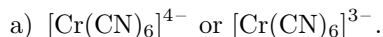
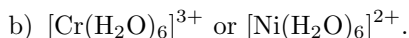


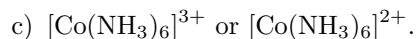
4/19: 1. For the following pairs of complexes, predict which should exchange more rapidly and justify your answer.



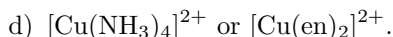
Answer. $[\text{Cr}(\text{CN})_6]^{4-}$ should exchange more rapidly. This is due to the lesser magnitude oxidation state on the chromium. \square



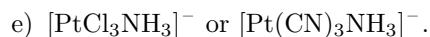
Answer. $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ should exchange more rapidly. This is because the nickel's d^8 configuration will be more labile than the chromium's d^3 configuration, despite the nickel's smaller size. The instability of the d^8 configuration comes from its partially filled antibonding 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 $[\text{Cu}(\text{NH}_3)_4]^{2+}$ doesn't. Indeed, even though the copper in $[\text{Cu}(\text{NH}_3)_4]^{2+}$ 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

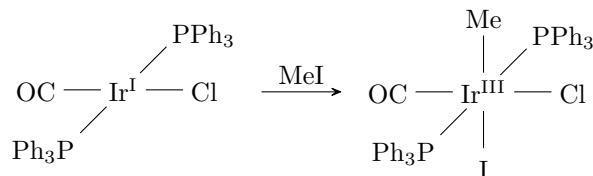
- ii. $[\text{Co}_2]^{5+}$ or $[\text{Fe}_2]^{5+}$ (all ions are low-spin).

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.

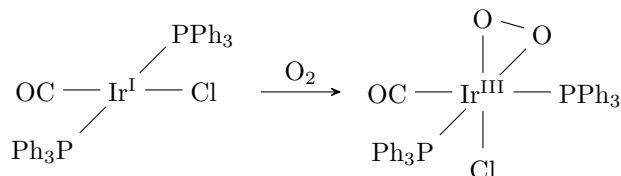
Answer. This reaction will proceed as follows ($\text{S}_{\text{N}}2$ mechanism).



\square

- b) O_2 .

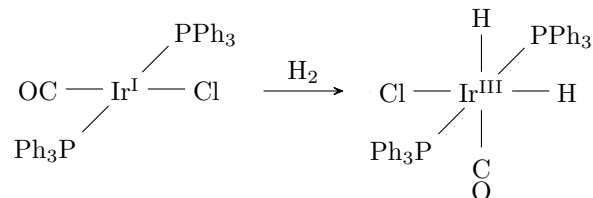
Answer. This reaction will proceed as follows (concerted mechanism).



\square

- c) H_2 .

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



\square

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.

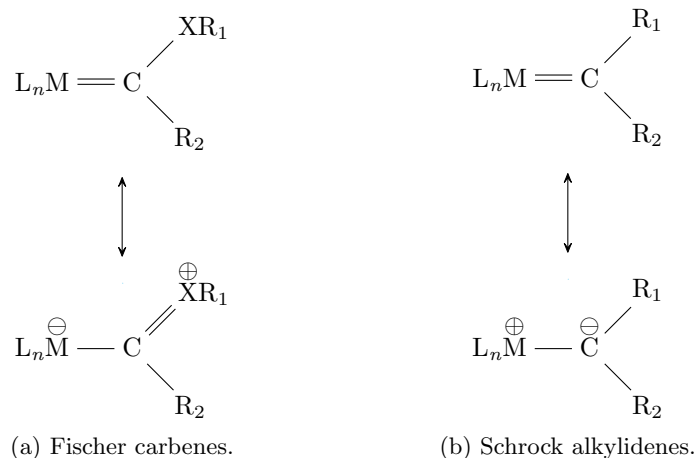
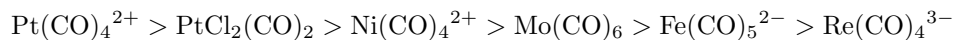


Figure 1: Carbene regime resonance structures.

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.

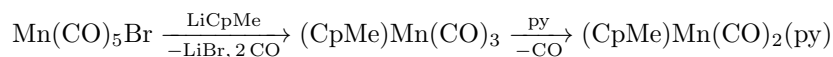
There are a number of differences between $\text{Mo}(\text{CO})_6$ and $\text{Fe}(\text{CO})_5^{2-}$. To begin with, Mo is lower and earlier in the periodic table than Fe. However, molybdenum also has a relatively higher oxidation state and more ligands to which it can backbond. As such, it backbonds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

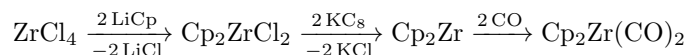
Answer.



\square

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

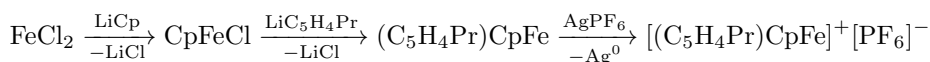
Answer.



\square

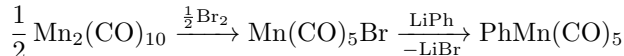
- c) $[(\text{C}_5\text{H}_4\text{Pr})\text{CpFe}]^+[\text{PF}_6]^-$ from FeCl_2 .

Answer.



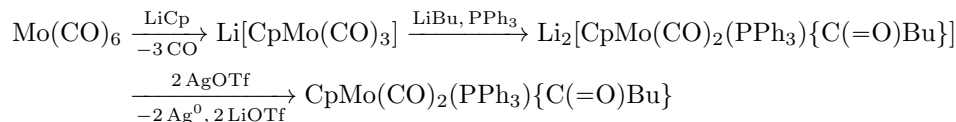
\square

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

Answer.

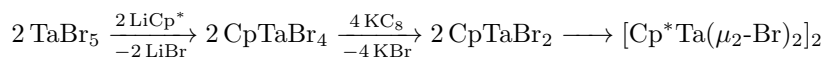
□

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

Answer.

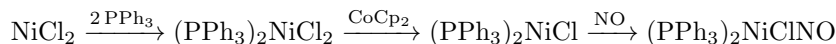
□

- 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
- .

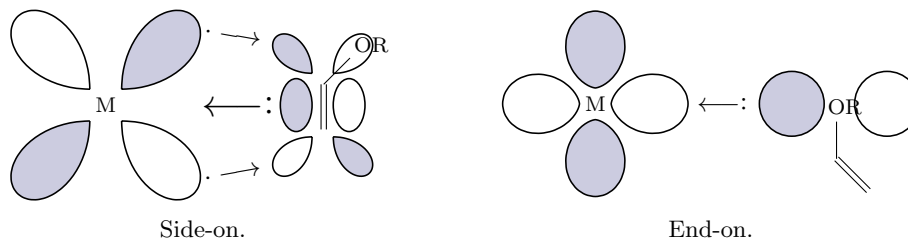
Answer.

□

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?

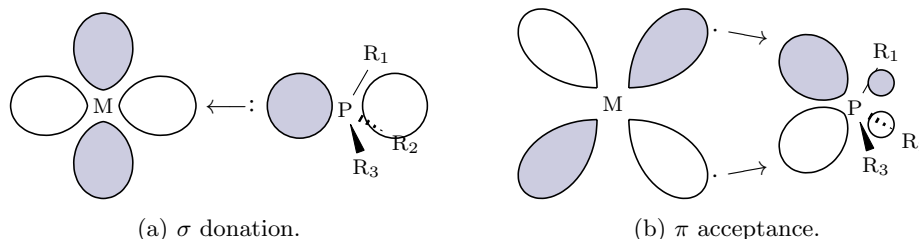
Answer. If the metal center is electron rich and soft, the side-on mode will be favored as it gives the metal center the chance to delocalize its electron density through $\text{M} \longrightarrow \text{L}$ π backbonding. If it is electron poor and hard, the end-on mode will be favored due to the dative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

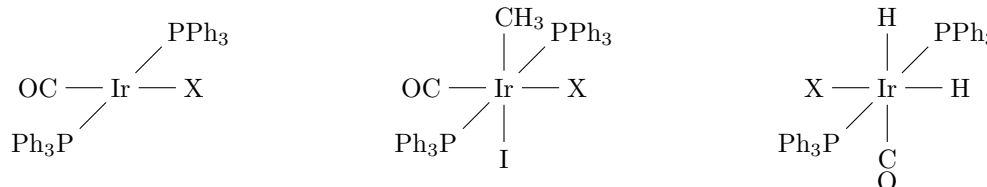
- c) Of these three phosphines, which will give the cobalt complex with the lowest energy carbonyl stretch in the infrared spectrum? Explain briefly.

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.

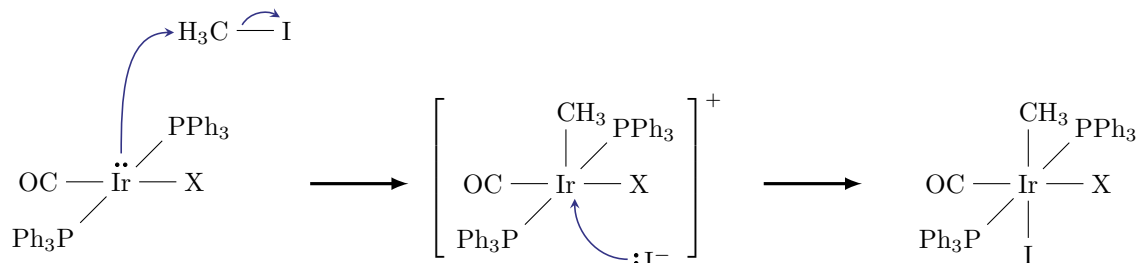
Answer.



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.

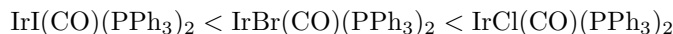
Answer.



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.



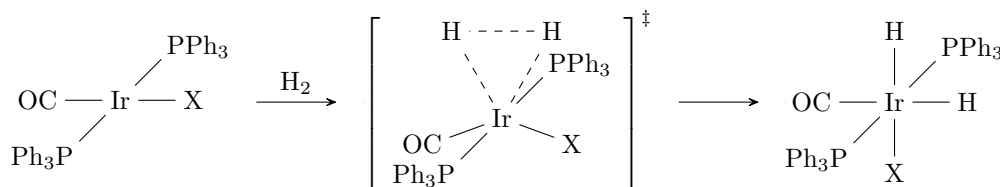
For the three forms of Vaska's complex (one with each halogen save fluorine), we have $\nu_{\text{CO}} = 1950, 1955, 1975 \text{ cm}^{-1}$ for $\text{X} = \text{Cl}, \text{Br}, \text{I}$, respectively. This implies that π backbonding follows the order $\text{Cl} > \text{Br} > \text{I}$. It follows that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