**Activation of η5-Cyclopentadienyl Ligands toward Nucleophilic Attack through η5 → η3 Ring Slippage. Kinetics, Thermodynamics, and NMR Spectroscopy**

Please complete these guiding questions to *Organometallics* **1998**, *17*, 2391-2393. <https://doi.org/10.1021/om9801195>

1. a) This article discusses the coordination of cyclopentadienyl (Cp) to a metal center with 3 different hapticities: 5, 3, and 1. Draw structures from the article that correspond to each of these situations.

|  |  |  |
| --- | --- | --- |
|  |  |  |
| 5 | 3 | 1 |

b) According to the authors, this article is the first direct observation of what phenomenon?

c) Why are 3-Cp ligands often invoked as intermediates in organometallic rearrangement reactions? Include in your explanation a comparison of 5-, 3-, and 1 -Cp ligand designations according to the covalent bond classification (CBC) method.

2. Why did the authors cite reference 2?

3. a) Fill in the table below using the CBC method.

|  |  |  |  |
| --- | --- | --- | --- |
| complex # | **3** | **6** |  |
| 5­­ - Cp CBC designation |  | N/A | N/A |
| 3­­ - Cp CBC designation | N/A |  | N/A |
| 1­­ - Cp CBC designation | N/A | N/A | X |
| cyclopentadienoneCBC designation |  |  |  |
| **L** = thiourea (SC(NH2)2)CBC designation |  |  |  |
| PMe3CBC designation | N/A |  |  |
| [ML*l*X*x*Z*z*]Q± designation |  |  |  |
| Equivalent neutral class [[ML*l*X*x*Z*z*] |  |  |  |
| m |  |  |  |
| VN/oxidation state |  |  |  |
| LBN |  |  |  |
| dn |  |  |  |
| total valence electron count |  |  |  |

b) Draw the complete Lewis structure for thiourea (SC(NH2)2) and explain why you assigned the CBC designation in the table above.

4. Consult the plots on the Parkin group website (<http://www.columbia.edu/cu/chemistry/groups/parkin/mlxz.htm>) to answer the following questions.

a) What percentage of Ru compounds have the [ML*l*X*x*Z*z*]Q± designation for complex **6** (3­­ – Cp)? For the complex with 1­­ – Cp (see Table for question 2)?

b) Comparing total electron counts from the table in question 2, which is more common for Ru?

5. How did the authors establish that the 3­­ – Cp ligand was in an *endo* orientation in complexes **4**-**6**?

6. a) What technique did the authors use to measure the kinetic and thermodynamic data in Table 1? Briefly describe this technique. (Hint: see this [link](https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_%28Physical_and_Theoretical_Chemistry%29/Kinetics/02%3A_Reaction_Rates/2.01%3A_Experimental_Determination_of_Kinetics/2.1.06%3A_Stopped_Flow) after determining your answer for more information to describe this technique.)

b) The authors state that the reactions to form complexes **4**-**6** from complexes **1**-**3** occur via associative mechanisms. What evidence do they cite to support this claim?

c) Write the chemical equation describing the synthesis of compound **6** from compound **3**. What is *K*, the equilibrium constant, in terms of reactants and products?

d) Compare the equilibrium constants for the reactions in Table 1. Hypothesize an explanation for why *K* is 1-2 orders of magnitude smaller for the formation of **6** than for **4** and **5**.

e) Based on the results presented in article, which interaction is enthalpically more favorable, a Ru(II)-L interaction where L = PMe3 or L = the pi bond from a Cp ring?