1. Define the term “pincer ligand” based on the following sentence taken from pg 2916 of the paper:

“As a **tridentate, meridionally chelating ligand**, it can also be characterized as a pincer ligand.”

1. How does the author define a “redox non-innocent ligand”? Please be sure to put this in your own words.
2. For Ni, Pd, and Pt,
   1. Use available resources to create a table of the redox potentials for

M2+ + 2e- → M.

|  |  |
| --- | --- |
| Half-reaction | Eo (V vs NHE) |
|  |  |
|  |  |
|  |  |

* 1. How do the potentials for Pt and Pd compare? How do the potentials for Ni and Pt compare? What is the range of potentials covered by these three metals?
  2. Which two metals are most similar in their redox potential? Does this agree with what you would predict based on periodicity?
  3. Look at the potentials presented in Table 6 in the paper. What is the electrochemical potential range for the 3-PdCl complex and the 3-NiCl complex?
  4. The change in electrochemical potential mentioned in part d is small compared to that in part b. Discuss how this supports the redox non-innocence of these ligands.

1. Classify complexes 14-RhCO, 15-RhCO, 8-RhCO, and 4-RhCO in Figure 5 according to the CBC rules. Determine the ligand bond number, valence number, electron count, and d-electron count.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Complex | Classification | Ligand Bond Number | Valence number | Electron Count | dn |
| 14-RhCO |  |  |  |  |  |
| 15-RhCO |  |  |  |  |  |
| 8-RhCO |  |  |  |  |  |
| 4-RhCO |  |  |  |  |  |

1. Complete this table using information from Table 2 and Figure 7:

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Complex | Sketch the Structure of the Pincer Ligand | Color of Rh Complex | 𝜈(CO) for Rh Complex | E1/2 for Pd Complex (V vs Fc/Fc+) |
| 3-M |  |  |  |  |
| 5-M |  |  |  |  |
| 11-M |  |  |  |  |

1. In which two complexes in question 5 do the phosphine substituents change and the pincer backbone remain constant? How do the values of 𝜈(CO) for these two complexes change?
2. Which phosphine substituent in these complexes do you expect to donate more electron density to the metal? Why?
3. Using what we’ve learned about molecular orbitals and back-bonding, explain the trend you see in IR frequencies between compounds 3-RhCO and 11-RhCO. Include sketches in your answer.
4. In which two Pd complexes in question 5 did the substituent on the ligand backbone change? How does this change the redox potentials of the Pd complexes?
5. Which ligand backbone substituent is capable of donating more electron density to the complex?
6. Recognizing that oxidation involves removing an electron, explain the observed correlation between ligand backbone substitution and redox potential for the PdCl complex.
7. According to the table in Question 5, what is the change in v(CO) for 3-Rh(CO) and 11-Rh(CO)?
8. According to the table in Question 5, what is the change in redox potentials for 3-PdCl and 11-PdCl?
9. Does changing the substituent on the phosphine have an effect on the v(CO) (and thus the “electron richness” of the metal center)? If the redox event were located on the metal center, would you then expect a correlated change in the redox potential of the complex? Why or why not?
10. Now let’s focus on the substituent on the pincer backbone. According to the table in Question 5, what is the change in v(CO) for 3-Rh(CO) and 5-Rh(CO)?
11. According to the table in Question 5, what is the change in the redox potentials of 3-PdCl and 5-PdCl?
12. Compare the two sets of data you just collected in the above questions. If the metal is where the redox event occurs (again, where an electron gets removed), would you predict a change in that substituent to affect the electron richness of the metal and thus the v(CO)? Is this what is observed based on your previous answers? How does this conclusion support the idea that these ligands are redox non-innocent?
13. Finally, using the data from your table and the text, which has the most effect on the color change: the pincer backbone substitution or the phosphine substituents? Describe the relationship between the nature of the substituent and the color of the complex.
14. Using what we’ve learned about colors of organometallic complexes, speculate on the correlation between the structure and electronics of the pincer ligands in the paper. What possible electronic transitions may be responsible for the colors of these complexes? Explain your reasoning.