# Literature Discussion on “*Pyridylamido Hafnium and Zirconium Complexes: Synthesis, Dynamic Behavior, and Ethylene/1-octene and Propylene Polymerization Reactions”*

by Jerzy Klosin et al, *Organometallics,* **2011,** *30,* 3318-3329. [dx.doi.org/10.1021/om200167h](https://pubs.acs.org/doi/abs/10.1021/om200167h)

This VIPEr Learning Object is dedicated to Dr. Klosin, the recipient of the ACS Award in Industrial Chemistry at the ACS National Meeting Spring 2022.

Questions for consideration:

1) In the introduction, the authors classify the catalysts they developed as related to imino-amido catalysts and contrast them to Cp-based catalysts.

a) The abbreviation “Cp” refers to 5-cyclopentadienyl. Draw the simplest Cp-based zirconocene compound, Cp2ZrCl2. Be sure that the geometry around Zr is represented in your drawing.

b) Draw the pyridylamide procatalyst **1** from Figure 1 and identify the parts of the ligand that make the compound related to imino-amido catalysts.

2) a) The crystal structure of pyridylamido zirconium procatalyst compound **3** is shown in Figure 3. Examine nitrogen N2. Does N2 appear to be pyramidal or planar?

b) Consider the pre-catalyst compound Cp2ZrCl2 and the pyridylamido zirconium pre-catalyst compound **3** (Scheme 1, Figure 3). Use the covalent bond classification (CBC) method of electron counting to fill in the table below. Table 1 in [J. Chem. Educ. 2014, 91, 807−816 (dx.doi.org/10.1021/ed400504f)](file:///C%3A%5CUsers%5Clin%5CDocuments%5Cdx.doi.org%5C10.1021%5Ced400504f) maybe useful.

|  |  |  |
| --- | --- | --- |
|  | Cp2ZrCl2 | Compound **3** |
| Cp CBC ligand classification |  | N/A |
| pyridylamido ligand classification | N/A |  |
| Cl CBC ligand classification (in Cp2ZrCl2) |  | N/A |
| Me CBC ligand classification (in **3**) | N/A |  |
| MLlXxZz classification |  |  |
| Valence number |  |  |
| Ligand bond number |  |  |
| Electron count from ligands |  |  |
| Electron count from metal |  |  |
| Total electron count |  |  |
| dn count for metal |  |  |

c) According to the experimental section of the article (page 3325), compound **3** and others similar to it are synthesized and handled in nitrogen-filled gloveboxes with rigorous drying of solvents. Use the results in the table from part (b) to explain why this is necessary.

3) A significant portion of this article is dedicated to discussing the difference between compounds **1** and **1’** and **3** and **3’**.

a) How are these compounds related?

b) How did the authors determine the relative amounts of **1** and **1’** formed?

c) Complete the table of the kinetic and thermodynamic parameters that were experimentally determined and calculated using density functional theory (DFT). Calculate G° from DFT computations using the values of H° andS° given on page 3322 and assuming T = 298 K (room temperature).

|  |  |  |
| --- | --- | --- |
| Parameter | Experimental | DFT |
| Hǂ (kcal/mol) |  |  |
| Sǂ (cal/(mol•K)) |  |  |
| G° (kcal/mol) |  |  |

4) a) Procatalysts **1** and **3** were activated and used in ethylene/1-octene polymerizations. Draw a segment of an ethylene/1-octene copolymer that contains 10 monomer units and 20 mol % octene content.

b) Use Table 2 to create a ranking of which catalyst incorporated the most 1-octene at 120 °C.

5) a) Draw a molecule of propylene and label the carbons with “1” and “2” according to nomenclature rules. Write the series of reactions showing the 1,2-insertion of 3 propylene monomers into the growing polymer chain of a catalyst [Zr+] – P (where P denotes the polymer chain, not phosphorus). (Hint: the result of a 1,2-insertion is that the carbon #1 is bonded to the metal and carbon #2 is attached to P.)

b) Explain why the carbons with the methyl groups in the polymer backbone are chiral.

c) In Table 3, the authors report that catalysts **1** and **3** make isotactic polypropylene. They report the % mmmm where the “m” denotes the relative stereochemistry of the methyl groups along the polypropylene chain. When two adjacent methyl groups are on the same side of the chain, the designation is “m”; two adjacent methyl groups on opposite sides of the chain are designated “r.” Sketch a segment of isotactic polypropylene that contains 5 monomer units where the relative stereochemistry of the all methyl groups is “m”.

6) Why did the authors cite reference (7) (see <https://pubs.acs.org/doi/10.1021/om101207a>)?