Reading[†] Guide for

"**Geometric Control of Carbon–Carbon Reductive Elimination from a Platinum(IV) Pincer Complex.**" Liberman-Martin, A. L.; Van Vleet, M. J.; Elenberger, T.; Cave, R. J. and Williams, N. S. B. *Organometallics*, **2022**, *41*, 3104-3108.
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Preliminaries
What is the reason why the authors carried out this study? Why is reductive elimination an important reaction and what were the authors trying to find out?

Why is reductive elimination the "irreversible product-forming step in a catalytic cycle? (see first paragraph of the article).

Prior work by the Love group is described by complexes **A**, **D**, and **G** in Scheme 1. Her work provide examples of both C_{sp2}-C_{sp3} (complexes **A** and **D**) and C_{sp3}-C_{sp3} RE reactions (complex **G**). perhaps the explanation for the differing reactivity comes from the electronic structure. Determine the CBC description of complexes **A**, **D**, and **G**. Include the VN, LBN, d^n count and total valence electron count of these molecules. Are they different from each other (we expect **A** and **D** to be the same…)

[†] The author thanks NSBW for helpful discussions while developing this learning object.

Similarly, the claim of a RE reaction from either complex **3** or **4** to give either complex **5**, **6**, or **7** should be evident from the CBC description. Provide the complete CBC description of complexes **3**, **5**, and **6**.

The authors use "ap" and "ba" as geometrical descriptors. What do these abbreviations stand for and what do they mean? Use the descriptors to differentiate complexes **3** and **4**.

NMR structural determination

a) the supplemental information for this paper gives complete NMR details for complexes **1** and **6**. In complex **1**, a signal is observed at 4.18 ppm in CD_2Cl_2 (NC**H**$_2$Ar) that is a singlet (note also the solvent effects; in C_6D_6, these protons appear at 3.66 ppm), while in complex **6**, also in CD_2Cl_2, the same protons appear as two sets of doublets at 4.77 and 3.94 ppm. Why does the signal split from a singlet into a two doublets? Can you rationalize the downfield shift of about ½ ppm for complex **6**?

b) Coupling constants

The authors use coupling constants to verify structure in a few places in the manuscript. On page 3105 above Scheme 3, complex **1** is described as having two different one-bond Pt-C coupling constants of 781 and 614 Hz. The coupling constants for complex **6** are not reported (presumably because they were not observable) but there should have been *one* observable coupling constant.

    i)   why is there a coupling constant observed between Pt and C?

    ii)   Which carbon should have retained its strong coupling constant? To help you answer this question, consider the text on page 3106 just below Scheme 4. The authors state that "the α−agostic methyl group in complex **6** appears as a singlet without ^{195}Pt coupling at 3.18 ppm in the ^{1}H NMR spectrum." Note, that the protons discussed in the previous part to this question also exhibit ^{195}Pt coupling.

Later, the authors state that the $^3J_{Pt-H}$ coupling constants increase from 34 Hz in **1** to 61 Hz in **6**. This opposite trend is harder to explain and relies on the fact that coupling through multiple bonds involves coupling constants with both positive and negative terms as well as an angle dependence. Table 11 of reference 13 provides a rationalization of this behavior but it is quite complicated.

Mechanistic things

An explanation for why the methyl-phenyl RE reaction is slow is explained by the conformational change required for an edge-on phenyl (slow) to rotate to a face-on phenyl (fast).

Why is face-on faster than edge-on from a mechanistic perspective?

Why is the phenyl ring constrained in complex **3** resulting in a slow RE reaction?

The authors state that some aromatic product is observed, benzene, not toluene, in the reaction of complex **3**. What is the source of the benzene? Given your answer, why is no methane observed?

To simplify the computations, complexes **3**, **4**, **6**, and **7** did not include the triflate anion. Is this a reasonable assumption? What is special about triflate in this context? Would the assumption be valid if the counterion were a halide?

Due to the highly exergonic nature of the RE reactions, they are stated to be under complete kinetic control in the 2nd paragraph on the left on page 3107. What is the alternative and why is the reaction not under that control?

The next paragraph in the paper states that the calculated trajectory from complex **3'** to **6'** has no substantial rearrangement of ligands and thus has a low barrier. On the other hand, going from **3'** to **5'** + toluene requires a substantial reorganization. Discuss what this means in the context of the rates of the reactions.

A possible problem with the computational study is described in the second to last paragraph of the paper. What is the problem, and why do the authors discount it?

The final paragraph of the paper addresses the concern that the isomerization of the 5-coordinate species is not fast. They claim that the isomerization *is* fast, but that the RE reactions are even faster. Why is isomerization in 5-coordinate complexes fast?
The barrier from **3'** to **4'** is 17.4 kcal/mol. How fast would you expect this reaction to go at 298 K? what about the reactions from **4'** to **7'**, **4'** to **5'**, or **3'** to **6'**? The Eyring equation relates the rate of a chemical reaction to physical constants and temperature:

$$k = \frac{k_B T}{h} e^{-\Delta G^{\ddagger}/RT}$$

h = Planck's constant = $1.584 \cdot 10^{-34}$ cal·sec
k_B = Boltzmann's constant, $0.330 \cdot 10^{-23}$ cal/K
R = gas constant, 1.987 cal/mol·K
k = rate constant