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Substitution Chemistry in Odd-Electron Ruthenium Carbonyl Complexes

Literature discussion of an article by Prof. Jason S. D'Acchioli. *Organometallics.* **2009** *28(2)*, 418-424. https://doi.org/10.1021/om800767g

This Learning Object is dedicated to Prof. D'Acchioli as part of the VIPEr LGBTQIAN+ LO collection created in celebration of Pride Month (June) 2022.

Introduction

1. Why would dissociation from a 19 e^- complex be expected to be faster than an 18 e^- complex?

2. Please explain in your own words how ETC (Scheme 2) is a special case of the ligand substitution mechanism shown in Scheme 1 that can be set off by just a catalytic amount of external reductant. Your explanation should use half-reactions and a full-cell reaction involving E^0_1 *and* E^0_2 and the sign of the overall ΔG^0 for the process.

3. The *indenyl effect* referenced on p. 419 needs a little explanation. Because a 17 e^-/19 e^- system can be a little confusing, please consider the $18e^-$ system $CpFe(CO)_2Cl$ (**1**) and its analog $(Ind)Fe(CO)_2Cl$ (**2**), and imagine that we are adding $[NBu_4]Br$ to form $CpFe(CO)_2Br$ (**3**) or $(Ind)Fe(CO)_2Cl$ (**4**).

a. Please give an electron count for **1**-**4** by the CBC method.

b. Please draw out a Lewis dot structure for the neutral Cp ligand, and circle the five electrons that normally bind to the metal.

c. Now please draw an η^3 version of **1** that we can call **1'**. What would be the electron count of this supposed intermediate? Why is this intermediate unfavorable relative to **1**?

d. Draw a mechanism for the conversion of **1** to **3** via **1'**, and give the electron count of each intermediate.

e. Please draw out a Lewis dot structure for the neutral indenyl ligand, and circle the five electrons that normally bind to the metal.

f. Now please draw an η^3 version of **2** that we can call **2'**. What would be the electron count of this supposed intermediate? Why is this intermediate more favorable than **1'**? How will this accelerate the conversion of **2**->**4** relative to the conversion of **1**->**3**?

Electrochemistry

4. Figure 4 presents the reductive electrochemistry of $[CpRu(CO)_3]^+$ in CH_3CN in (a) and the same compound in the presence of excess PPh_3 in (b). At the bottom of p. 421, the authors describe a reaction in which $[(Cp)Ru(CO)_3]^+$ is converted by reduction in the presence of PPh_3 to $[(Cp)Ru(CO)_2(PPh_3)]^+$ by, "loss of CO from the 19-electron radical generated at -1.15 V, addition of PPh_3, and ETC oxidation."

a. The authors describe the reduction shown in (a) as chemically irreversible. What does this mean?

b. What is the initial (unstable) product that is formed upon reduction? Provide an electron count for this compound and postulate why the compound is unstable.

c. The final resting fate of the metal after reduction is unclear, however, the authors suggest a likely first step in the decomposition pathway. A hint to this can be found in the second paragraph in section 3.3. What is the likely first step in decomposition and why does reduction favor this step?

d. In the presence of excess PPh_3, what likely happens to the product of the first step in the decomposition. Be sure to carefully track your electrons.

e. in Figure 4, CV (b) shows two irreversible waves. Again, the second paragraph in section 3.3 provides some insight into what species is responsible for this wave. What compound gives the second reduction wave which occurs at -1.34 V?

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f. The reduction of $[CpRu(CO)_2(PPh_3)]^+$ occurs at more negative potentials than the reduction of $[CpRu(CO)_3]^+$. What does this suggest about the electron donor ability of PPh_3 compared to CO? Why?

g. Consider the region between the two reduction waves in (b) (from about -1.15 V to -1.34 V). Based on your answers to b and d, what species are present in solution at this time.

h. Consider your answers to parts d and e. Is the phosphine-containing product that you generate in d. the same as the species that is reduced in e.? How do you know that it is or isn't the same?

i. In cyclic voltammetry, you are only observing species near the electrode surface. So, even though the potential is negative enough to reduce $[CpRu(CO)_3]^+$, only those molecules near the electrode surface are reduced. This is important because it means that $[CpRu(CO)_3]^+$ is still present in the solution and could be used as a reactant. Suggest a chemical reaction that could convert the neutral PPh_3 compound to the cationic PPh_3 compound. (Hint: See Scheme 2!).

j. Based on the electron donor ability of the PPh_3 and CO ligands, why would you expect your answer in part i to be a spontaneous reaction?

DFT Investigations

5. Why would adding an electron to a LUMO that is predominantly CO π^* lead to ready CO dissociation? What does this suggest about the importance of back-donation or back-bonding to the metal-CO complex?

6. Why, in the $[(Ind)Fe(CO)_3]^+$ case would the reducing electron being delocalized over the indenyl ligand reduce the likelihood of CO dissociation relative to the $[CpFe(CO)_3]^+$ analog?