Literature discussion of "CO_2 activation by permethylpentalene amido zirconium complexes," Hamilton, E. A., Kilpatrick, A. F. R., Turner, Z. R., Fraser, D. A. X., Buffet, J.-C., and O'Hare, D. *Dalton. Trans.*, 2021, **50**, 4494. http://dx.doi.org/10.1039/d1dt00770j

The following questions are designed to guide the reader though this paper which discusses CO_2 activation by zirconium complexes.

The first paragraph of this paper provides a very concise and readable introduction to early metal amidos. The CBC electron counting method is summarized which is useful for subsequent paragraphs that rely on this information.

1) use the CBC method to provide electron counts for complexes **1**, **2**, and **3** (see question 9).

The next few paragraphs detail the prior work using the Pn* ligand and includes a discussion of the long history of early metal amides reacting with CO_2 to form carbamates, which has been known since the mid 1960s.
2) Write a balanced chemical equation for the reaction of a metal amide ($Zr(NR_2)_4$) reacting with one equivalent of CO_2.

3) What is the driving force for this reaction, entropic or enthalpic factors? Why?

4) What aspects of the Pn* ligand allow it to stabilize the metal center so that it can undergo the reaction? Include in your discussion an explanation as to why homoleptic metal amide complexes are less likely than Pn* complexes to undergo the reaction (this question relates to question 10, so maybe wait until you answer that question before this one).

The next paragraphs discuss the synthesis and characterization of the zirconium complexes.

5) the ^{1}H NMR spectrum of **1** and **2** are reported to have 5 sharp singlets in a 5:6:6:6 integration ratio. What protons do those integrals correspond to and why are they singlets?

6) the authors report that the solution structures of molecules **1** and **2** are "consistent with C_s molecular symmetry," while **3** has "signals consistent with solution phase C_{2v} symmetry." Explain how the molecules have these symmetries and why **3** has more symmetry than either **1** or **2**.

7) the X-ray crystal structure of **1** and **2** also have C_s symmetry, but that of **3** has only C_2 symmetry. Why does the solid state structure have lower symmetry than the solution structure?

8) what do the authors mean by "pentalene fold angles," and how is this number used to characterize the bonding in the complexes? In other words, what would cause a larger (or smaller) fold angle?

9) the bond angles around the amide nitrogens sum to approximately 360°. What does this indicate about the bonding between the Zr and the amide nitrogen? Is it consistent with the CBC notation you reported in question 1? Why do the authors state that in complexes **1** and **2**, the amides are best described as X ligands, while in **3** the amide is best described as an XL ligand, given the very similar geometries around each nitrogen?

The paper then goes on to discuss the reaction of complexes **1**, **2**, and **3** with CO_2.

10) given the information in the paper (top right of page 4496, in the paragraph that starts with 'The generally accepted mechanism…') draw an arrow pushing mechanism for the reaction of **1** with CO_2; simplify **1** as $X_3L_5Zr\text{-}NMe_2$ (this question relates to question 4).

11) What is the author's rationale for the lack of reactivity of **2** with CO_2 given the mechanism? There are two; do both make sense given the reaction of complex **3** with CO_2?

12) Complex **3** reactions with CO_2 to form complex **5**, which was able to be characterized by single crystal X-ray diffraction, but the most important comparison was a different spectroscopic technique. Contrast the proposed structure of **4** with that of **5**. How does IR spectroscopy provide the authors with evidence of the structures of **4** and **5**? Explain.

13) in the conclusion, the authors discuss both similarities and differences between a $(Cp)(NR_2)$ and a $(NR_2)_2$ ligand set. What are they?

The supporting information gives additional information, including a complete synthesis and characterization of each of the complexes.

14) Complex **1** did not give a "satisfactory elemental analysis." Why might that be? What do the reported analysis results suggest for the composition of the product? Does this mean they did not actually make complex **1** or is there another explanation?