type; both phosphines are L-type; both bridging hydroxides (μ -OH) are LX-type).
- (ii) Pd^{2+} is d^8 .
- (iii) Both phenyl groups are 1-electron donors, both phosphines are 2-electron donors, and both μ -OH groups 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 $\frac{12+2 \cdot 10}{2} = 16$ as the electron count at each palladium. Since this is a $16e^-$ square planar complex, there will be no Pd–Pd bonds even though the palladiums have the electrons to form them.

□

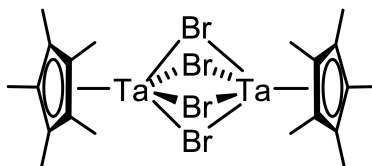
13)

*Answer.*

- (i) Re^+ (the [linear] nitrosyl group is LX-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 L_2X -type).
- (ii) Re^+ is d^6 .
- (iii) The nitrosyl group is a 3-electron donor (it will bond linearly to facilitate an $18e^-$ count), 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.

□

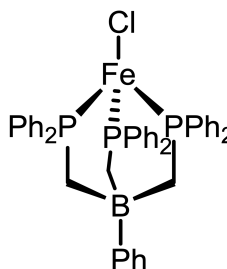
14)

*Answer.*

- (i) Ta^{3+} (both Cp^* groups are L_2X -type; each bridging bromine ($\mu\text{-Br}$) is LX-type).
- (ii) Ta^{3+} is d^2 .
- (iii) Both Cp^* groups are 5-electron donors, and both $\mu\text{-Br}$ groups are 3-electron donors. 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.

□

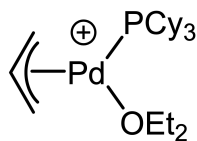
15)

*Answer.*

- (i) Fe^{2+} (the chloride is X-type; the tris(phosphino)borate group 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 tris(phosphino)borate group 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.

□

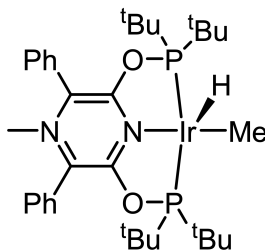
16)

*Answer.*

- (i) Pd^{2+} (the phosphine is L-type; the ether is L-type; the aryl is LX-type; the charge is 1+).
- (ii) Pd^{2+} is d^8 .
- (iii) The phosphine is a 2-electron donor, the ether is a 2-electron donor, and the aryl 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.

□

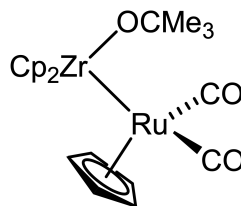
17)

*Answer.*

- (i) Ir^+ (the methyl is X-type; the hydride is X-type; the other ligand (PNP) is L_3 -type but carries a positive formal charge).
- (ii) Ir^+ is d^8 .
- (iii) The methyl group is a 1-electron donor, the hydrogen is a 1-electron donor, and the PNP group 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.

□

18)

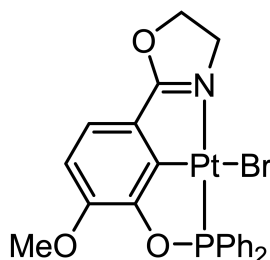
*Answer.*

- (i) Zr^{4+} (the tert-butoxide ($t\text{-Bu}$) is X-type; both Cp groups are L_2X -type; the Zr–Ru bond takes 1 electron), and Ru^{2+} (both carbonyls are L-type; the Cp is L_2X -type; the Zr–Ru bond takes 1 electron).
- (ii) Zr^{4+} is d^0 , and Ru^{2+} is d^8 (before Zr–Ru bonding).

- (iii) For the zirconium atom, the *t*-Bu 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).

□

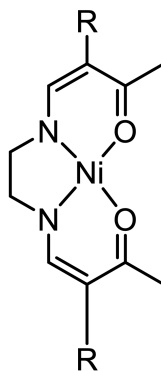
19)

*Answer.*

- (i) Pt^{2+} (the bromine is X-type; the other ligand (NCP) is L_2X -type).
 (ii) Pt^{2+} is d^8 .
 (iii) The bromine is a 1-electron donor, and the NCP group 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.

□

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 (and it is d^0), whereas 2 already has 18 electrons, and thus is more basic relatively. Also note that Co–H is acidic while Zr–H is hydridic. \square

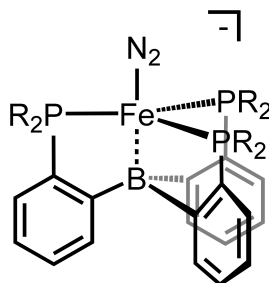
b) Which complex is more likely to be reduced or oxidized between 4 and 15 (both Fe)?

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. \square

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 because its M–C bond is more polarized. \square

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 and the negative charge balances out the borate.

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). \square

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

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

$\text{Fe} \equiv \text{N}^{\oplus} - \ddot{\text{N}}^{\ominus 2}$ exhibits no changes in oxidation state, d count, or type.

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

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

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

¹As 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.

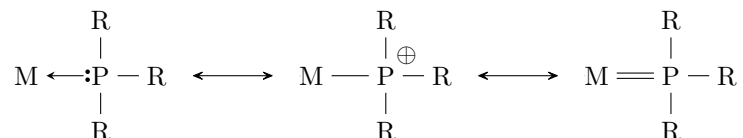
- c) How might the valence of the species differ from the oxidation state in the resonance structure depicted in the chem draw above?

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). \square

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:

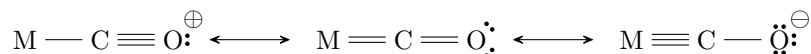


2-electron donor.

L-type ligand. \square

- b) CO.

Answer. Resonance structures:

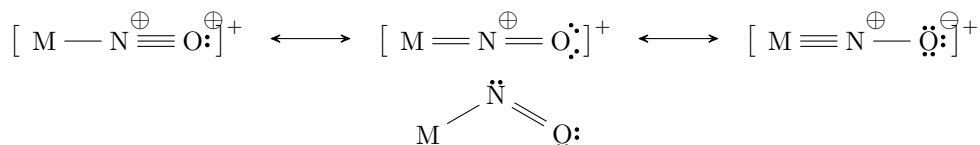


2-electron donor.

L-type ligand. \square

- c) NO.

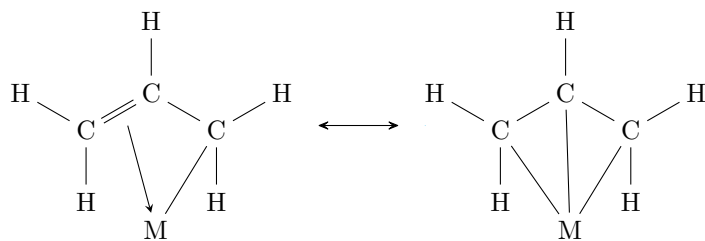
Answer. Resonance structures:



The top set of resonance structures are 3-electron-donating LX-type ligands. The bottom structure is a 1-electron-donating X-type ligand. \square

- d) C_3H_5 .

Answer. Resonance structures:

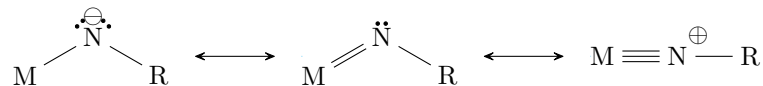


3-electron donor.

LX-type ligand. \square

e) "NR."

Answer. Resonance structures:



2-electron donor.

X₂-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,

$$\begin{aligned} \mu_{\text{eff}} &= 2\sqrt{\frac{5}{2}\left(\frac{5}{2} + 1\right)} & \chi T &= \frac{2^2}{8}\left(\frac{5}{2}\left(\frac{5}{2} + 1\right)\right) \\ &= \sqrt{35} & &= \frac{35}{8} \end{aligned}$$

□

b) Octahedral Ir(III).

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

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

□

c) Octahedral Ru(III).

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

$$\begin{aligned} \mu_{\text{eff}} &= 2\sqrt{\frac{1}{2}\left(\frac{1}{2} + 1\right)} & \chi T &= \frac{2^2}{8}\left(\frac{1}{2}\left(\frac{1}{2} + 1\right)\right) \\ &= \sqrt{3} & &= \frac{3}{8} \end{aligned}$$

□

d) Square planar Co(II).

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

$$\begin{aligned} \mu_{\text{eff}} &= 2\sqrt{\frac{1}{2}\left(\frac{1}{2} + 1\right)} & \chi T &= \frac{2^2}{8}\left(\frac{1}{2}\left(\frac{1}{2} + 1\right)\right) \\ &= \sqrt{3} & &= \frac{3}{8} \end{aligned}$$

□

e) Square planar Pt(II).

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

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

□

f) Octahedral Ni(II).

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

$$\begin{aligned}\mu_{\text{eff}} &= 2\sqrt{1(1+1)} & \chi T &= \frac{2^2}{8}(1(1+1)) \\ &= 2\sqrt{2} & &= 1\end{aligned}$$

□

g) Tetrahedral Cr(II).

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

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

□

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). □

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

Answer. Mn(II) has a larger radius than Mn(III) because it has more antibonding electrons. □

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). □

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

Answer. Zr(III) has a larger radius than Zr(IV) because it has populated d orbitals. □

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 $\text{M} = \text{N} \cdot$ and $\text{M} = \ddot{\text{C}} - \text{R}$ 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. □

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, $\text{Mo}(\text{CO})_6$, $\text{Mo}(\eta\text{-C}_6\text{H}_6)(\text{CO})_3$, and $\text{Mo}(\eta\text{-C}_6\text{H}_6)_2$ have coordination numbers of 6, 9, and 12, respectively). \square

- 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). \square

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

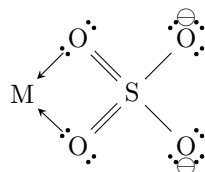
Answer. L-type: Two electrons are donated from a ligand-based orbital to an empty orbital on the metal center via the formation of a single dative bond.

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.

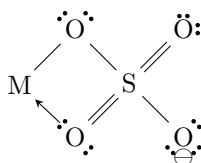
Z-type: An empty ligand orbital accepts an electron pair from the metal via the formation of a single bond. \square

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

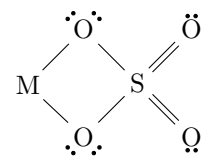
Answer.



(a) L_2 form.



(b) LX form.



(c) X_2 form.

Figure 1: Different ways sulfate can bind to a metal center. \square

- 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., $\text{M}-\text{M}$) 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.*

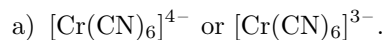
The L.B.N. and C.N. differ when the metal ligand bonding is more complex. For example, one place where the two differ is in any coordination complex with a double bonded ligand (that's two X-functions but only one ligand). □

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

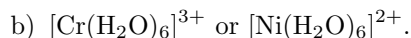
Answer. It means that they have similar steric and electronic properties. Although ligands in the same domain may not be isolobal (or isoelectronic) and have *that* kind of close similarity, they do share more than a passing resemblance. □

2 Intro to Reactions and Ligands

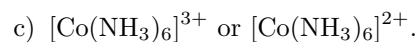
- 4/19: 1. For the following pairs of complexes, predict which should exchange more rapidly and justify your answer.



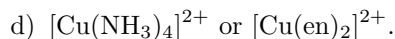
Answer. $[\text{Cr}(\text{CN})_6]^{4-}$ should exchange more rapidly. This is due to the lesser magnitude oxidation state on the chromium. \square



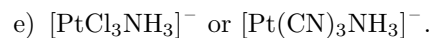
Answer. $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ should exchange more rapidly. This is because the nickel's d^8 configuration will be more labile than the chromium's d^3 configuration, despite the nickel's smaller size. The instability of the d^8 configuration comes from its partially filled antibonding orbitals, and the stability of the d^3 configuration comes from its half-filled t_{2g} set. \square



Answer. $[\text{Co}(\text{NH}_3)_6]^{2+}$ should exchange more rapidly. This is due to the lesser magnitude oxidation state on the cobalt. \square



Answer. $[\text{Cu}(\text{NH}_3)_4]^{2+}$ should exchange more rapidly. This is due to the chelate effect, which $[\text{Cu}(\text{en})_2]^{2+}$ has but $[\text{Cu}(\text{NH}_3)_4]^{3+}$ doesn't. Indeed, even though the copper in $[\text{Cu}(\text{NH}_3)_4]^{3+}$ 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 $[\text{Cu}(\text{en})_2]^{2+}$ even more. \square



Answer. $[\text{Pt}(\text{CN})_3\text{NH}_3]^-$ 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. \square

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 . \square

- 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 $[\text{ML}_6]$ and $[\text{L}']$. Is this consistent with your answer from part (a)? What dependence should be observed for associative/dissociative mechanisms?

Answer. A first order dependence on $[\text{ML}_6]$ and $[\text{L}']$ 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 $[\text{ML}_6]$, alone, upon swamping the reaction with $[\text{L}']$. \square

3. In the electron transfer reaction between $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ and $[\text{Cr}(\text{H}_2\text{O})_5]^{2+}$, the rate of the reaction depends strongly on the X^- ligand. When $\text{X} = \text{Cl}^-$, the rate is 60 000 and when $\text{X} = \text{H}_2\text{O}$ (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 (for an inner sphere mechanism, which this likely is). Ligand size helps because the extra diffusion of the electron cloud literally generates more overlap area. 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). \square

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 $[(\text{NH}_3)_5\text{Fe}-\text{pyz}-\text{Fe}(\text{NH}_3)_5]^{5+}$ 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. \square

- 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. $[\text{Cr}_2]^{5+}$ or $[\text{Cr}_2]^{7+}$.

Answer. $[\text{Cr}_2]^{7+}$ 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. \square

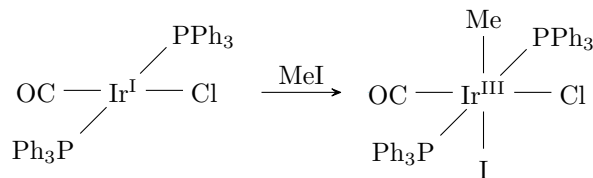
- ii. $[\text{Co}_2]^{5+}$ or $[\text{Fe}_2]^{5+}$ (all ions are low-spin).

Answer. $[\text{Fe}_2]^{5+}$ will be more delocalized. Even though it has fewer electrons than $[\text{Co}_2]^{5+}$, it has a larger radius, so it can more easily share them. \square

5. Predict the reactivity of $\text{Ir}(\text{CO})(\text{Cl})(\text{PPh}_3)_2$ with the following reagents.

- a) MeI.

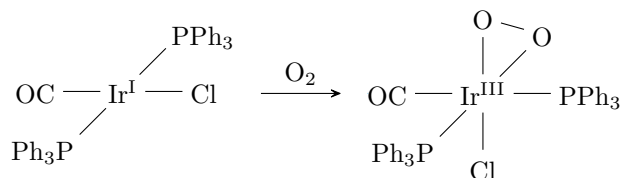
Answer. This reaction will proceed as follows ($\text{S}_{\text{N}}2$ mechanism).



\square

- b) O_2 .

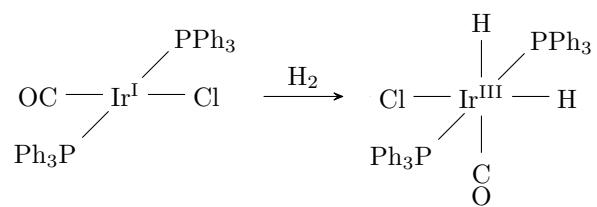
Answer. This reaction will proceed as follows (concerted mechanism).



\square

- 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. \square

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. \square

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. \square

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 1, and O.S. does not change.

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

Nucleophilic attack: e^- count does not change, C.N. does not change, and O.S. does not change. \square

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.

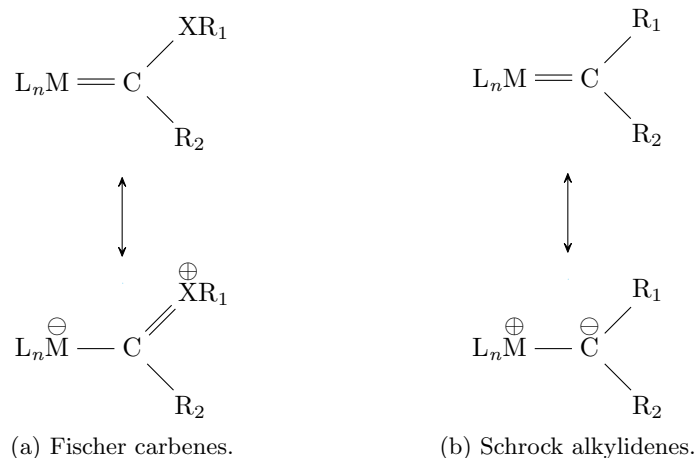
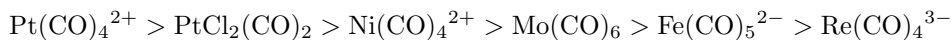


Figure 2: Carbene regime resonance structures.

Fischer carbenes are electrophilic at C, their heteroatom is stabilized, and they typically react with late metals. Schrock alkylidenes are nucleophilic at C, have no heteroatom, and typically react with early metals. \square

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

Answer.



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. $\text{L} \longrightarrow \text{M}$ 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 $\text{Pt}(\text{CO})_4^{2+}$ and $\text{PtCl}_2(\text{CO})_2$ 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 $\text{PtCl}_2(\text{CO})_2$ and $\text{Ni}(\text{CO})_4^{2+}$, we will focus on the differences in the metal center and neglect the ones in the ligands. Indeed, platinum has a higher electronegativity than nickel, so it will hold onto its electrons more tightly. Thus, it engages in less backbonding.

To compare $\text{Ni}(\text{CO})_4^{2+}$ and $\text{Mo}(\text{CO})_6$, 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.

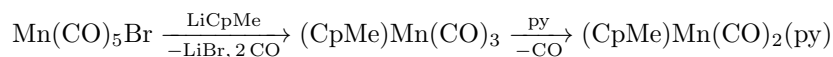
There are a number of differences between $\text{Mo}(\text{CO})_6$ and $\text{Fe}(\text{CO})_5^{2-}$. To begin with, Mo is lower and earlier in the periodic table than Fe. However, molybdenum also has a relatively higher oxidation state and more ligands to which it can backbond. As such, it backbonds less to each ligand overall.

Lastly, we must discuss $\text{Fe}(\text{CO})_5^{2-}$ and $\text{Re}(\text{CO})_4^{3-}$. 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) $(\text{CpMe})\text{Mn}(\text{CO})_2(\text{py})$ from $\text{Mn}(\text{CO})_5\text{Br}$.

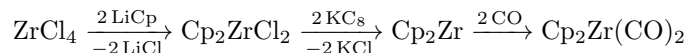
Answer.



\square

- b) $\text{Cp}_2\text{Zr}(\text{CO})_2$ from ZrCl_4 .

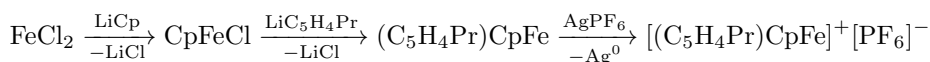
Answer.



\square

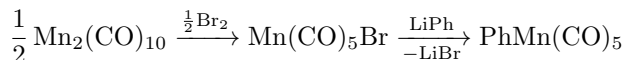
- c) $[(\text{C}_5\text{H}_4\text{Pr})\text{CpFe}]^+[\text{PF}_6]^-$ from FeCl_2 .

Answer.



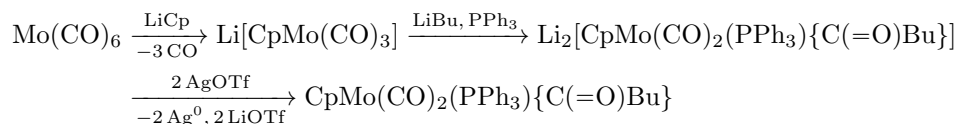
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- d)
- PhMn(CO)_5
- from
- $\text{Mn}_2(\text{CO})_{10}$
- .

Answer.

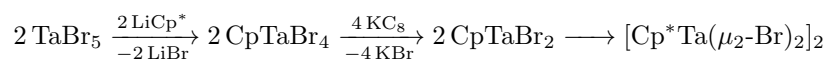
□

- e)
- $\text{CpMo(CO)}_2(\text{PPh}_3)\{\text{C(=O)Bu}\}$
- from
- Mo(CO)_6
- .

Answer.

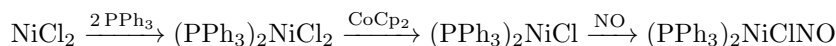
□

- f)
- $[\text{Cp}^*\text{Ta}(\mu_2\text{-Br})_2]_2$
- from
- TaBr_5
- .

Answer.

□

- g)
- $(\text{PPh}_3)_2\text{NiClNO}$
- from
- NiCl_2
- .

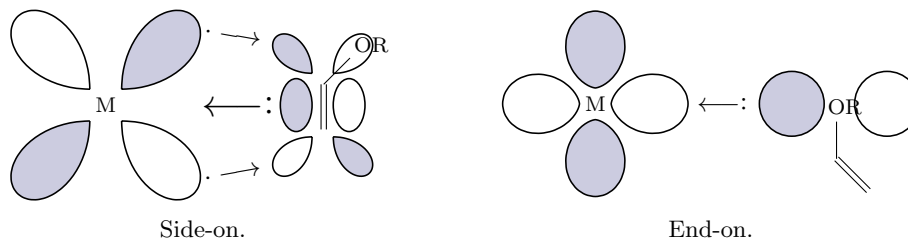
Answer.

□

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



- 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.

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?

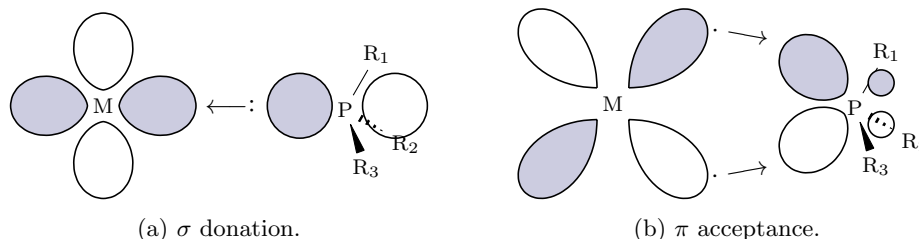
Answer. If the metal center is electron rich and soft, the side-on mode will be favored as it gives the metal center the chance to delocalize its electron density through $\text{M} \longrightarrow \text{L}$ π backbonding. If it is electron poor and hard, the end-on mode will be favored due to the dative nature of the bond from the ether and the hardness of the oxygen atom. □

12. Equilibrium constants for the reaction $\text{Co}(\text{CO})\text{Br}_2\text{L}_2 \longrightarrow \text{CoBr}_2\text{L}_2 + \text{CO}$ 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.



□

- b) Account for this trend in equilibrium constants.

Answer. Phenyl groups have stronger electron withdrawing effects than ethyl groups. As such, with them, backbonding is weakened, so it is easier for cobalt to dissociate a carbonyl. Additionally, steric effects from the larger phenyl groups help push the carbonyl off. □

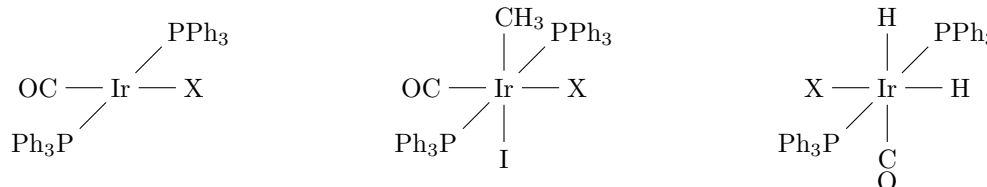
- c) Of these three phosphines, which will give the cobalt complex with the lowest energy carbonyl stretch in the infrared spectrum? Explain briefly.

Answer. PEt_3 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 $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ 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 $\text{IrX}(\text{CO})(\text{PPh}_3)_2$ complexes studied for CH_3I and H_2 reactivity. Classify each ligand as σ/π and as donor/acceptor.

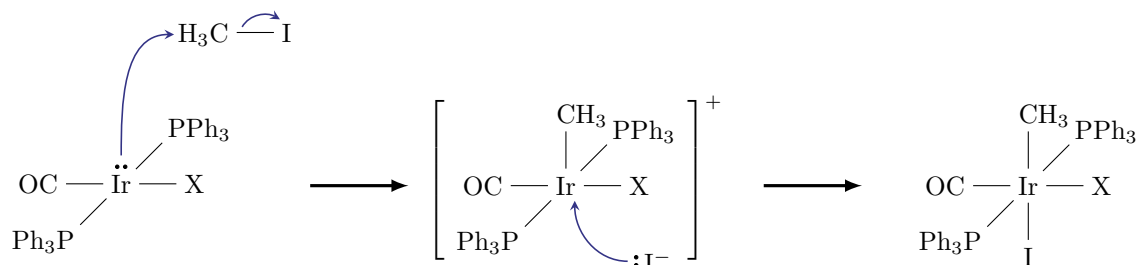
Answer.



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 $\text{IrX}(\text{CO})(\text{PPh}_3)_2$. Explain each step in your own words and label species as a nucleophile or an electrophile as appropriate.

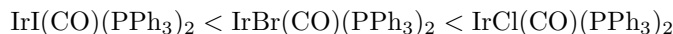
Answer.



The first step is $\text{S}_{\text{N}}2$, 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. \square

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

Answer.



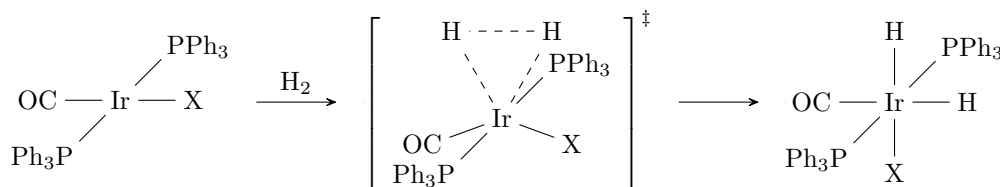
For the three forms of Vaska's complex (one with each halogen save fluorine), we have $\nu_{\text{CO}} = 1950, 1955, 1975 \text{ cm}^{-1}$ for $\text{X} = \text{Cl}, \text{Br}, \text{I}$, respectively. This implies that π backbonding follows the order $\text{Cl} > \text{Br} > \text{I}$. It follows that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

- d) Which $\text{IrX}(\text{CO})(\text{PPh}_3)_2$ complex reacts with CH_3I the fastest?

Answer. $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ reacts with CH_3I the fastest. \square

- e) Give a general mechanism for the oxidative addition of H_2 to $\text{IrX}(\text{CO})(\text{PPh}_3)_2$ 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 $\text{H}-\text{H}$ bond itself begins to break. \square

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

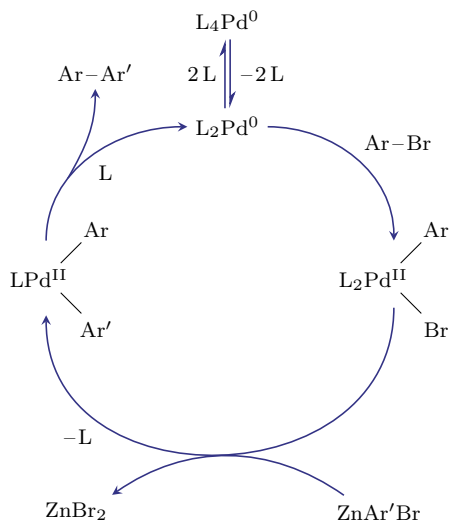
Answer. $\text{IrI}(\text{CO})(\text{PPh}_3)_2$ reacts with H_2 the fastest. This could be the iridium in this complex has the least electron density, meaning it is most keen for the σ donation of the incoming H_2 molecule. \square

3 Intro to Catalysis

5/3: 1. Address the following questions.

- a) Draw a typical mechanism for a Pd catalyzed cross-coupling reaction of an aryl bromide and an aryl zinc reagent.

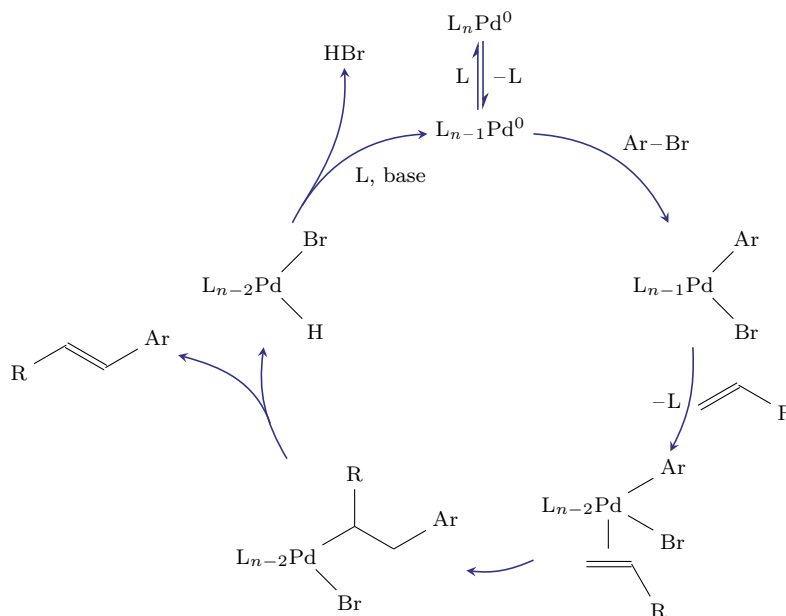
Answer.



□

- b) Show how this mechanism may differ with a Mizoroki-Heck type reaction involving the coupling of an aryl bromide with an olefin. What additive might be necessary to drive this reaction?

Answer.

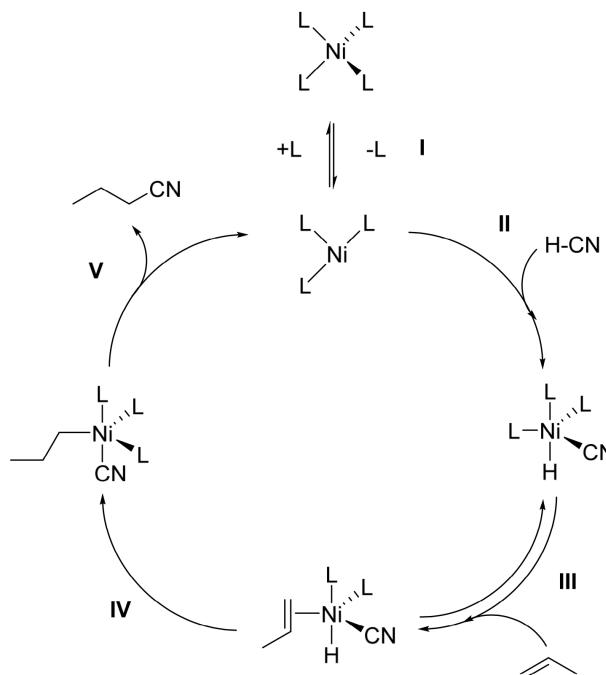


With this mechanism, the activation and oxidative addition steps are the same, but then things start to differ. Instead of a transmetalation step, we now have a ligand substitution followed by a 1,2-migratory insertion. Now things start to look a bit similar again as we kick the product out, but here we have a *regular* elimination step, whereas before we had *reductive* elimination.

Finally, we need one additional last reductive elimination/ligand addition step to regenerate the catalyst. Note that the eliminated acid is neutralized by the added base.

As to the second part of the question, said base is the necessary additive. \square

2. A simplified catalytic cycle for hydrocyanation of propylene by NiL_4 ($\text{L} = \text{P}(\text{OR})_3$) is drawn below. Classify each mechanistic step in the cycle (**I-V**) using the classifications discussed in class.



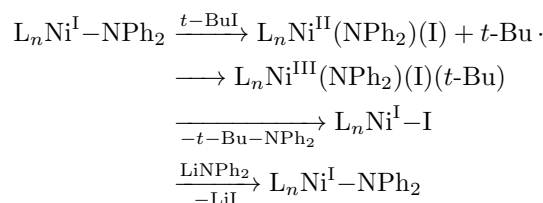
Answer.

- I** Activation (by dissociation).
- II** Oxidative addition.
- III** Ligand substitution.
- IV** 1,2-migratory insertion; ligand addition.
- V** Reductive elimination.

\square

3. Pd-catalyzed cross couplings with aliphatic groups are typically difficult, especially with bulky alkyl-halides. Ni catalysts are typically more effective for these transformations. Starting with a generically ligated Ni^{I} amide complex, $\text{L}_n\text{Ni}-\text{NPh}_2$, show a mechanism for the cross coupling between LiNPh_2 and *tert*-butyliodide that explains this discrepancy.

Answer. I propose the following radical mechanism:



First off, aliphatic cross couplings are rare because they depend on alkyl electrophiles, and β -H elimination can be a problem. As such, if they do occur, they generally proceed through a radical mechanism. Thus, since first-row transition metals are more likely to participate in one-electron redox chemistry, the first-row metal nickel is favored as a catalyst over the second-row metal palladium. ☐

4. Show generic reactions for the following olefin metathesis processes:

a) Cross metathesis.

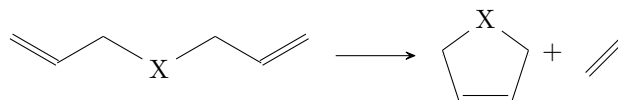
Answer.



☐

b) Ring-closing metathesis.

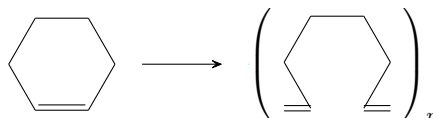
Answer.



☐

c) Ring-opening metathesis polymerization.

Answer.



Note that although a six-membered ring is pictured, this reaction can proceed with rings containing any number of carbons. Something similar can also happen with alkyne rings. ☐

d) What byproduct is common to many of these reactions?

Answer. Ethylene gas.

☐

4 More Catalytic Processes

5/10: 1. We have discussed various mechanisms for nitrogen fixation, one of which is a Chatt/distal type of mechanism.

a) Using orbital diagrams, explain why N_2 is a much weaker ligand than CO.

Answer.

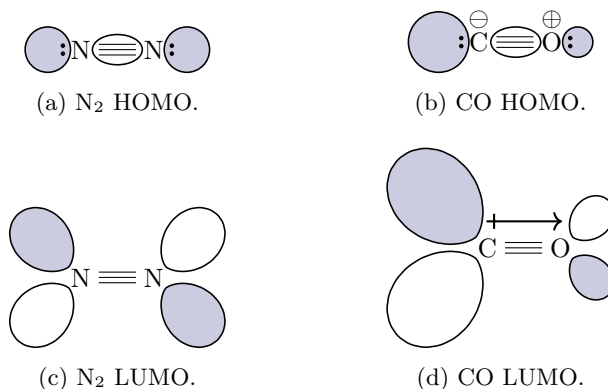


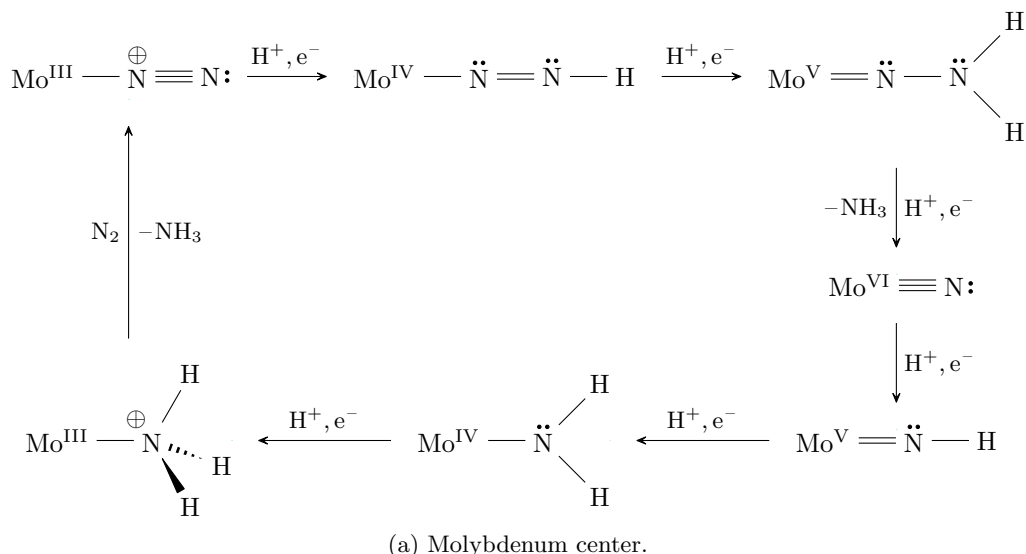
Figure 7: CO vs. N_2 as a ligand.

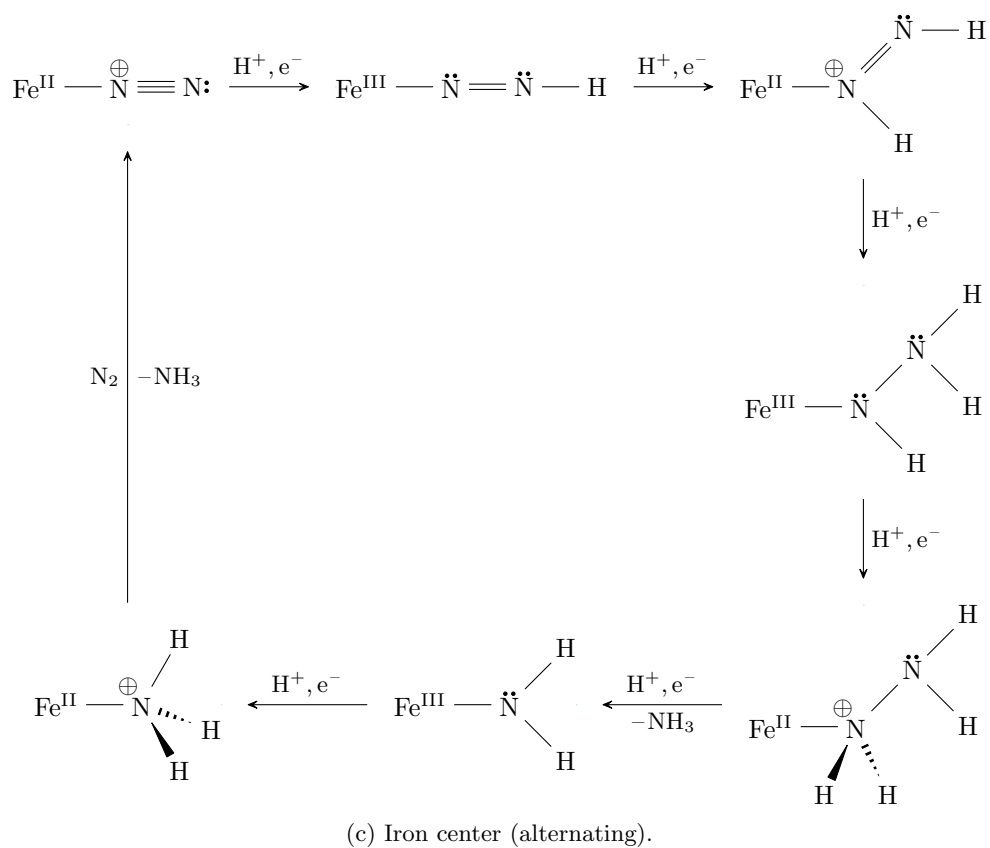
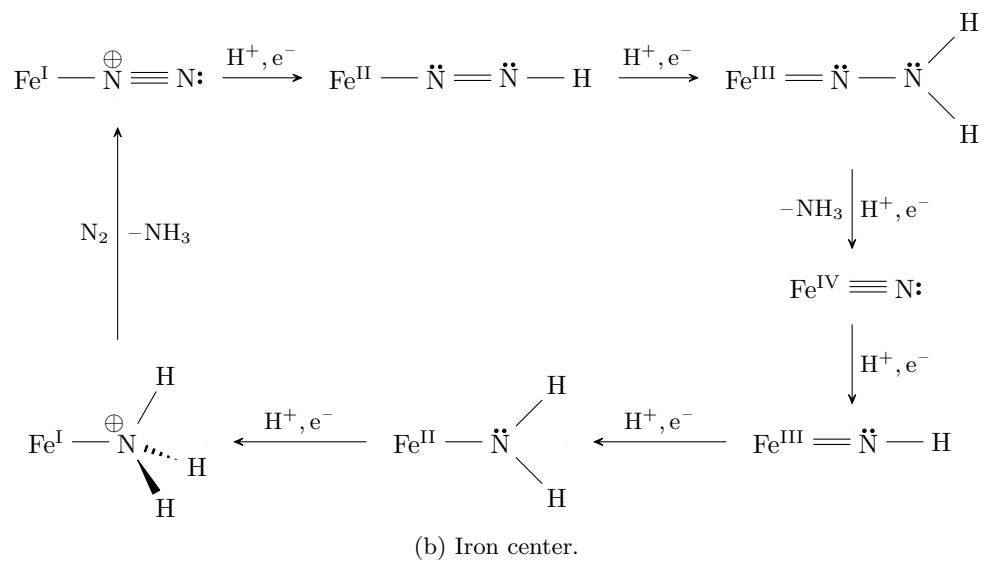
First off, we will compare the HOMOs in N_2 and CO (see Figures 7a and 7b). In N_2 , the triply bonded resonance structure means that it can be a σ donor. However, in the analogous resonance of CO, there is a negative charge on the carbon, meaning that CO is a stronger σ donor.

Additionally, there are differences in the LUMOs (Figures 7c and 7d). Whereas the π^* orbital coefficients on N_2 are the same for both atoms, they are much larger on the carbon in CO due to the polarization of the triple bond. This makes CO a better π acceptor, too. \square

b) Draw out a Chatt-type mechanism for Fe and Mo, indicating oxidation states at the metal center.

Answer. As mentioned in the lecture, molybdenum has an X_3 -type ligand in this type of reaction. However, for the sake of space, this ligand will not be shown and only its effect on the oxidation state (making the oxidation state start at 3+) will be indicated. As for iron, we can show a Chatt-type mechanism, but it will more likely alternate between 2+ and 3+ (iron's most stable oxidation states) via the alternating mechanism.

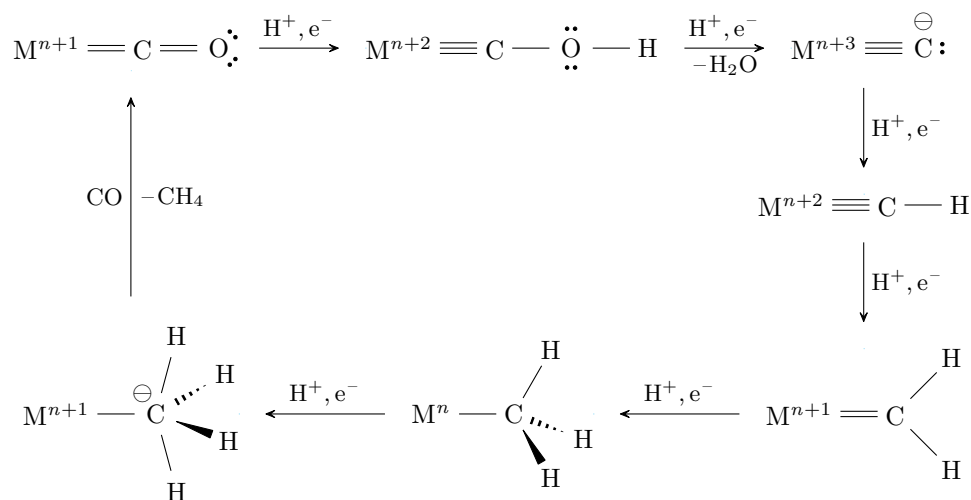




□

- c) Using this mechanism as a template, predict what a similar mechanism for CO reduction would look like. Make sure to show which products are formed and to balance the overall reaction.

Answer.



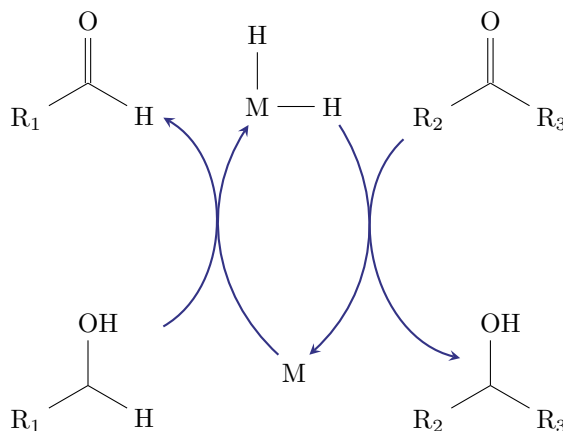
□

- d) Using your answer from part (b), why might a distal mechanism be more favorable for Mo than for Fe?

Proof. Mo has more readily accessible oxidation states, so it has no problem alternating between 3+ and 6+ as well as everywhere in between. Fe can only easily access Fe²⁺ and Fe³⁺ as a later, first row transition metal. □

2. Write out a detailed mechanism for a transfer hydrogenation between an aldehyde and a ketone. Which way would this reaction be expected to go for the combination of a benzaldehyde/benzyl alcohol and isopropanol/acetone?

Proof.

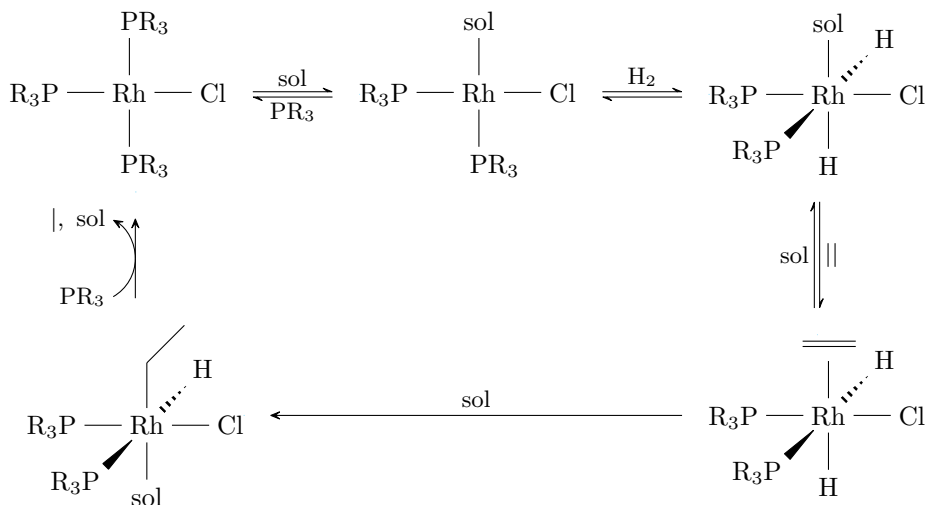


The products benzyl alcohol and acetone are favored because the aryl alcohol will not dehydrogenate as easily as isopropanol (i.e., the thermodynamics are not comparably favorable). □

3. Show the mechanism of hydrogenation for the following catalysts.

a) $\text{Rh}(\text{PR}_3)_3\text{Cl}$.

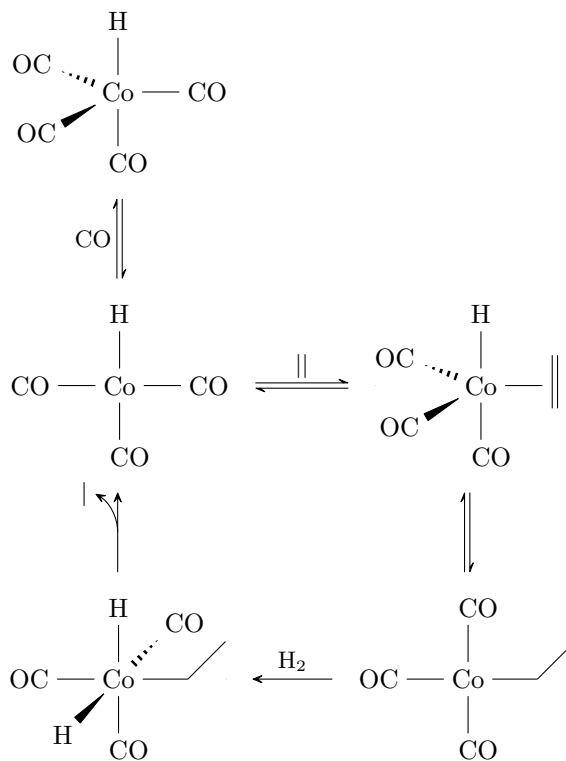
Answer. Dihydride mechanism:



□

b) $\text{HCo}(\text{CO})_4$.

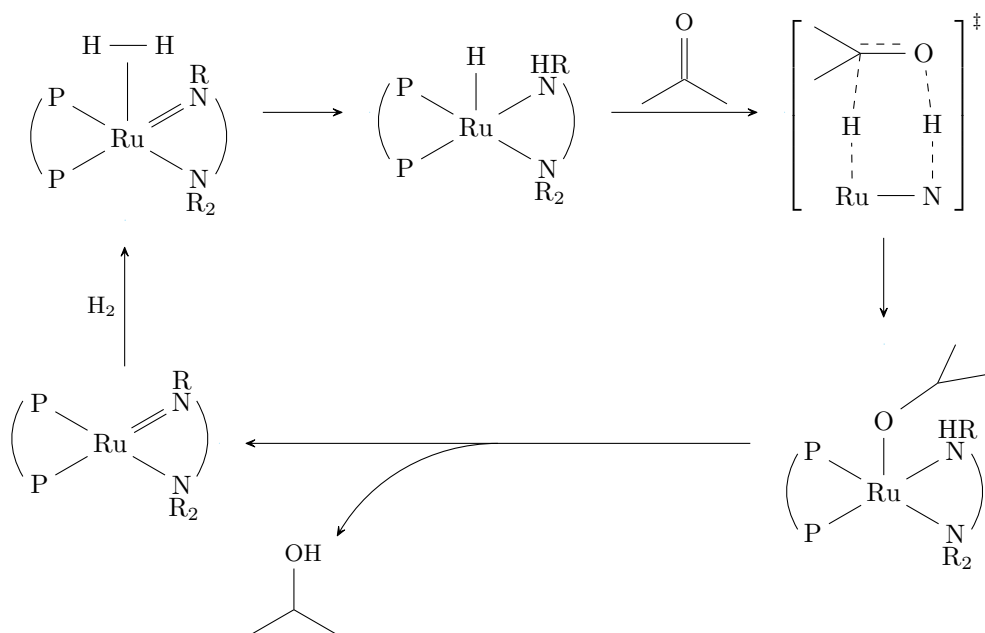
Answer. Monohydride mechanism:



□

c) Noyori's catalyst.

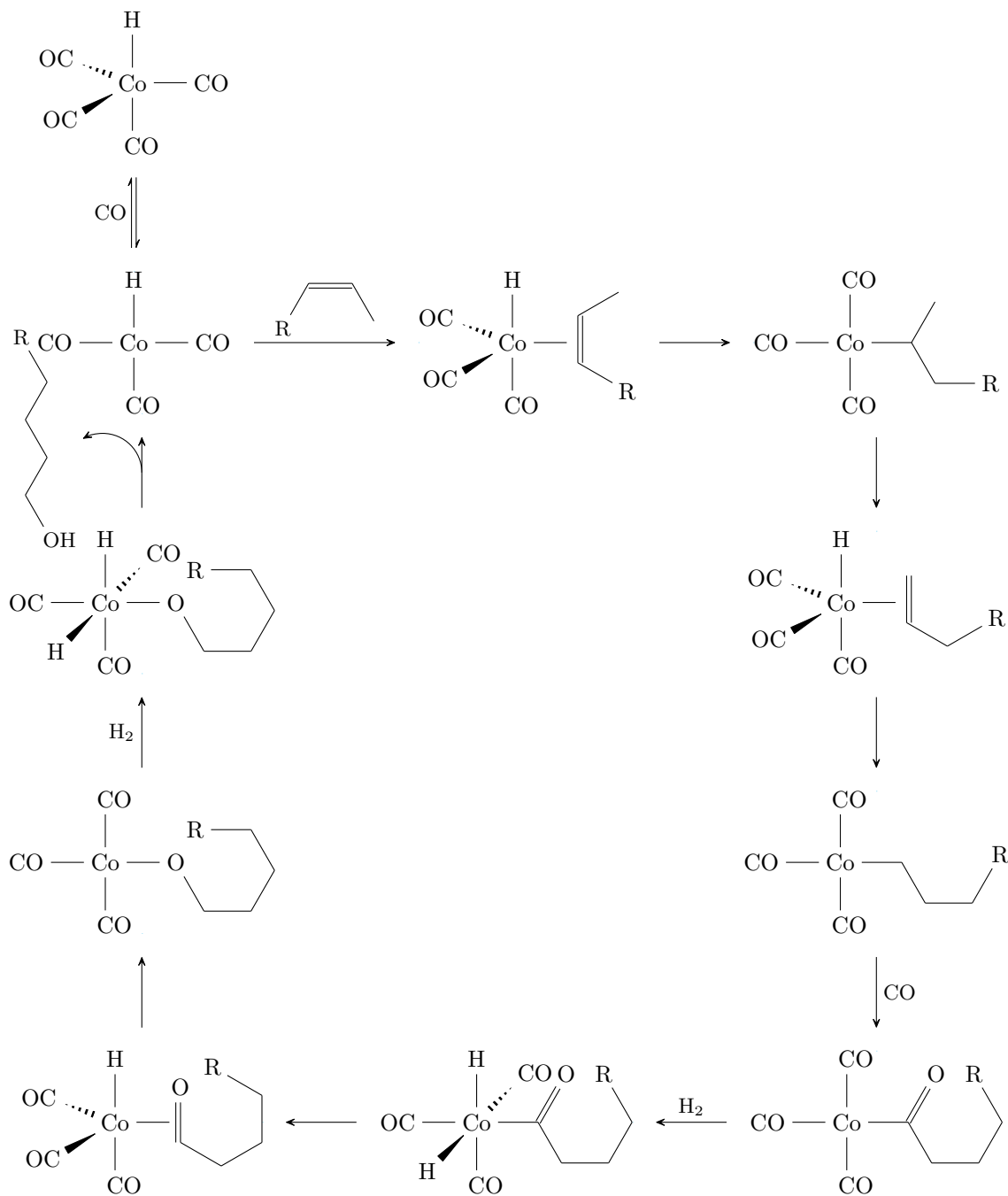
Answer. Cooperative mechanism with bound amines.



□

4. One use of hydroformylation catalysis is the conversion of internal olefins into terminal alcohols. Show a mechanism for this process.

Answer.



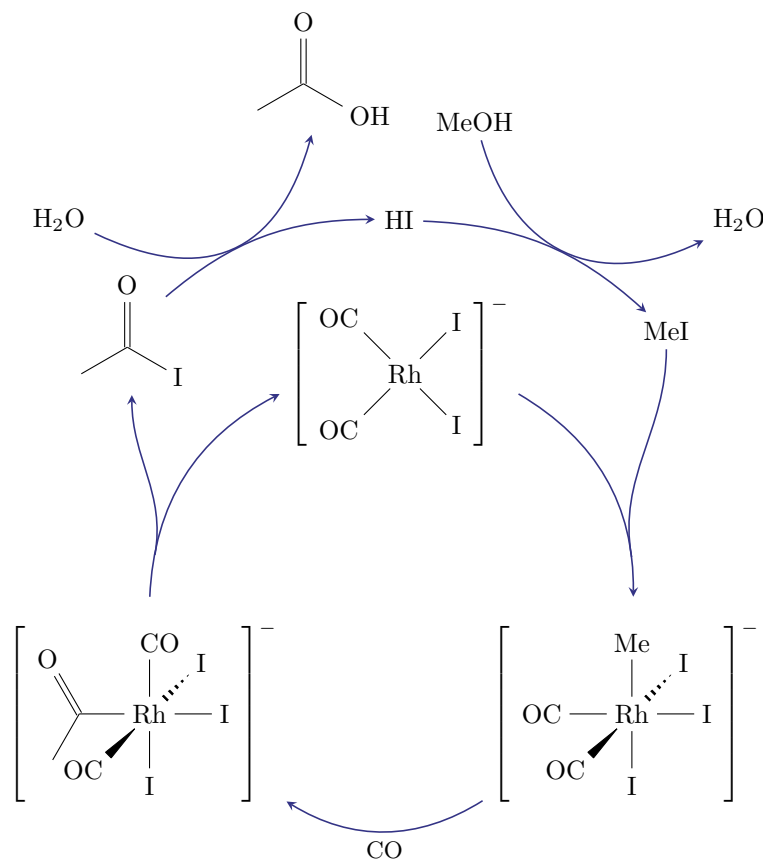
□

5 Even More Catalytic Processes

5/21: 1. Answer the following questions.

a) Draw a mechanism for the Monsanto acetic acid process.

Answer.



□

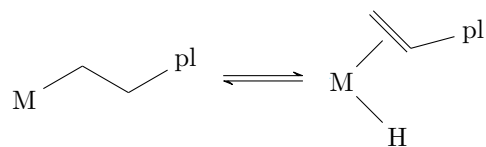
b) Explain how this mechanism differs for BP's Cativa process.

Answer. The most obvious difference is that although the catalysts are similar, the Cativa process uses an iridium center instead of a rhodium one. Additionally, whereas the catalyst from the Monsanto process is purely anionic, the catalyst of the Cativa process has a proton as a counterion. This is notably important when hydroiodic acid is removed from an intermediate. Furthermore, there are a couple alternate pathways and off-cycles to be aware of with the Cativa process. Most notably, the intermediate $\text{Ir}(\text{CO})_2\text{I}_2\text{Ac}$ can be captured and transformed into $\text{Ir}(\text{CO})_3\text{I}_2\text{Ac}$ or $[\text{Ir}(\text{CO})_2\text{I}_3\text{Ac}]^- \text{H}^+$. Note that the latter off-cycle product can be generated slowly from the intermediate three steps earlier in the cycle, i.e., $[\text{Ir}(\text{CO})_2\text{I}_3\text{Me}]^- \text{H}^+$. Beyond these differences, it is worth noting that the final product (AcOH) is pulled directly off of the catalyst by H_2O , as opposed to through a reductively eliminated AcI species. Lastly, the cycle for regenerating MeI from HI is more complicated in the Cativa process; indeed, while the Monsanto process only uses MeOH in one step with H_2O as a byproduct, the Cativa process uses MeOAc , AcOH , MeOH , and H_2O in a two-step cycle.

□

2. Consider both early and late metal olefin polymerization processes. What is the resting state of the catalyst in each case and why? Predict whether early or late metals should favor linear or branched polyethylene and show a mechanism that explains this.

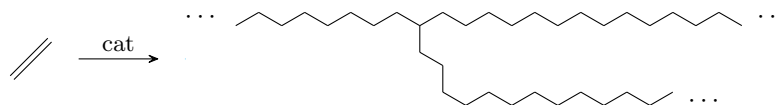
Answer.



Early metal resting state: Metal alkyl intermediate. This is because early metals are terrible backboners (not enough d electrons) and thus do not form olefin adducts easily. Hence, insertion of an olefin is very fast and a bound olefin is almost never observed in these systems. This favors linear polyethylene because inhibition of olefin adducts precludes chain walking.

Late metal resting state: Metal-olefin adduct. This is because late metals can backbond and will more readily form an olefin adduct. This favors branched polyethylene because metal-olefin adducts are a necessary intermediate to chain walking. Additionally, olefins are more likely to dissociate than alkyls, making chain transfer a more likely possibility. \square

3. Some catalysts polymerize ethylene to HDPE that contains a few long branches (ca. 1-2 per chain). Explain how the long branches might form. What distribution of branch lengths do you expect for your mechanism?



Answer. The long branches most likely form through chain transfer. If we use early metal catalysts that do not chain walk or dissociate olefins very easily, then we can expect to build only a few very long chains in solution before the inevitable termination step. Once a chain has terminated though, since it has a terminal olefin, there's no reason that a catalyst currently working on another chain couldn't pull in the previously terminated chain at the olefin instead of just another ethylene and then continue on. Indeed something like this would lead to a polymer with only a few very long branches. \square

4. Provide a concise explanation of the stereocontrol mechanism for the formation of isotactic and syndiotactic polypropylenes by metallocene catalysts of appropriate symmetry. Provide clear drawings to support your discussion.

Answer.

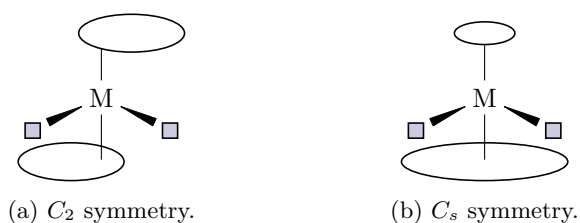


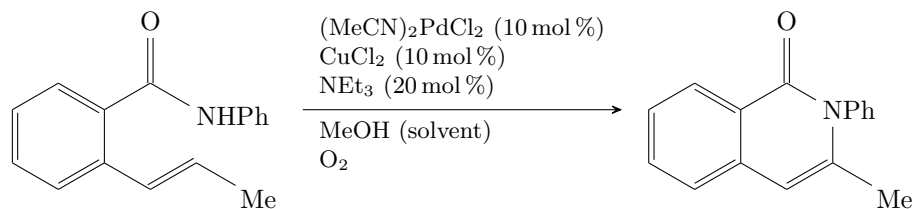
Figure 9: Polypropylene-type catalysts.

Metallocene catalysts of C_2 symmetry will generate isotactic polypropylene. This is because propylene bonds with the same pro-chiral face to each coordination site on Figure 9a (for the left coordination site, sterics force the methyl group to point upward, and vice versa for the right coordination site). As such, when the chain transfers during a growth step, the methyl group always aligns the same way (always R or always S, depending on whether the pro-R or pro-S face bonds to the catalyst).

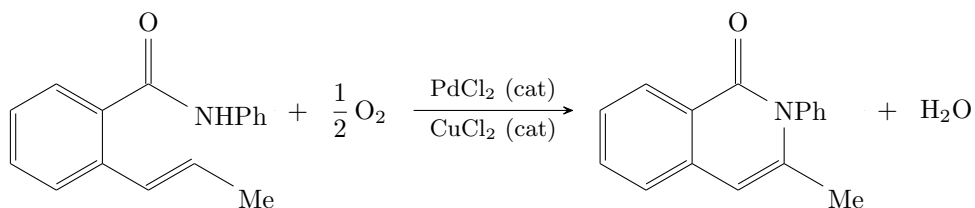
On the other hand, metallocene catalysts of C_s symmetry will generate syndiotactic polypropylene. This is because propylene bonds with different pro-chiral faces to each coordination site on Figure 9b

(at both coordination sites, sterics force the methyl group to point upward). As such, when the chain transfers during a growth step, the methyl group always aligns opposite to the way it aligned last time. \square

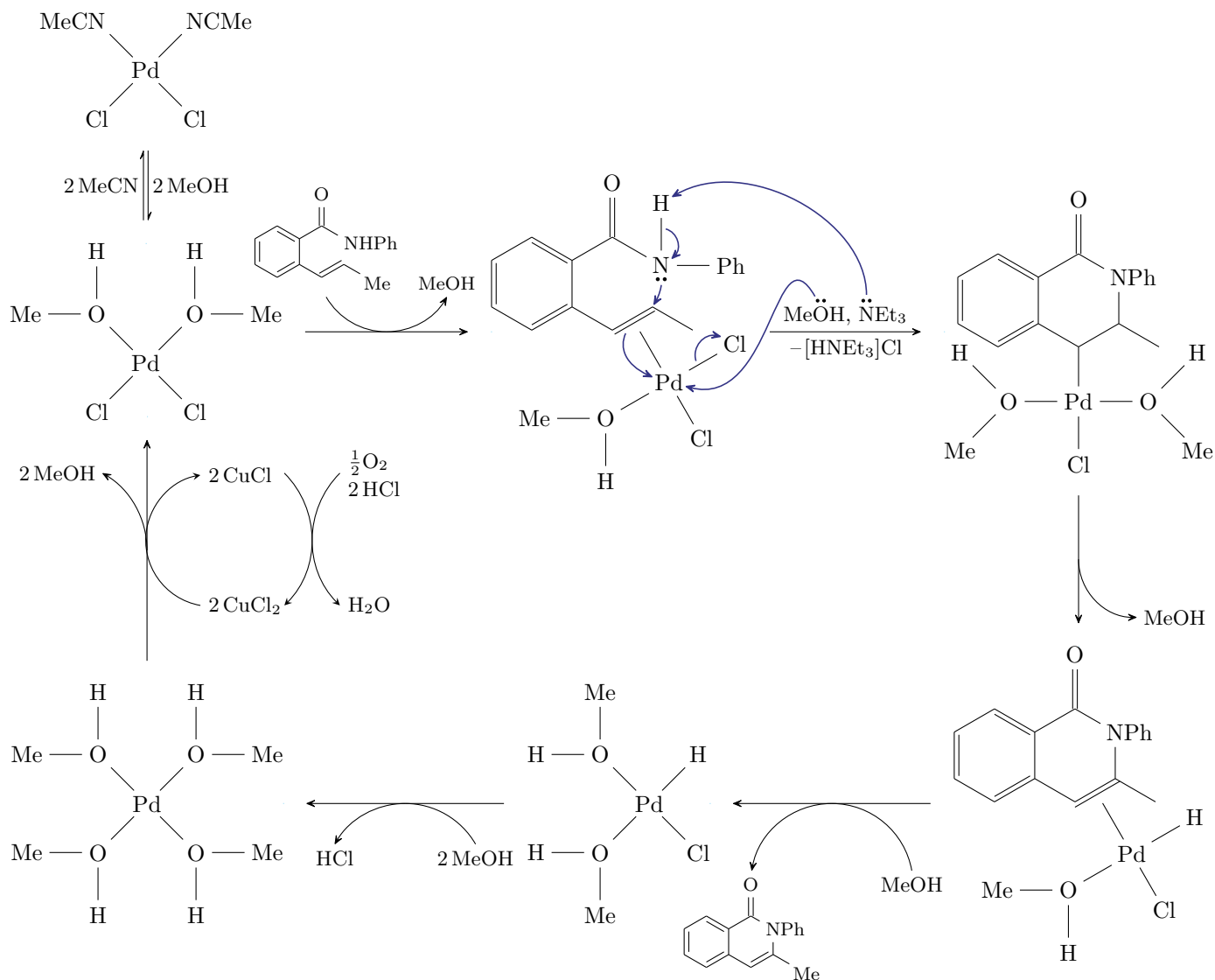
5. Variants of the Wacker oxidation reaction have been developed for the synthesis of fine chemicals and pharmaceuticals. Provide a balanced equation and mechanism for the following intramolecular aza-Wacker cyclization reaction.



Answer. Balanced equation:

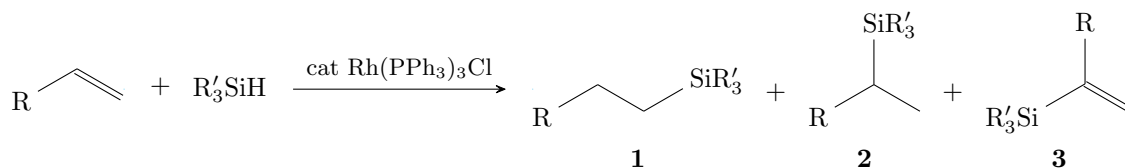


Mechanism:

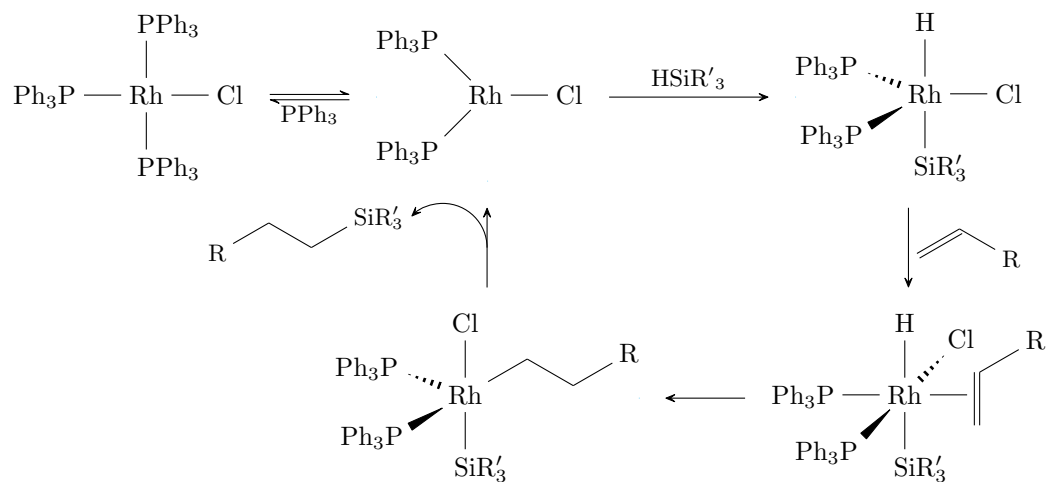
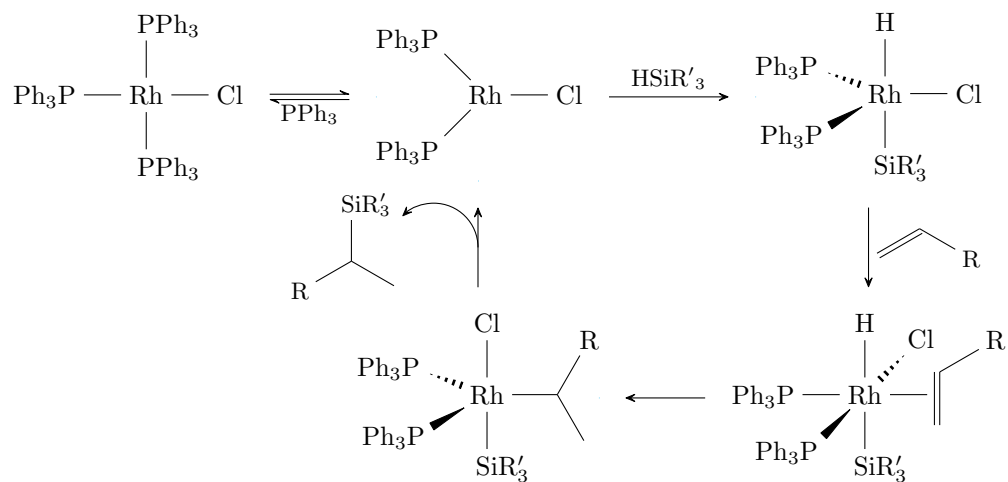


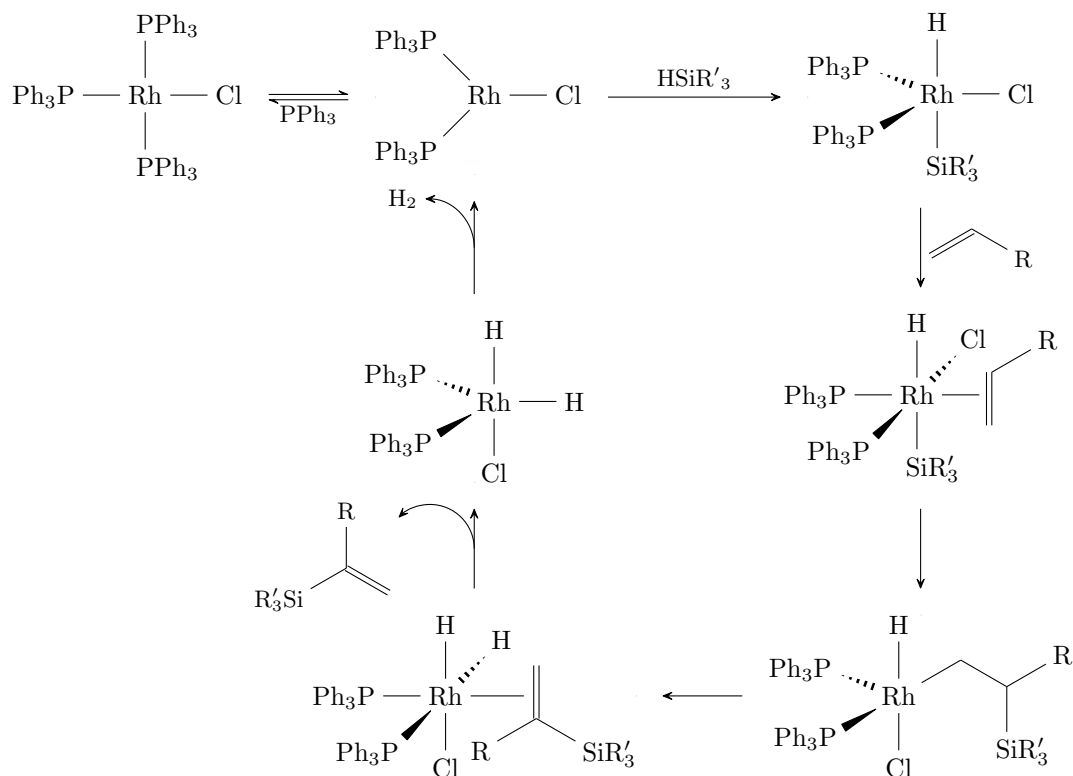
□

6. Wilkinson's catalyst catalyzes the hydrosilylation of α -olefins, as shown below. Two isomers of the product (**1**, **2**) are usually observed and vinylsilanes **3** are sometimes formed as byproducts. Provide a mechanism for the reaction and the formation of **1-3**.



Answer. Product **1**:

Product **2**:Product **3**:

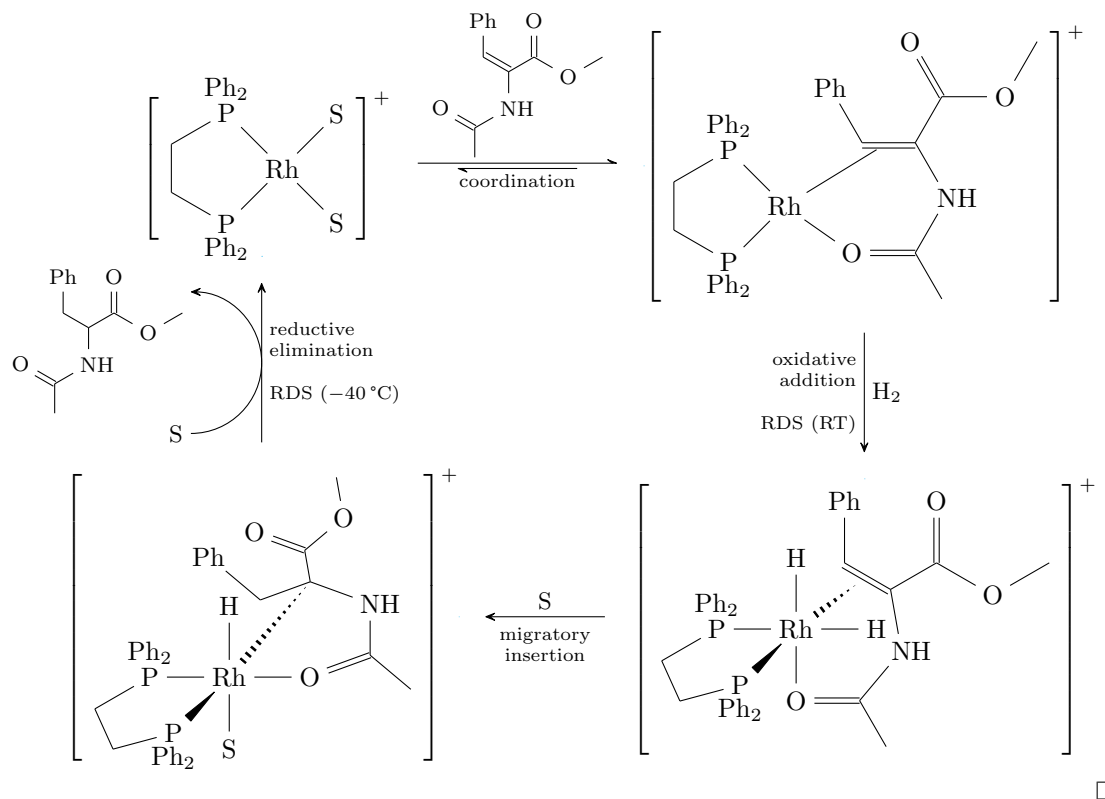


□

7. This question is meant to guide you through Prof. Jack Halpern's paper studying the enantioselective hydrogenation of methyl-(Z)- α -acetamidocinnamate (mac) mediated by $[\text{Ru}(\text{dipamp})(\text{MeOH})_2]^+$ (Landis & Halpern, 1987). These questions will focus on the introduction, results, and discussion (not the experimental section).

- a) Figure 1 depicts a previously published achiral hydrogenation catalyst. Draw the cycle in Figure 1 and label the mechanism for each step. When drawing arrows between intermediates, indicate whether the step is reversible and, if so, which intermediate is favored. Label the rate determining step at room temperature (RT) and at -40°C .

Answer.



- b) Figure 2 depicts two possible catalytic cycles for the asymmetric catalyst $[\text{Ru}(\text{dipamp})(\text{MeOH})_2]^+$. In this scheme, why is one labeled the “major manifold” and the other the “minor manifold?” Why does the minor manifold lead to the major product? Depict the differences in energy for each pathway with a reaction coordinate diagram (we used these to talk about catalysis on May 1) and indicate the resting state of the catalyst.

Answer.

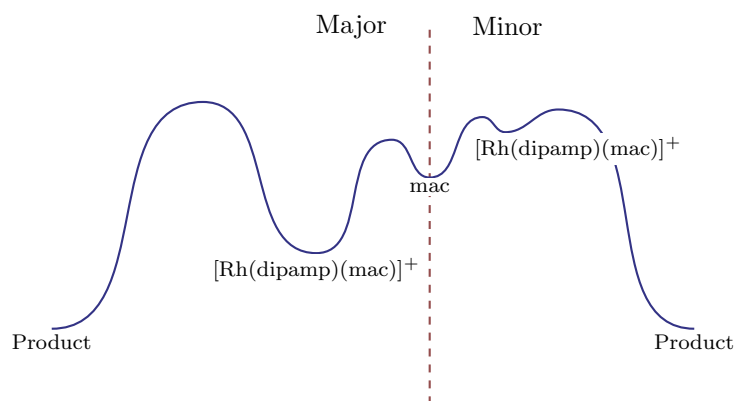


Figure 10: Reaction coordinate diagram.

This whole paper centers around the chirality of the $[\text{Rh}(\text{dipamp})(\text{mac})]^+$ adduct and, thus, the stereochemistry of the product. Of course, sometimes diastereomers (such as the two possible $[\text{Rh}(\text{dipamp})(\text{mac})]^+$ adducts) can have slightly different properties. As such, the major manifold follows the catalysis using the more thermodynamically stable “major” $[\text{Rh}(\text{dipamp})(\text{mac})]^+$ adduct (probably called major since its thermodynamic stability means that there is relatively more of it in solution), and likewise for the minor manifold.

It is exactly this variability in stability that causes the minor manifold to yield the major product and vice versa; indeed, since the minor adduct is less thermodynamically stable and much more reactive with H_2 , it reacts faster and creates more of its product.

The reaction coordinate diagram shows that the energy of the minor adduct is higher and the energy of the major adduct is lower, affecting their relative concentrations in solution as discussed. However, this also means that the remainder of the steps are harder, since we've overstabilized the intermediate and it's already less reactive with H_2 . \square

- c) The substrate *mac* can form two different isomers by associating with the metal catalyst. These complexes are termed 2^{min} and 2^{maj} . Provide an example of a spectroscopic technique where the two complexes can be differentiated and an example where they appear identical.

Answer. As stereoisomers, NMR can differentiate between them, but they would appear identical to mass spectroscopy. \square

- d) To gain insight on the mechanism of hydrogenation and the origin of enantioselectivity, the influence of varying H_2 pressures on the rates of catalysis is explored. Under what conditions is the oxidative addition the rate determining step, and under what conditions is isomerization between 2^{maj} and 2^{min} the rate determining process? These studies are shown in Figure 6; explain the changes in the rate of formation of the S-product observed upon changing the pressure of H_2 .

Answer. Oxidative addition is the RDS at sufficiently low pressures of H_2 , since there it finally becomes slower than reductive elimination. Isomerization between 2^{maj} and 2^{min} is the RDS at sufficiently high pressures of H_2 , since in the limit of infinitely high H_2 pressure, oxidative addition finally becomes faster than isomerization.

As $[\text{H}_2]$ increases, the reaction rate increases. As it does, since the S-product is the major product, as formed by the less thermodynamically stable, more reactive minor adduct, the differences in how much more of it is formed will be exaggerated. \square

- e) What does it mean for the selectivity of a reaction to be "product controlled?"

Answer. In the sense of the Hammond postulate, it means that the stability of the products determines the activation energy of the reaction (esp. the energy of the transition state). With respect to the catalytic method under study here, it is applied to the fact that the greater stability of the minor *dihydride* adduct (see Figure 9 in Landis and Halpern (1987)) causes the process of conversion to it to be less energy intensive than the analogous process for the major *dihydride* adduct. \square

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