Literature discussion for “Synthesis and characterization of a formal 21-electron cobaltocene derivative.” *Nat. Commun.* **2023**, *14*, 4979.

Read the [paper mentioned above](https://www.nature.com/articles/s41467-023-40557-7), using these questions as a guide. Do research outside of the paper where needed to answer the questions below. Work on this individually before class, and then in small groups once class meets. You will turn in a group sheet before reviewing as a class.

1. What is a “metallocene”? Why do the authors claim that they are important?
2. Ferrocene was the first metallocene reported, as the authors mention. Draw the structure for ferrocene, and provide an electron count, valence number, and dn. The formula is Cp2Fe, where Cp = η5-cyclopentadienyl, C5H5.
3. Before this current report, what compound had the highest electron count? How many electrons did it have? Draw the compound, and use CBC electron counting to prove the electron count, valence number, and dn.
4. The following questions deal with how ligands with various binding modes bind to a metal. If the answers are not apparent, do some research to get to the bottom of these!
   1. What does the word “hapticity” mean/refer to?
   2. What is “ring-slip”? Draw a figure to help demonstrate what it is, and determine what type of ligand it is for electron counting purposes.
   3. The authors indicate that others have made claims to have made 21-electron complexes. Why, then, is this report so important, in the context of others? (Hint: Mentioning ring-slip here may be a good idea!)
   4. What structural evidence do the authors provide for the assignment of compound **1** as a 21-electron compound? Consider both the Cp and N-based ligands.
   5. What spectroscopic evidence do the authors provide for the claim that there is a N-Co electronic interaction?
5. Consider the structure in Figure 2.
   1. What is the point group of compound **1**?
   2. Does it make sense that you would observe 2 signals in the 1H NMR spectrum for the Cp protons?
   3. Why is the range of chemical shifts in the 1H NMR so large for compound **1**?
   4. Why are some signals missing in the 13C NMR?
6. Use CBC electron counting to demonstrate that compound **1** is indeed a 21-electron compound. Provide the valence number and dn as well.
7. The authors report that compound **1** has an effective magnetic moment μeff of 4.33 and 3.99 μB, depending on the method employed for the measurement. Consider μeff = 3.99 μB. How many unpaired electrons does compound **1** have.
8. The authors used density functional theory (DFT) calculations to probe the electronic structure, and determine the environments of those unpaired electrons.
   1. You’ve heard of HOMOs and LUMOs before. What are SOMOs?
   2. Describe the nature of the SOMOs in compound **1**. Why do these make **1** possible?
   3. The authors claim that they reacted regular 19-electron cobaltocene with pyridine, and did not get the 21-electron analog of compound **1**. Why does that compound not form, but compound **1** with the pincer ligand does?
9. The authors use EPR to characterize compound **1**.
   1. What is EPR? Do some research, and provide a brief explanation of the technique, and why it is useful here.
   2. What can the authors conclude based on their observation of 59Co hyperfine splitting?
   3. The nuclear spin for 59Co is 7/2. Does the splitting make sense for this nucleus? Show how you know.
10. The authors tried to make the 22-electron version of this complex by using nickel in lieu of cobalt. What happened?
11. Oxidation of 21 electron compound **1** results in an 18-electron cation, compound **3**.
    1. After oxidation, what would the electron count be?
    2. How do the authors know that this is an 18-electron compound, and why is it not simply a 20-electron compound?
    3. The oxidant chosen is the cation Cp2Fe+. What stands out about this compound that may make it prone to being reduced by one electron?