**Literature Discussion: The Organometallic Chemistry Behind the “Polymer of Squares”**

A recent publication by the Chirik group (*Nature Chemistry*, **2021**, DOI: 10.1038/s41557-020-00614-w) details the discovery of a new way to polymerize butadiene through iron-catalyzed [2+2] cycloaddition. This polymer of cyclobutanes (aka, the “polymer of squares”) can also be reversibly deconstructed back to butadiene using the same iron catalyst used in its synthesis. This represents a new plastic-like material that can be chemically recycled back to its constituent monomer.

Below are questions related to the iron-catalyzed [2+2] cycloaddition that makes the polymer of squares:

1. This paper focuses on a new way to use olefin monomers to generate a unique polymer structure that can be chemically recycled, which contrasts the known olefin-derived resins shown in Figure 1b. Using Figure 1b as a guide, draw the olefin monomers that make up plastic resin codes 2-6.



1. a) Using Figure 2a as a guide, draw coordination-insertion mechanisms generating the two isomers of linear polybutadiene. Starting from a generic metal hydride, incorporate two molecules of butadiene into the polymer.
	1. Using Figure 2a as a guide, draw an oxidative cyclization/reductive elimination mechanism to generate a “polymer of squares” incorporating two cyclobutyl groups, starting from a generic metal butadiene complex. Indicate the oxidation state of the metal center in your mechanism.
	2. What are the differences between the metal catalyst used in part a) and the metal catalyst used in part b)? What implications does this have for the mechanism?
	3. *Challenge question:* There is an assumption that must be made in the way that two butadienes coordinate to the metal center in the mechanism of part b) in order to obtain the correct polymer of squares. What is it? What happens when the butadienes coordinate the other way?

3. Each cyclobutane unit in the polymer squares can exist in either a *syn* or *anti* conformation (see Figure 4a). Based on the computational results in the paper, the polymerization process produces an alternating *syn* and *anti* distribution of cyclobutanes in the chain. Given this information, draw a sequence of 5 cyclobutyl rings that is consistent with this distribution.



4. The metal catalyst used to make the polymer of squares is an iron complex ligated by a tridentate, pyridine(diimine) ancillary ligand (“PDI ligand”) shown below. When it ligates butadiene, it exists as complex **1**. After oxidative cyclization, it exists as metallacycloheptene complex **2** (for a crystal structure of an analogue, see Russell, *J. Am. Chem. Soc.* **2011**, *133*, 8858, DOI: 10.1021/ja202992p).



* 1. In complex **1**, what type of ligand is the butadiene molecule? What is its hapticity?
	2. What is the oxidation state and d electron count of the iron in complex **1**? What is the total electron count?



* 1. What type of ligand is the allyl group in **2**? Hint:

* 1. What is the oxidation state and d electron count of the iron in complex **2**? What is the total electron count?
1. The allyl portion of metallacycle **2** can exist in two isomeric forms (see the hint in question 4C). Draw the two isomers and the resulting products when reductive elimination occurs. Based on the results of this paper, which isomer is favored?
2. The formation of the polymer of squares is reversible, such that the polymer can be chemically recycled. What does this mean for the overall thermodynamics of the polymerization process?

7. These iron complexes are also known to oxidatively add carbon-carbon bonds of strained 4-membered ring systems (Darmon, *J. Am. Chem. Soc.* **2012**, *134*, 17125 DOI: 10.1021/ja306526d). With this information and the information in Figure 5, draw a plausible mechanism for the following reaction:



8. *Challenge Question:* PDI ligands are “redox active”, meaning that they can act as neutral, monoanionic, or dianionic ligands. In each of the following molecules, assign the formal oxidation state at iron, the d electron count, and the total electron count.

