Literature Discussion Learning Object:

**Effects of Cyclopentadienyl and Phosphine Ligands on the Basicities and Nucleophilicities of Cp′Ir(CO)(PR3) Complexes.**

Wang, D.; Angelici, R. J. *Inorg. Chem.* **1996**, *35*, 1321-1331.

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1. Two reactions are shown on the first page of the paper. They are labeled (1) and (2) and referred to as eq 1 and eq 2 in the text. Determine the classification, valence number, ligand bond number, electron number and dn count for the Ir containing reactants and products in these reactions.

|  |  |  |  |
| --- | --- | --- | --- |
|  | **CpʹIr(CO)PR3** | **[CpʹIr(CO)(PR3)H]+** | **[CpʹIr(CO)(PR3)CH3]+** |
| **Classification** | ML4X | ML4X2+ | ML4X2+ |
| **Equivalent neutral class** | ML4X | ML3X3 | ML3X3 |
| **Valence number** | 1 | 3 | 3 |
| **Ligand bond number** | 5 | 6 | 6 |
| **Electron number** | 18 | 18 | 18 |
| **dn count** | 8 | 6 | 6 |

1. How is basicity defined? How is nucleophilicity defined? How are the reactions associated with the basicity study related to the reactions associated with the nucleophilicity (what changes during the reaction?)?
2. What is the ultimate goal of this paper?
3. The focus of this activity is going to be on the protonation study presented in this paper (approximately the first half of the paper). The technique employed to study the protonation was titration calorimetry. Describe this technique to a first-year chemistry student.
4. The acid used in this study was triflic acid, CF3SO3H. Suggest why this acid may have been used. You may need to use additional sources to answer this question. Include appropriate citations.
5. The Cpʹ ligands are varied in the experiment. The two Cp ligands examined are Cp and Cp\*. What are the identities of these two ligands?
6. There is a substantial amount of experimental and spectroscopic detail presented in this paper (Experimental Section). What are the infrared CO stretching frequencies, νCO for compounds 9 and 16? From this data determine which ligand, Cp or Cp\*, is more electron donating. Describe how you reached this conclusion.
7. Similar reasoning, using νCO values, can be used to rank the electron donating ability of the various phosphine ligands that are used in this study. Based on the data presented for the Cp compounds, which PR3 ligand is the most electron donating? The least? Briefly explain how you arrived at these conclusions.
8. The paper describes another method of measuring the donor ability of the PR3 ligands, –ΔHHP (see equation 3, bottom of first column on p 1325, and Table 3). Briefly describe how –ΔHHP was measured and how this measurement correlates to the IR data discussed in the previous questions.
9. Table 3 also presents another metric often associated with PR3 ligands, cone angle. Briefly define cone angle and how it is relevant to this study. You may need to use additional sources to answer this question. Include citations.
10. How does the electron donor ability of the Cpʹ ligands influence the basicity of the compounds? Explain.
11. Does the electron donor ability of the PR3 ligands impact the basicity of the Ir compounds? Explain.
12. Upon protonation, the νCO bands shift dramatically to higher wavenumbers. For example, the νCO for compound 9 occurs at 1916 cm-1 while the band for 9H+ CF3SO3- occurs at 2052 cm-1. Account for this change.