Migratory Insertion Reaction Mechanisms in Cyclopentadienyl Tantalum Complexes

Rachel Pincus, Megan Flood

April 21, 2013

1 Relevant figures

Abstract, Scheme I, Scheme II (note the substituents are different), Scheme VI, Figure 1, Figure 2, Figure 3, Figure 4, Figure 5, Figure 6, Figure 7, Figure 8, Figure 9, Table 2 (only complex 1)

2 To read

1. **Introduction** up to **Scheme II**. The rest of the introduction until the final sentence (which we enclose here) we find unnecessary:

   > "Aiming to shed light on the reaction mechanism, we have performed a DFT study of the migratory insertion of methyl isocyanide into the tantalum–carbon bonds of [TaCpMe$_2$(κ^3-tbmp)] (tbmp = 2,2'-thiobis(4-methyl)phenolato) (1) and
   > [TaCpMe2(κ^3-tbcp)] (2). The results of this study, reported in the present article, give also some hints of the structural versatility and flexibility of thiobisphenolate ligands coordinated to early transition metal atoms."

2. 7054-7060 (**Possible Mechanisms for Migratory Insertion** up to (not including) **Substituent Effects**)

3. **Concluding Remarks**

3 To ignore

1. Computational Details

2. 7054 (up until Possible Mechanisms for Migratory Insertion)

3. Scheme III (and all references to Zn or Zr complexes), Scheme IV, Scheme V, Table 1, Figure 10

4. References

4 Questions to Consider

1. Which route (of A or B) do you favor for the migratory insertion of methylisocyanide? This is not a trick question (as there is no trick answer). Quoth the authors: 'Calculations show that the dissociative (first *fac* $\rightarrow$ *mer* rearrangement, then migratory insertion) and the associative (first migratory insertion, then *far* $\rightarrow$ rearrangement) pathways are in principle competitive. So we're asking how you *feel* about the two proposed paths.

2. Consider closely Figure 1. Which isomer do you think lends itself better to attack by the methylisocyanide HOMO? Does your answer based on this illustration reflect your gut feeling in 1?

3. Given the "optimized structures" on pp 7056 - 7059, are you surprised by any of the calculated energies depicted in Figure 6?

4. We asked you to ignore any calculations or comparisons the group made with different solvents or central atoms other than tantalum. If you had to hazard a rough prediction, what would you say?

5 Important Information

- tbmp = 2,2'-thiobis(4-methyl)phenolato)
- Summary of Computational Details:
  - DFT calculations on reaction intermediates and transition states of insertion process
  - geometry optimizations using B3LYP on Gaussian 03
  - transition states characterized by frequency analysis
  - intrinsic reaction coordinate towards corresponding minima calculated for each transition structure
  - solvent effects computed with CPCM model by single-point calculations on gas-phase-optimized geometries