**Mechanistic Study of Competitive sp3-sp3 and sp2-sp3 Carbon-Carbon Reductive Elimination from a Platinum(IV) Center and the Isolation of a C-C Agostic Complex**

Literature discussion of an article by Prof. Nancy S. B. Williams. *J. Am. Chem. Soc.* **2007** *129***,** 9538-9539. <https://doi.org/10.1021/ja066195d>

This Learning Object is dedicated to Prof. Williams as part of the VIPEr LGBTIAN+ LO collection created in celebration of Pride Month (June) 2022. A profile of Prof. Williams from the *Chemical & Engineering News* Out and Proud article can be found at <https://cen.acs.org/careers/diversity/LGBTQ-diversity-Trailblazers-2022/100/i12>.

1. In the first paragraph of the article, the authors allude to the difficulty of breaking C-H and C-C bonds that are not otherwise activated. What are the average bond enthalpies of C-H and C-C bonds? How do these values compare to those of other single bonds involving carbon? Be sure to cite your source.

2. Which specific groups are reacting that correspond to competitive sp3-sp3 and sp2-sp3 coupling in the title of the article?

3. a. Why did the authors cite reference 5?

b. After consulting reference 5, please describe the interaction that takes place between the metal and the C-H bond.

c. In the context of reference 5, what type of ligand is the C-C interaction with the metal according to the Covalent Bond Classification (CBC) method?

4. a. Complete the classification of the table of ligands appearing in the article using the CBC method.

|  |  |
| --- | --- |
| Ligand | CBC ligand classification |
| [NCN] pincer ligand |  |
| Cl |  |
| CH3 |  |
| OTf |  |
| C-C agostic |  |

b. Apply CBC to determining the following characteristics of complexes **1**, **3**, **4 (Scheme 1)** and intermediate **I** (Scheme 2). Note that in Scheme 2, compound **4** is drawn incorrectly with an OTf in place of the Me. Use Scheme 1 for the correct structure of compound 4.

|  |  |  |  |
| --- | --- | --- | --- |
|  | compounds **1 & 3** | intermediate **I** (Scheme 2) | compound **4** (Scheme 1) |
| [MLℓXxZz]Q± designation and equivalent neutral class if applicable |  |  |  |
| valence number /oxidation state of metal |  |  |  |
| dn |  |  |  |
| ligand bond number |  |  |  |
| total valence electron count |  |  |  |

5. Consult the plots on the Parkin group website on covalent bond classification (<http://www.columbia.edu/cu/chemistry/groups/parkin/mlxz.htm>) to answer the following questions.

a. What percentage of Pt compounds have the [MLℓXxZz]Q± designation for compound **4** determined in 4(b)? For intermediate **I**?

b. What percentage of Pt compounds have the valence number for compound **4** determined in 4(b)? For intermediate **I**?

c. What percentage of Pt compounds have the ligand bond number for compound **4** determined in 4(b)? For intermediate **I**?

d. What percentage of Pt compounds have the total electron count for compound **4**? For intermediate **I**?

6. a. Based upon the dn determined in 4(b) and Crystal Field Theory, briefly explain why Pt complexes with this number of d electrons favor a square planar geometry rather than a tetrahedral geometry.

b. How does the pincer ligand in complexes **1**-**4** also encourage a square planar geometry?

c. What is the geometry of intermediate **I**?

7. The formation of complex **4** from intermediate **I** is a ***reductive*** ***elimination***. The term *elimination* refers to the loss of ligand. Use the CBC results in the table from 4(b) to explain why the formation of complex **4** from intermediate **I** is a ***reductive*** elimination.

8. The authors state that complex 1 has *C2v* symmetry. List the symmetry elements of the *C2v* point group and identify them in complex **1**.

9. Describe the evidence the authors cited for compound **4** being a C-C agostic complex rather than an arenium species (Chart 1).

10. Consider Scheme 2 showing 3 possible mechanisms for how compounds **3** and **4** are formed.

a. Which experiment allowed the authors to eliminate Mechanism C as a possibility?

b. How did the authors distinguish between Mechanism A and Mechanism B?

11. After the communication was published in July 2007, the authors published an addendum in October 2007. View the addendum at <https://doi.org/10.1021/ja0799514>. What is the content of this addendum?