Literature Discussion Learning Object:

**Structurally Similar, Thermally Stable Copper(I), Silver(I), and Gold(I) Ethylene Complexes Supported by a Fluorinated Scorpionate.**

Dias, H. V. R.; Wu, J. *Organometallics* **2012**, *31*, 1511-1517.

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1. This paper employs a B-phenylated tris(pyrazolyl)borate ligand (see figure 1). Tris(pyrazolyl)borate ligands are commonly abbreviated as Tp-. Why are these ligands popular?
2. The title refers to the ligands as scorpionates. What does that term mean? This may require you to use other sources.
3. Consider compounds 2 and 3 in figure 1. Determine the classification, valence number, ligand bond number, electron number and dn count for the M in each compound.

|  |  |  |
| --- | --- | --- |
|  | **Cu** | **Ag** |
| **Classification** | ML3X | ML3X |
| **Valence number** | 1 | 1 |
| **Ligand bond number** | 4 | 4 |
| **Electron number** | 18 | 18 |
| **dn count** | 10 | 10 |

1. After analyzing the compounds in the previous questions, what common organometallic ligand is tris(pyrazolyl)borate similar to? Why?
2. The primary focus of the paper is on compounds 4-6 shown in Figure 1. Determine the classification, valence number, ligand bond number, electron number and dn count for the M in each compound.

|  |  |  |  |
| --- | --- | --- | --- |
|  | **Cu** | **Ag** | **Au** |
| **Classification** | ML2X | ML2X | ML2X |
| **Valence number** | 1 | 1 | 1 |
| **Ligand bond number** | 3 | 3 | 3 |
| **Electron number** | 16 | 16 | 16 |
| **dn count** | 10 | 10 | 10 |

1. Describe the bonding interaction(s) between the coordinated ethylene ligand and the coinage metal. It would likely be helpful to include pictures of the orbitals involved in this interaction.
2. In Table 2, select crystallographic and NMR data are presented. In looking at the C=C bond lengths, rank the metals from strongest to weakest interaction(s) with the ethylene ligand? Describe how you reached this conclusion.
3. The paper reports that the peak in the 1H NMR spectrum for free ethylene occurs at 5.39 ppm while the peak in the 13C{1H} NMR spectrum occurs at 123.3 ppm. Data for the coordinated ethylene ligands in this study is presented in Table 2. In which direction does coordination to a coinage metal shift the 1H and 13C{1H} signals of coordinated ethylene compared to free ethylene? Why? This might require looking at additional sources.
4. The limited NMR data presented in Table 2 also supports the conclusion you reached in question 7. Describe how this data supports that conclusion.
5. On page 1515 the authors use the term coalescence to describe what is observed when the NMR spectra of the compounds are taken under an atmosphere of ethylene. Define coalescence as it applies to this study. This might require looking at additional sources.
6. The 1H NMR spectra for the ethylene protons in the Cu, Ag and Au compounds in the presence of excess ethylene are presented in the supporting information. Briefly describe why these spectra look significantly different. As a reminder, the signal for free ethylene is observed at 5.39 ppm.
7. How does the NMR data in the previous question relate to the strength of the interaction between the coinage metal and ethylene?
8. Rank the monovalent coinage metals in overall donor ability to ethylene.
9. Account for your ranking in question 13.