This work comes from the Fieser lab at the University of Southern California (*Mater. Horiz.* **2023**, *10*, 2047) and describes the catalytic hydrodechlorination of PVC using a rhodium pincer complex.

1. In your own words, briefly summarize the reason this work is being performed.
2. Define polymers and monomers. If you use an external source, be sure to cite it appropriately.
3. What is the structure of PVC?
4. At the end of the second paragraph of the introduction, the authors mention one of their recent studies in which they were able to convert PVC to poly(ethylene-*co*-stryenic) copolymers. Draw the structure of styrene and describe what you think the term to poly(ethylene-*co*-stryenic) copolymers means. While an interesting study, why do the authors suggest that there are limitations to this method?
5. The proposed active catalyst in this work is [Rh(Xantphos)Cl] which is shown in Fig. 1b. Using the CBC method, classify the catalyst, provide an electron count, the ligand bond number, the valence on rhodium and the dn count for rhodium.
6. If you dig into the supporting information, you discover that the authors do not actually isolate [Rh(Xantphos)Cl], but rather isolate [Rh(Xantphos)(cod)Cl] where cod is η4-cyclooctadiene. This product is shown in Fig. S3. This compound is an 18-electron species. Using the CBC method, suggest how this can be an 18-electron species being sure to account for the ligand coordination and bond number, the valence on rhodium and the dn count for rhodium.
7. The 31P{1H} NMR spectrum of [Rh(Xantphos)(η4-cod)Cl] is shown in Fig. S2. In looking at the structure (Fig. S3) are the two phosphorus atoms in equivalent environments? Why or why not? How do you then account for the two peaks in the 31P{1H} spectrum?
8. Although the exact method of synthesis is not exactly clear, the structure of [Rh2(Xantphos)2(μ-Cl)2] has been reported (*Catal. Sci. Technol.* **2014**, *4*, 3409). This compound has an electron count of sixteen. Using the CBC method, classify this dimer, provide an electron count, the ligand bond number, the valence on rhodium and the dn count for rhodium. Note that the dimer is symmetric, so you need only determine half of the molecule and that we have seen two different coordination modes of the Xantphos ligand.
9. The addition of H2 to [Rh2(Xantphos)2(μ-Cl)2] results in the formation of [Rh(Xantphos)(H)2Cl] (*Organometallics* **2015**, *34*, 711). This compound has an electron count of eighteen. Using the CBC method, classify this compound, provide an electron count, the ligand bond number, the valence on rhodium and the dn count for rhodium. Note that the Xantphos ligand has displayed two different coordination modes so far.
10. Shown below are the average Rh-O distances and the P-Rh-P angles for the three compounds mentioned previously. What is suggested by these differences and how do you explain why they are observed?

|  |  |  |
| --- | --- | --- |
| **Compound** | **Rh-O in Å** | **P-Rh-P** |
| [Rh(Xantphos)(η4-cod)Cl] | 3.518 | 105.20 |
| [Rh2(Xantphos)2(μ-Cl)2] | 3.450 | 102.38 |
| [Rh(Xantphos)(H)2Cl] | 2.248 | 163.85 |

1. The authors suggest two different methods/mechanisms of chloride removal in the second and third paragraphs of the introduction. The second one is hydrodechlorination (HDC), which is the focus of this paper. The specific product for HDC is shown at the top of Fig. 1. There is a little less information provided about the other, dehydrochlorination (DHC), but there are some hints provided. The authors state that “the organic polymer fragment is not prioritized”. From the following sentences, suggest how the product of DHC might be different from that of HDC.
2. The proposed mechanism for the catalytic process is proposed in a computational study by the authors (*Phys. Chem. Chem. Phys* **2022**, *24*, 3518). This mechanism is shown in the figure below with 1-chloropropane as the substrate. Suggest what reactions are taking place for each step in the mechanism and provide support for you answers.

[Insert Fig. 1 from *Phys. Chem. Chem. Phys* **2022**, *24*, 3518 here]

1. Figure 3 displays the IR results of four different catalytic studies. Which source of hydrogen and solvent appears to be best in this system? Why? Which is the worst? Why?
2. Several techniques that you may not be familiar with are used to characterize the polymer product of this reaction. The first is thermalgravimetric analysis (TGA). Briefly explain TGA being sure to cite any external source you use.
3. The TGA of the products obtained from the various hydrogen sources was compared to PVC as shown below. Suggest how the TGA results are in agreement with those from IR spectroscopy.

[Insert Fig. S48 here]

1. In your own words, describe the technique of differential scanning calorimetry (DSC) and how it can be useful in characterizing polymers. Be sure to cite any external sources you use.
2. What do the authors learn about the product of their reaction from the DSC analysis?

[Insert Fig. 4B here]

1. Although it does not appear in the main article, the authors also use gel permeation chromatography (GPC) to characterize their polymer. In your own words, describe what can be learned by GPC. Be sure to cite any external works you use.
2. The GPC analysis of the product obtained after treatment with the rhodium catalyst and sodium formate was compared to that of PVC. How do the masses of these two materials compare and why is that significant to this study? The PD is a measurement of the distribution of the lengths of the polymer chains. If all of the polymer chains were exactly the same length, the PD would be 1. How do the PD values of these two materials compare and what are the implications of this measurement?

[Insert Fig. S46 and S47 here]

1. What is the significance of Fig. 5?

[Insert Fig. 5 here]