# **Literature Discussion on**

# **“Catalytic Carboalumination of Olefins with Cyclopentadienylamidotitanium Dichloride Complexes*”***

by Dan B. Millward et al, *Organometallics* **2000**, *19*, 1870-1878, <https://doi.org/10.1021/om990707y>

**Guiding Questions**

1. On page 1870, the authors state that “CpA ligands differ from their *ansa*-metallocene analogues in that they are formally 10 rather than 12-electron donors and tend to be more open about the metal center.”

1. Use the ionic method of electron counting to demonstrate how the Cp ligands in *ansa*-metallocenes are 12 electron donors and whereas the CpA ligand is a 10 electron donor.
2. Rationalize why CpA ligands are more open about the metal center than *ansa*-metallocenes.

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1. Would replacing the Me2Si bridge in the CpA ligand with a -Me2Si-SiMe2- bridge increase or decrease the openness about the metal center?

2. On page 1870, why did the authors cite reference 10?

3. a) Use the covalent bond classification (CBC) method of electron counting to fill in the table below for complex **2** and the activated complex, [Cp\*ATi-CH2CH3]+shown in Scheme 1.

|  |  |  |
| --- | --- | --- |
|  | h5-(C5Me4)SiMe2N(tBu)Ti(Bu)Cl | [Cp\*ATi-CH2CH3]+ |
| Cp\* CBC ligand classification |  |  |
| amido CBC ligand classification |  |  |
| Cl CBC ligand classification |  |  |
| alkyl CBC ligand classification |  |  |
| MLlXxZz classification |  |  |
| Valence number |  |  |
| Ligand bond number |  |  |
| Electron count from ligands |  |  |
| Electron count from metal |  |  |
| Total electron count |  |  |
| dn count for metal |  |  |

b) What is an agostic interaction? A helpful review may be found at <https://www.pnas.org/content/104/17/6908>.

c) How does the crystal structure of complex **2**, h5-(C5Me4)SiMe2N(tBu)Ti(Bu)Cl, support the assertion that CpA metal complexes are less prone to b-hydride elimination?

d) Starting with Cp\*ATiCl2 (**1**), the precatalyst, write the series of reactions that lead to the formation of the active catalytic species, [Cp\*ATiMe]+. Be sure to show all reagents and products for each step.

4. List the similarities between carboalumination, discussed in this article, and hydroboration, an often-taught reaction in organic chemistry.

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5. Tables 1 and 2 on page 1872 list percent conversion and percent yields for a series of ethylalumination reactions. What is the difference between conversion and yield? How did the authors measure these quantities?

6. Table 3 on page 1871 shows data for the enantioselective ethylalumination of a-olefins with pre-catalyst **4**.

a) What is the symmetry of pre-catalyst **4**?

b) Identify the chiral center(s) in the product 2-benzyl-1,4-butanediol **10.**

7. According to the experimental section, what mass of substrate was used for the synthesis of 2-benzyl-1,4-butanediol **10**? What mass of pre-catalyst Cp\*ATiCl2 **1** was used?