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Computationally Assisted Mechanistic Analysis of the Protonolysis of a Pt–Me Bond

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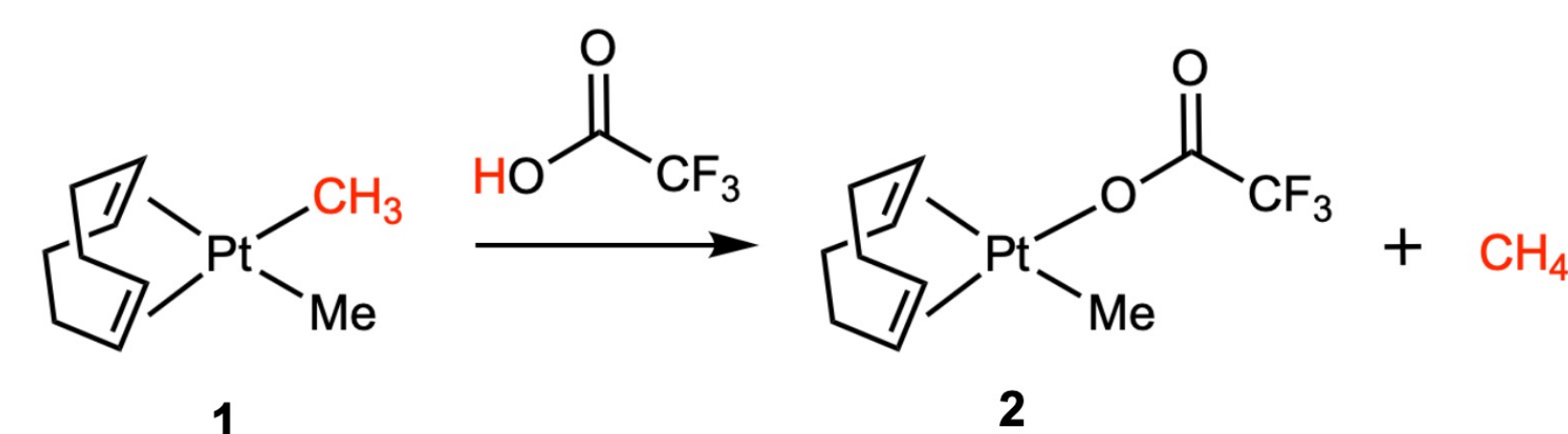
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Computationally Assisted Mechanistic Analysis of the Protonolysis of a Pt–Me Bond

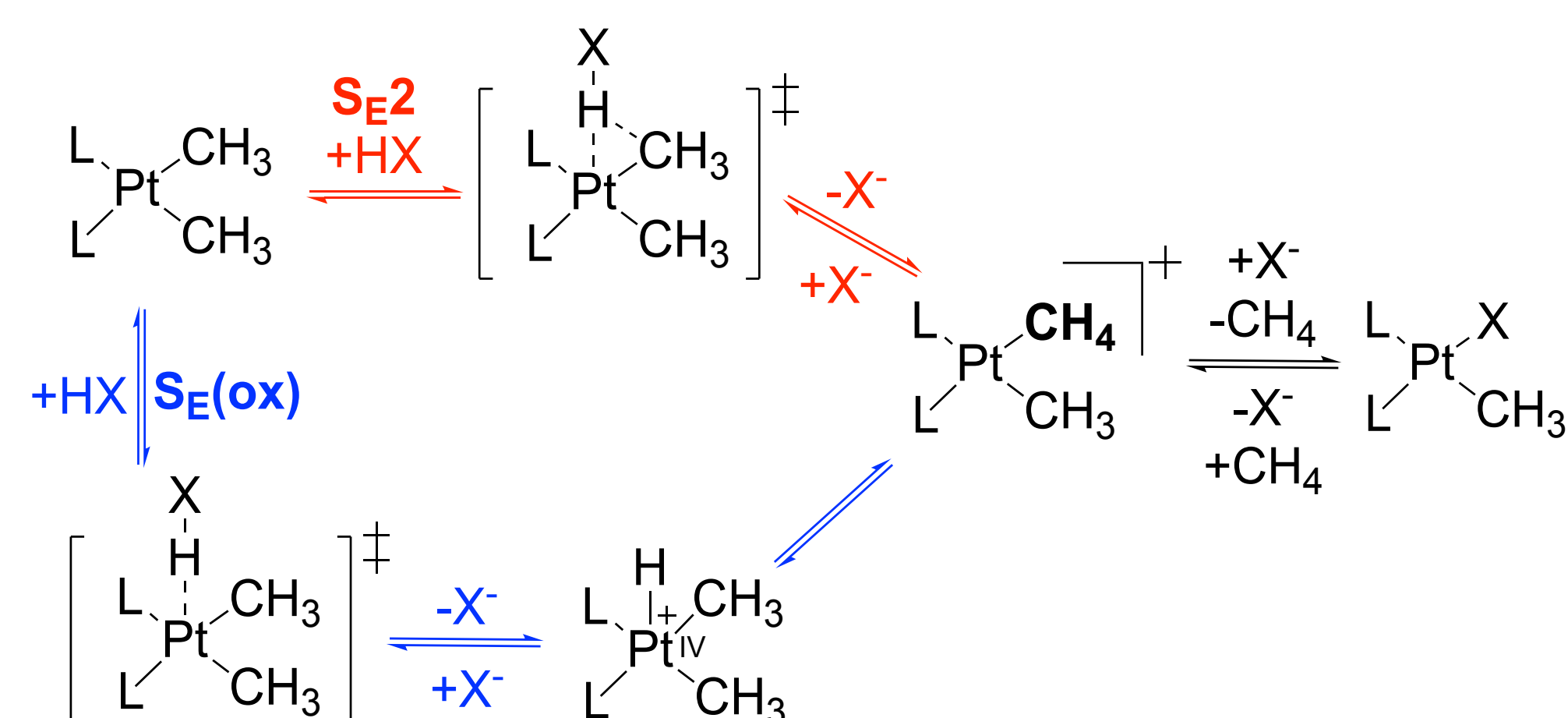
Clement M. DaSilva, Abriana J. Ferguson, Elon A. Ison, Irving D. Rettig, Miriam A. Bowring

Bowring Lab, Reed College Chemistry Department

Introduction

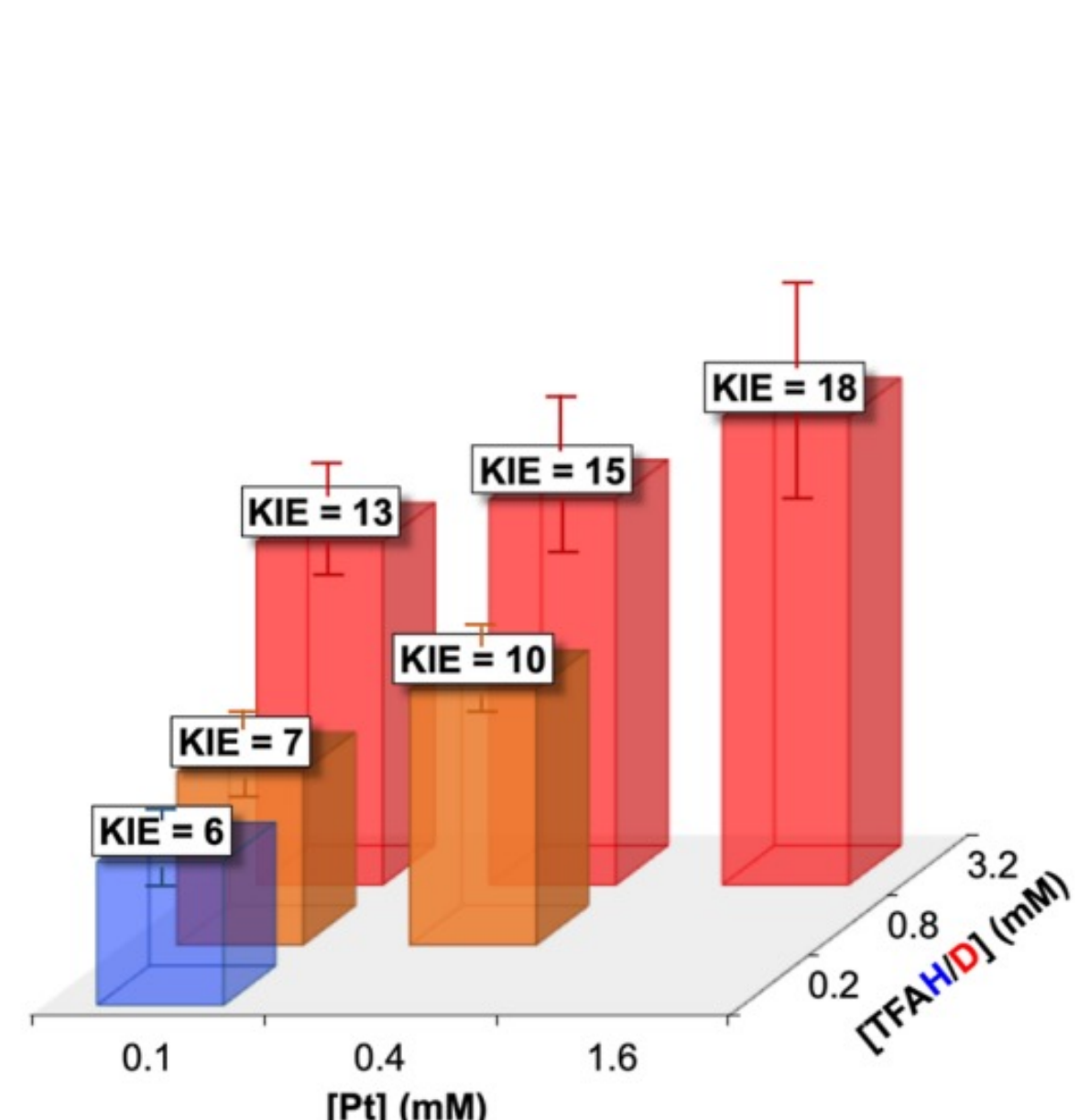


The protonolysis reaction of (cod)PtMe₂ (1) could give insight into C–H activation of methane because it is the microscopic reverse. Two mechanism types have been proposed in the literature for protonolysis of Pt–Me bonds of this type.¹⁻³

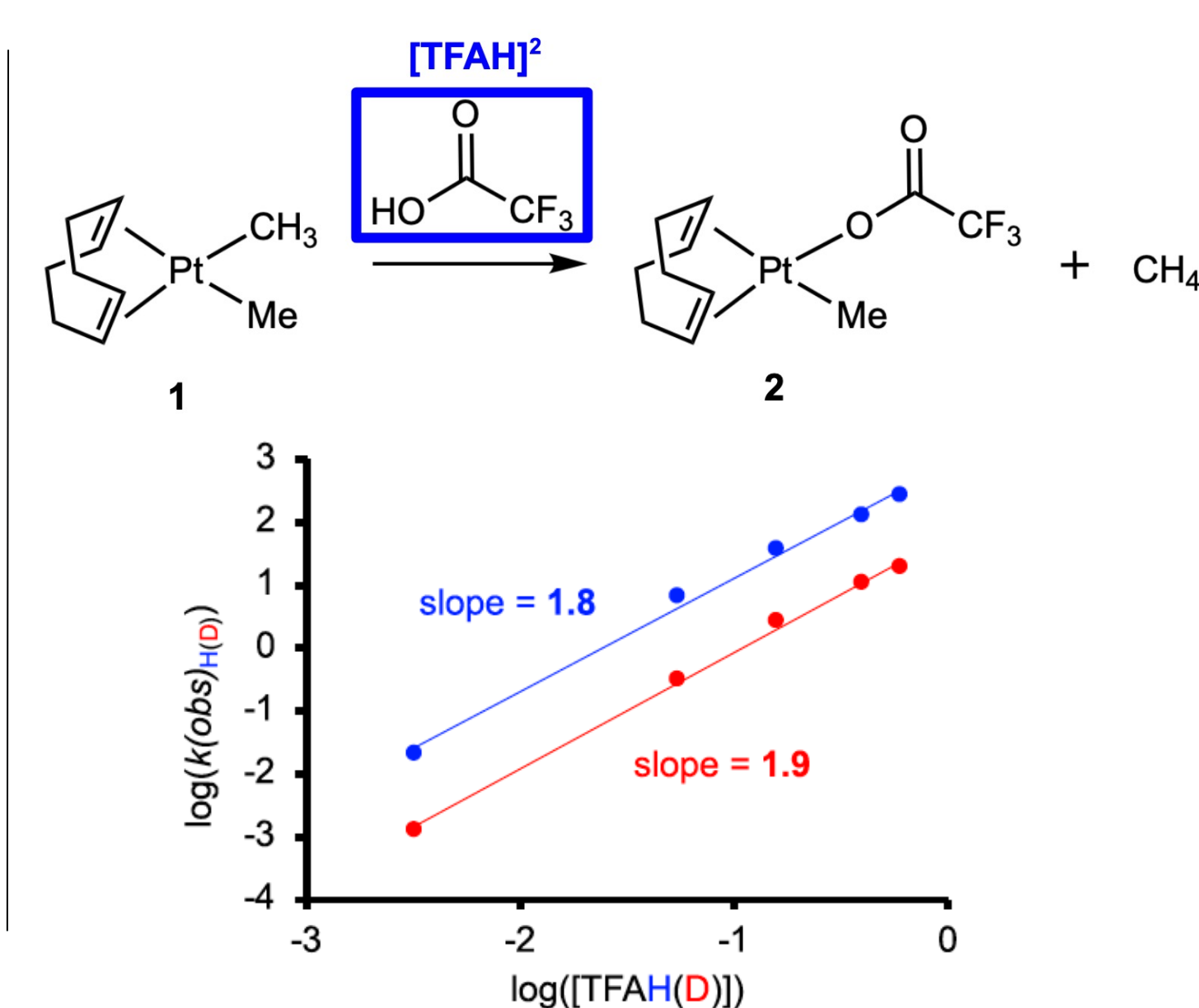


The two proposed mechanisms above are a concerted, single-step mechanism (S_{E2}), and a multi-step oxidative mechanism ($S_{E(ox)}$). For (cod)PtMe₂ protonolysis, previous experimental and computational work supported the S_{E2} pathway.¹⁻³

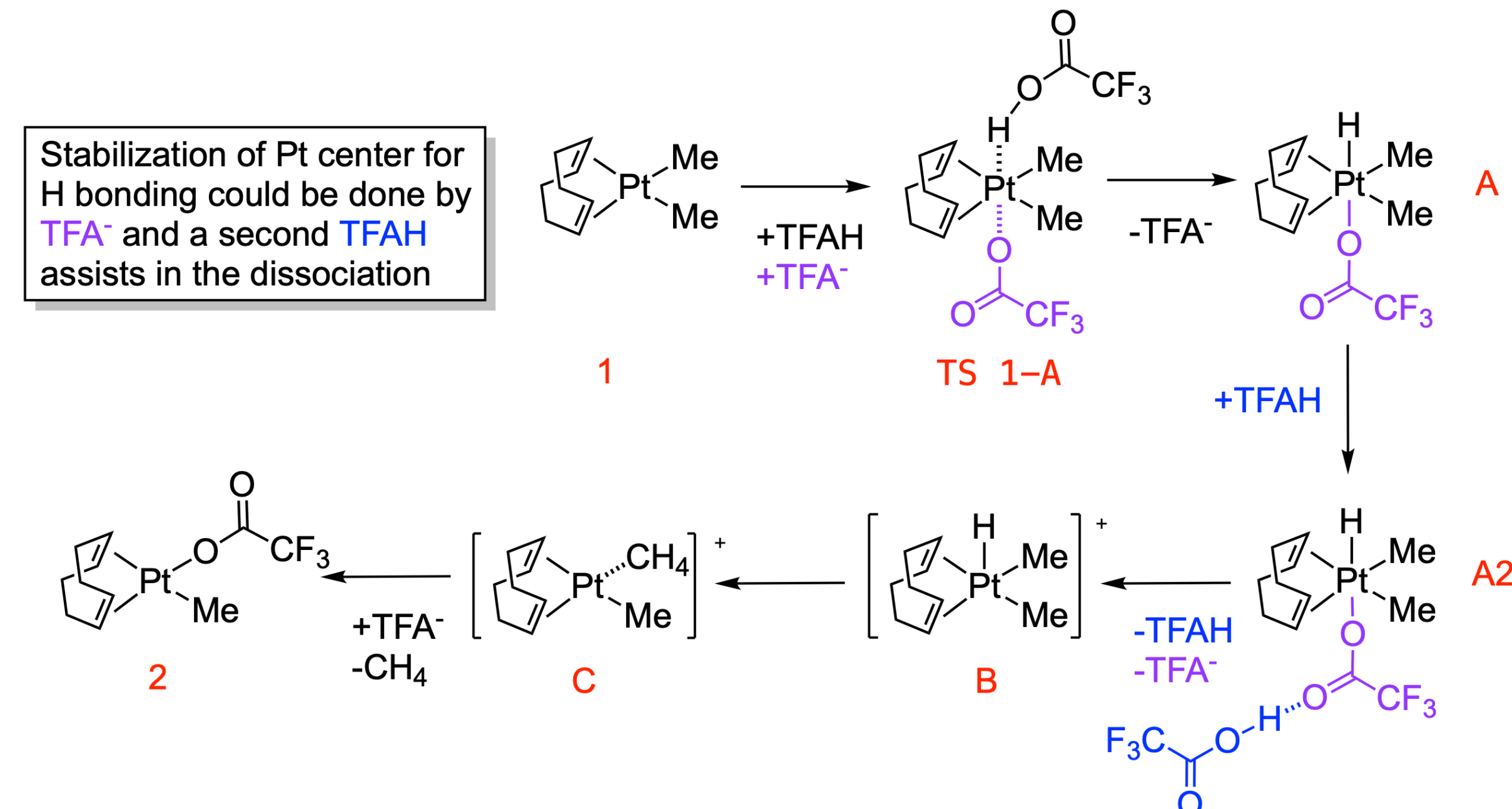
Variable KIE



Second order in acid



Experimental results from the Bowring group suggests that a **multi-step mechanism** involving **two equivalents** of TFAH is at play for the protonolysis of (cod)PtMe₂.⁴



Previous computational work on the $S_{E(ox)}$ pathway for 1 found that a 5-coordinate (B) Pt(IV) hydride intermediate would be too high in energy. We proposed a new $S_{E(ox)}$ pathway incorporating a TFA to stabilize the proton transfer and a TFAH to preform assisted dissociation. We believe that modeling the $S_{E(ox)}$ pathway with a second molecule of acid may aid in differentiating between the S_{E2} and $S_{E(ox)}$ mechanisms for describing the protonolysis of 1 with TFAH.

RESEARCH QUESTION:

Can computational experiments help explain experimental results and develop a plausible mechanism for protonolysis of 1?

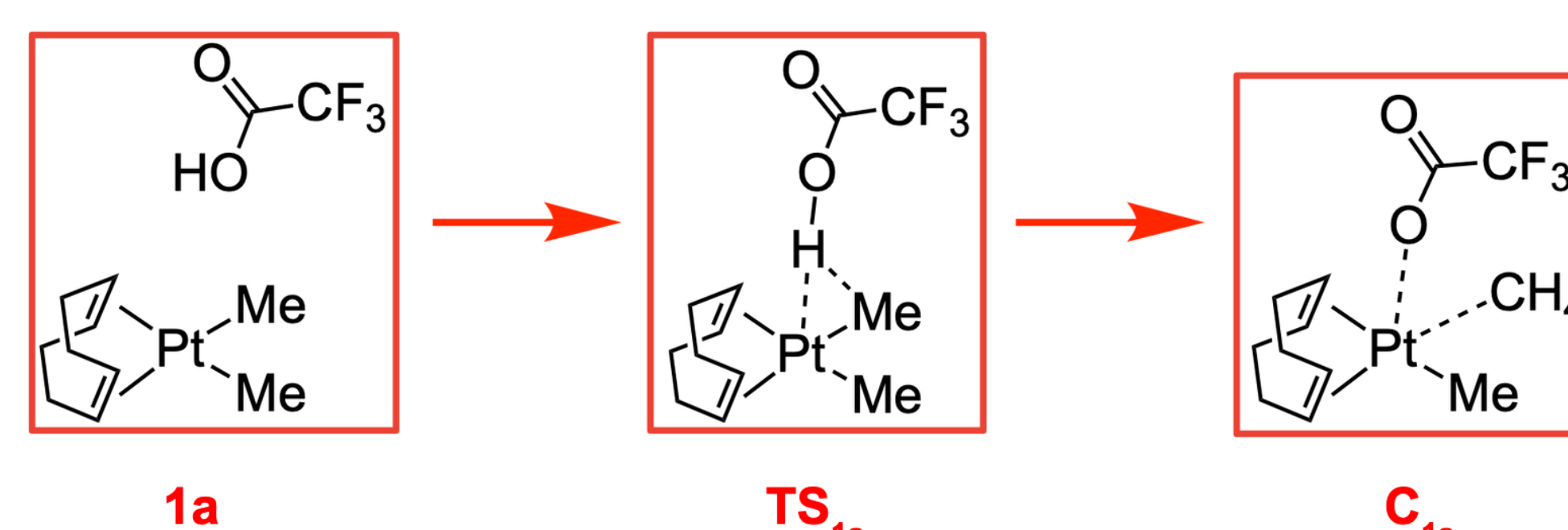
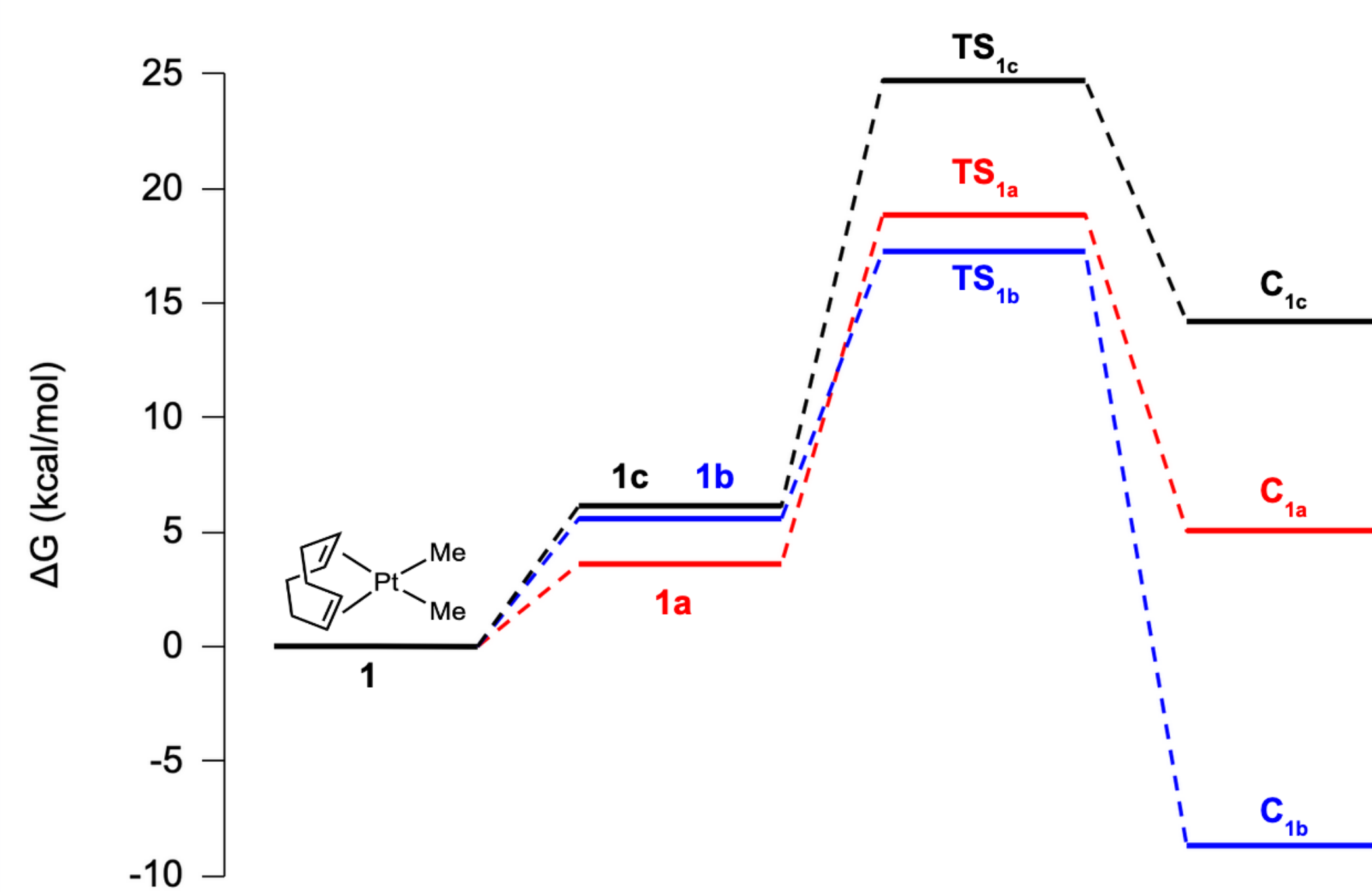
Methods

All calculations were carried out with DFT using the Gaussian 16 package. The B3LYP level of theory was used with a split basis set (Lan12dz for Pt; 6-311+G(d,p) for all other atoms). Final calculations were carried out in DCM solvation (CPCM).⁵ TS were confirmed to have a single negative frequency and were connected to starting material and product by optimizing the displacement of the single negative frequency towards starting material and product.

Results

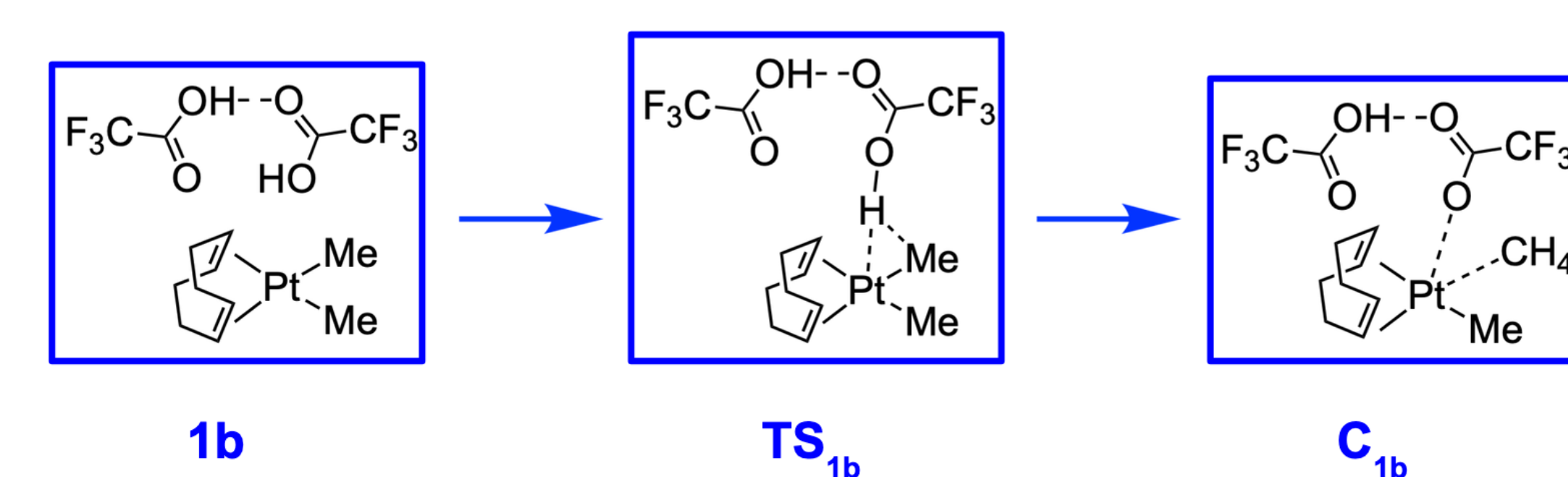
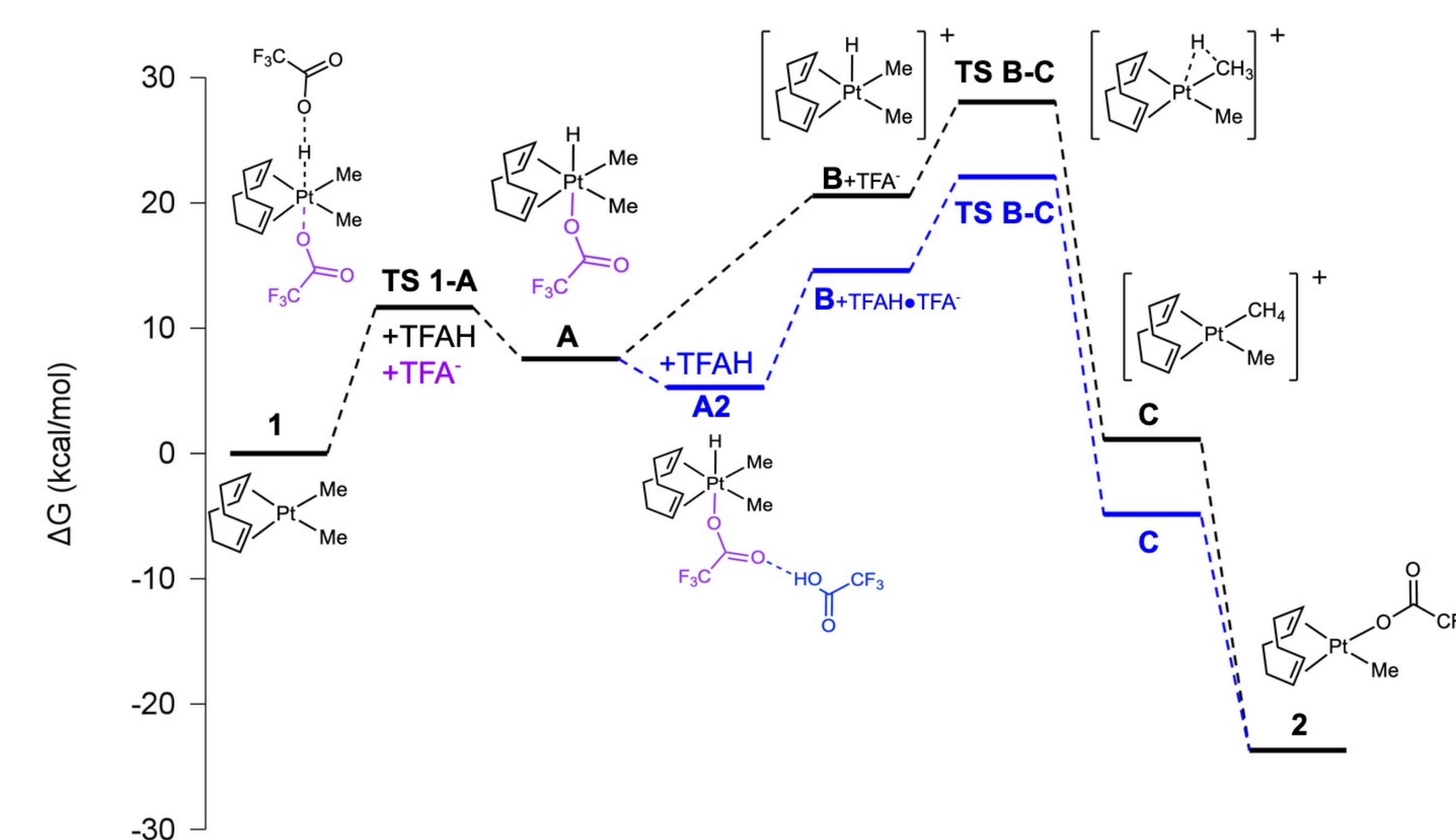
S_{E2} Pathway

Transition states were found for three variations on the S_{E2} pathway: with no additional acid (1a), with the additional acid hydrogen bonded to the first acid molecule (1b), and with the additional acid approaching the Pt center from the opposite face (1c). 1a and 1b were found to have activation energies within error range of each other. The activation energy of 1c was significantly higher in energy.



$S_{E(ox)}$ pathway

- The $S_{E(ox)}$ pathway has been modeled with intermediates and the and B-C TS.
- Adding a second TFAH lowers the energy of the highest TS B-C by 5.97 kcal/mol via assisted dissociation.
- Proton transfer TS 1-A was modeled with a TFA⁻ anion stabilizing it



Conclusions

- Optimized geometries and energies were calculated for all intermediates of various pathways of methane protonolysis, including S_{E2} and $S_{E(ox)}$ with and without inclusion of a second acid molecule
- All TS geometries and energies were calculated for S_{E2} pathways
- Some TS geometries and energies were calculated for $S_{E(ox)}$
- S_{E2} E_a does not show a dependence on two equivalents of TFAH
- $S_{E(ox)}$ E_a decreases by 5.97 kcal/mol with second TFAH molecule
- $S_{E(ox)}$ E_a is still 3.21 kcal/mol higher in energy than S_{E2} even with a second TFAH molecule
- S_{E2} and $S_{E(ox)}$ mechanism types seem unlikely, but TFAH-TFAH interactions seem significant
- TFAH-TFAH interactions could play a crucial role in the mechanism

Future Work:

- Modeling protonolysis with TFAH with molecular dynamics

Acknowledgments



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