

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.

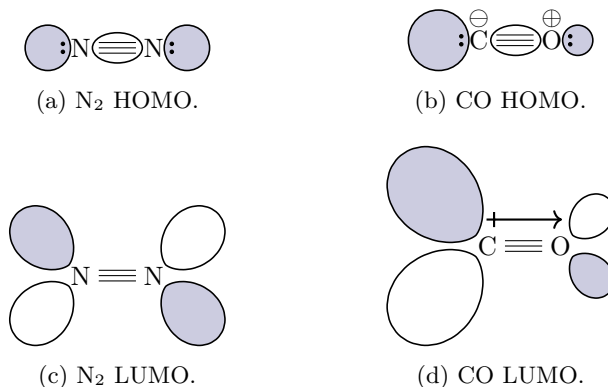


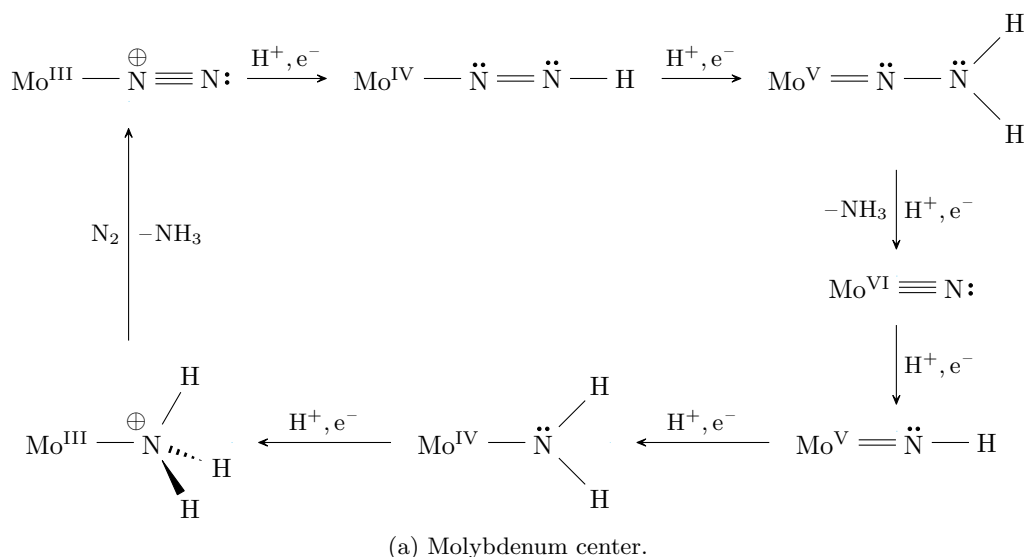
Figure 1: CO vs. N_2 as a ligand.

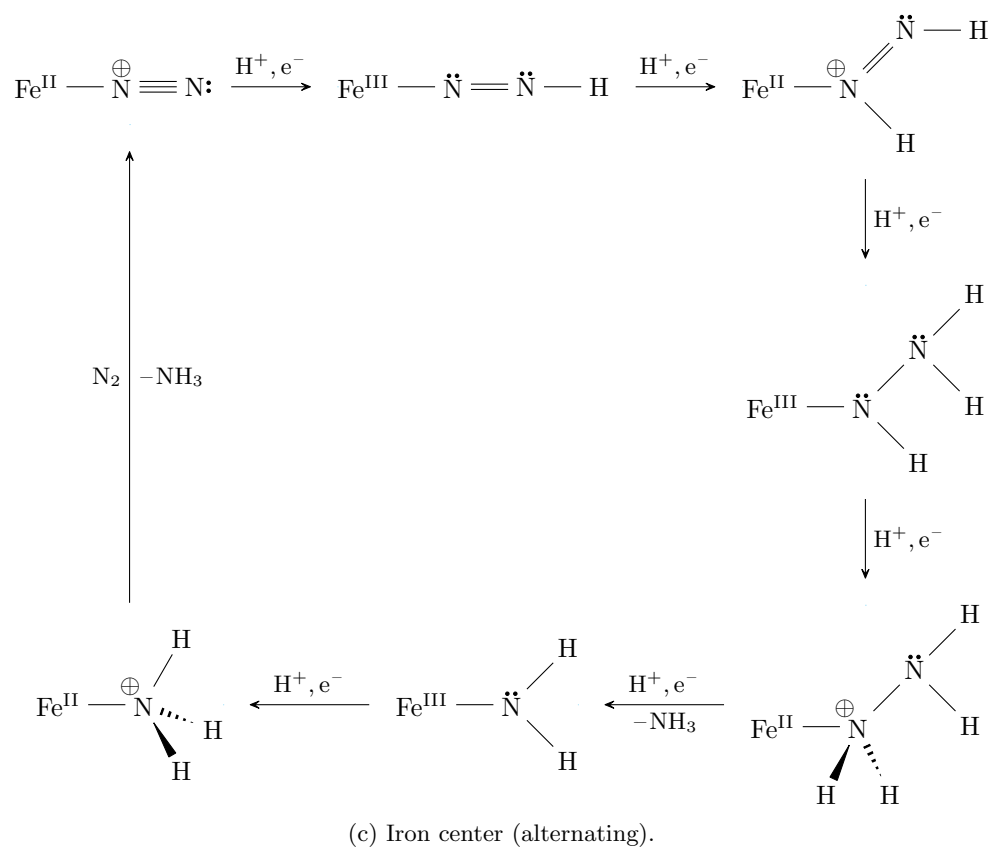
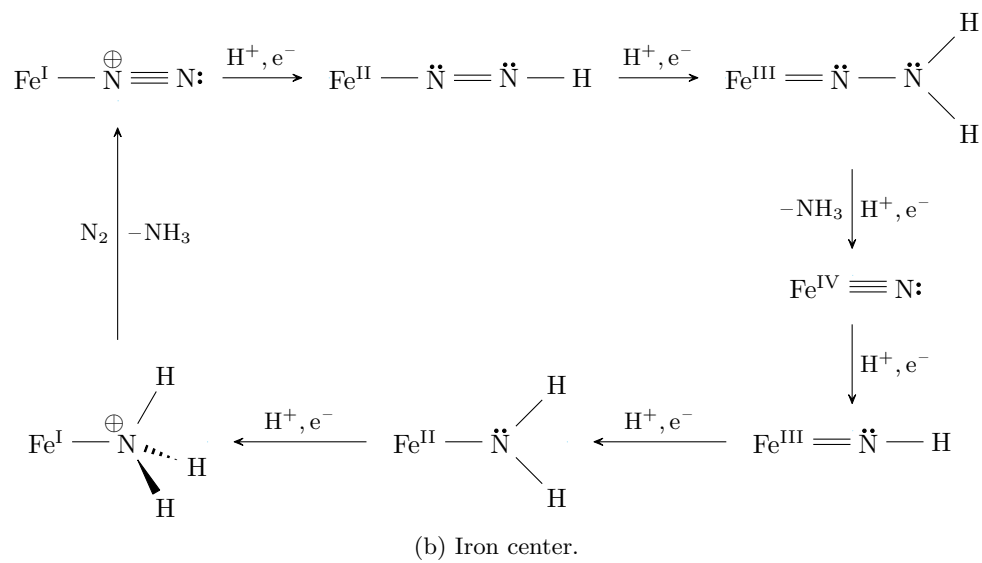
First off, we will compare the HOMOs in N_2 and CO (see Figures 1a and 1b). In N_2 , the triply bonded resonance structure means that it can be a σ donor. However, in the analogous resonance of CO, there is a negative charge on the carbon, meaning that CO is a stronger σ donor.

Additionally, there are differences in the LUMOs (Figures 1c and 1d). 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.

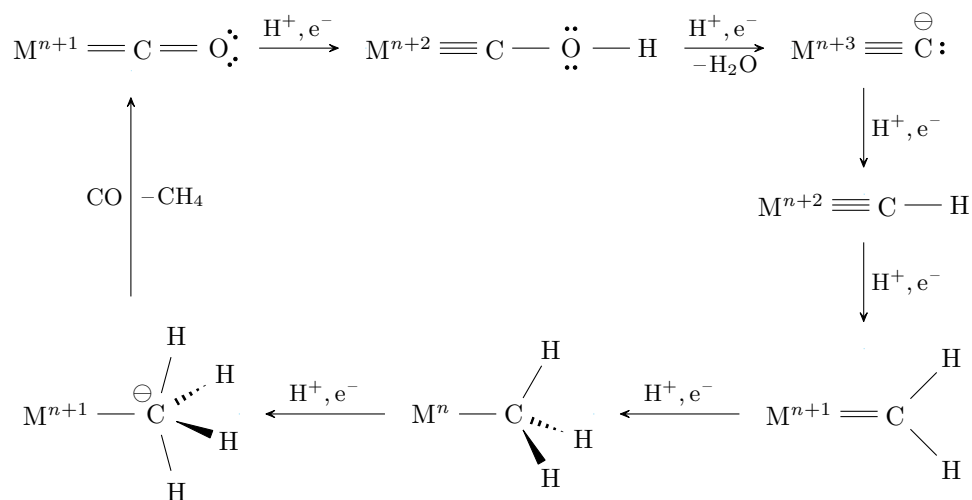




□

- 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.



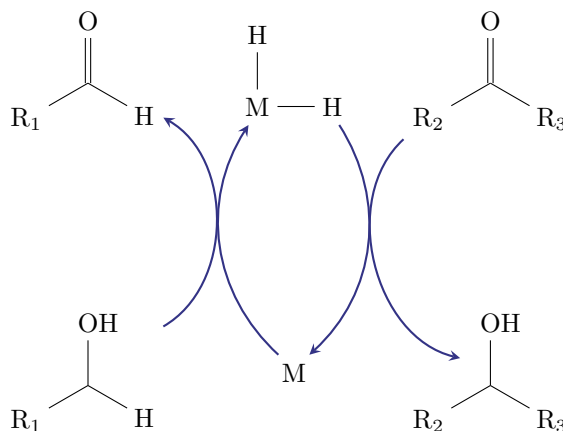
□

- 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 Fe^{2+} and Fe^{3+} 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.

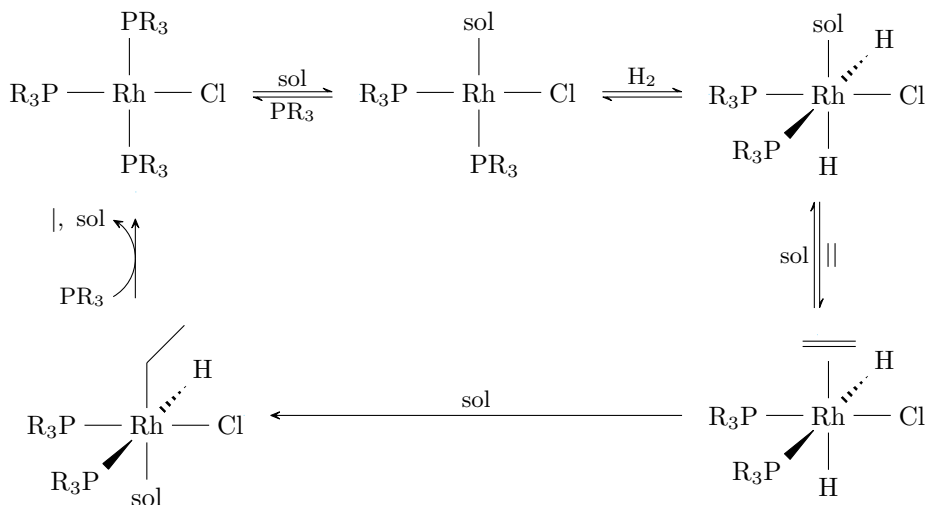


The products benzyl alcohol and acetone are favored because the aryl alcohol will not dehydrogenate as easily as isopropanol (i.e., the thermodynamics are not comparably favorable). □

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

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

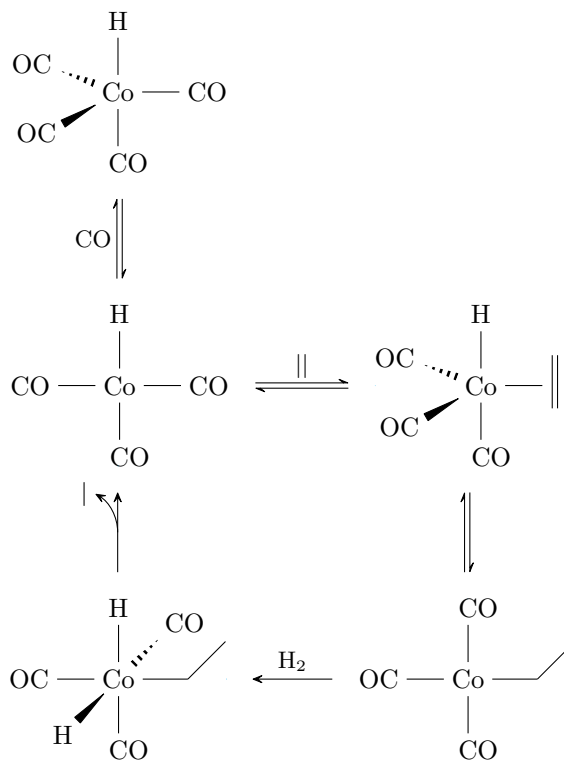
Answer. Dihydride mechanism:



□

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

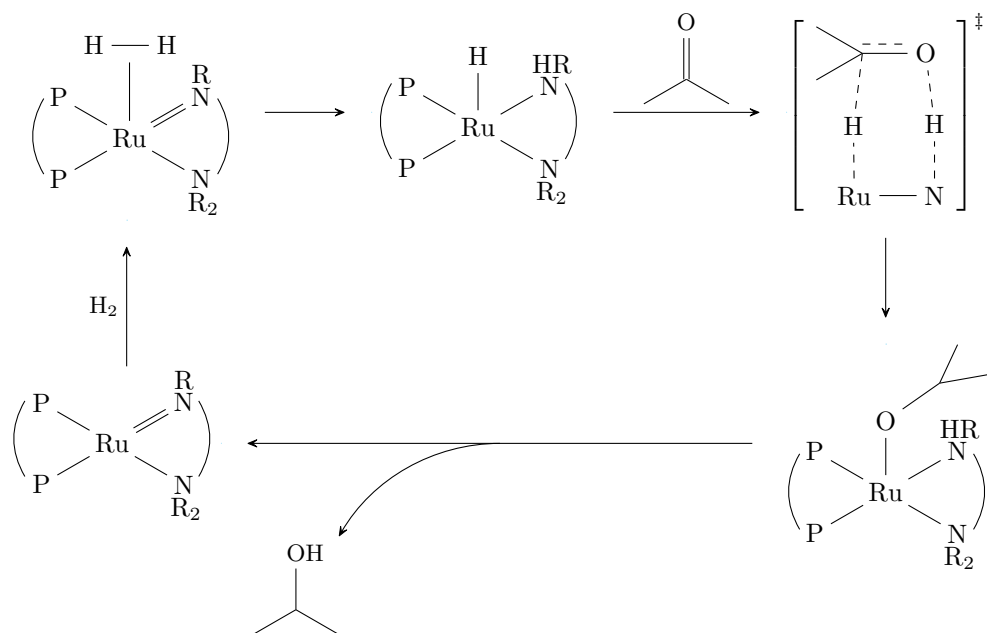
Answer. Monohydride mechanism:



□

c) Noyori's catalyst.

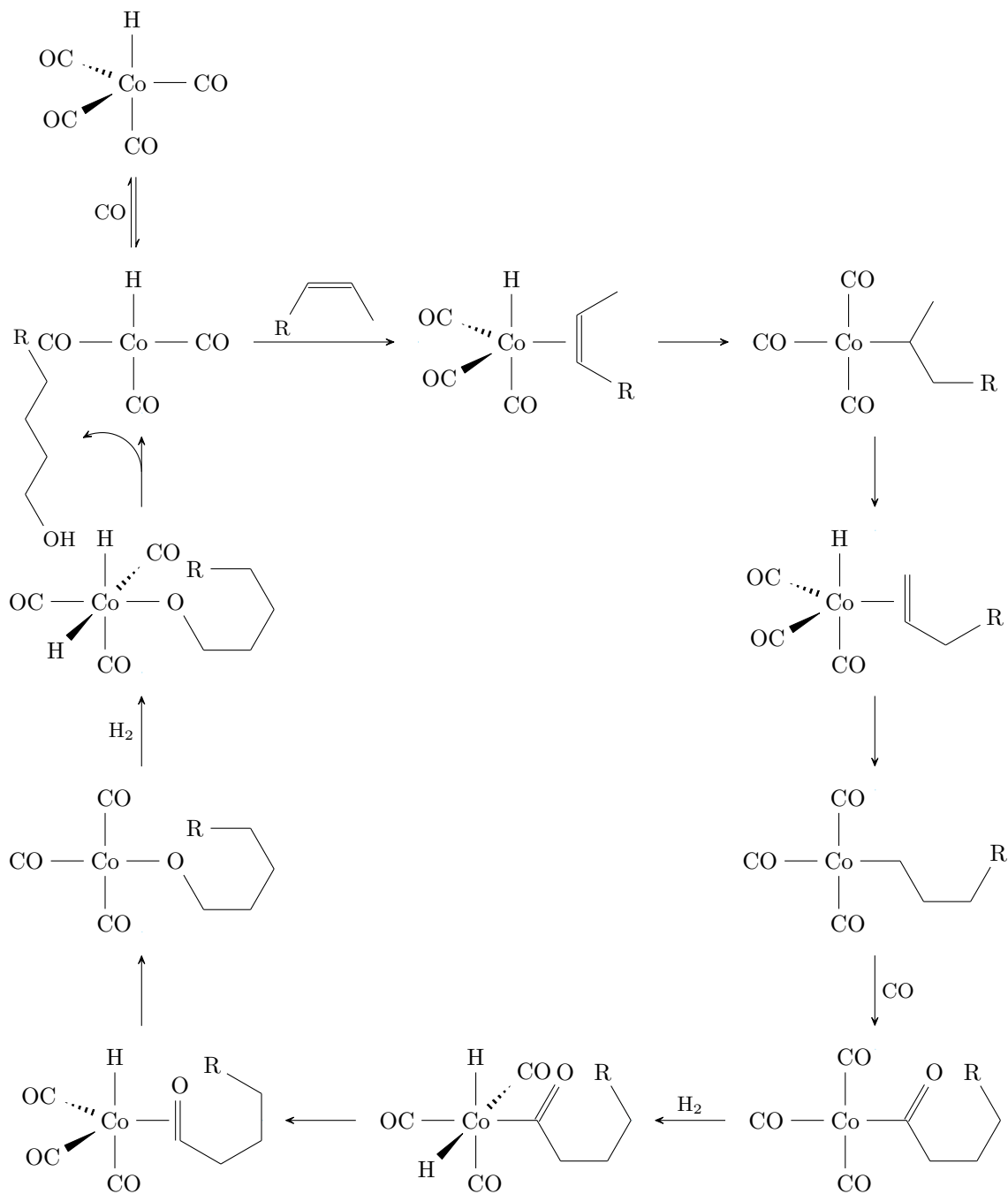
Answer. Cooperative mechanism with bound amines.



□

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

Answer.



□