

Progress Report for:
PRF # 57849-DNI3

Converting Methane to Higher Alkanes via Boron Homologation with Metal Methylidenes

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Overview of Project Goals and Progress. The original objective of this proposal was to develop a catalytic system for methane polymerization by exploiting metal methylidenes, generated by methane activation, and boron homologation (Figure 1). The project aims are to (1) study methane dehydrogenation at early transition metals (Year 1-2), investigate the insertion of metal methylidenes into boron—carbon bonds (Year 1-2), and identify conditions that are amenable for combining these two processes into a catalytic cycle (Year 2). During this first year of the project, we have made significant progress related to Aims 1 and 2.

Progress Relevant to Aim 1: Reaction of Methane and Other Hydrocarbons with Early Transition Metals.

We have used DFT calculations to explore the feasibility of methane dehydrogenation with tantalocene hydrides. As a benchmark, we first evaluated the energetics of benzene activation by Cp_2TaH_3 , a reaction that is known experimentally and proceeds by initial formation of Cp_2TaH upon reversible loss of H_2 . We next calculated the energetics of the analogous activation of methane and other hydrocarbons such as toluene by Cp_2TaH_3 (Figure 2). Intriguingly, the intrinsic free energy barrier to C—H activation of methane at Cp_2TaH is predicted to be only a few kcal/mol higher than that of benzene (15.0 for CH_4 vs. 11.2 for benzene), and is very similar to the barrier for benzylic C—H activation (16.0 for $\text{PhCH}_2\text{—H}$).

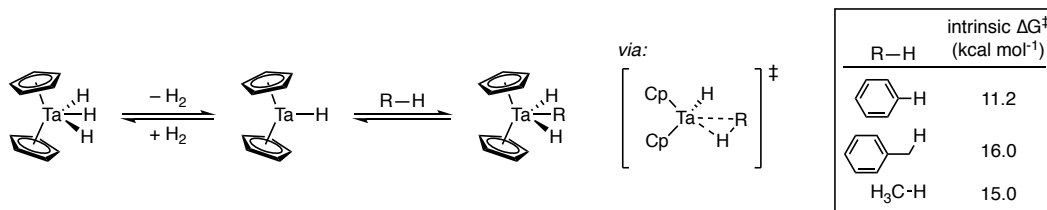
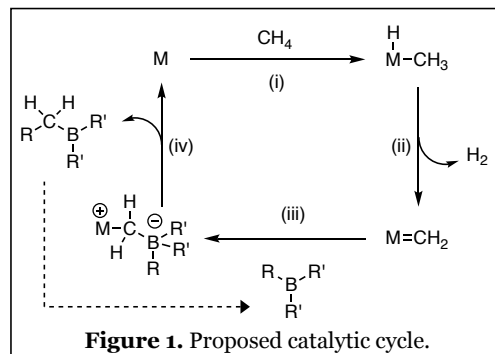


Figure 2. Examples of calculated barriers to C—H activation of hydrocarbons at Cp_2TaH .

Because liquid hydrocarbons are technically easier to work with than gaseous methane, we initiated experimental H/D exchange studies using liquid hydrocarbons (Figure 3). We were particularly interested in toluene because of the similar calculated barriers for benzylic and methane C—H activation. Excitingly, H/D exchange between Cp_2TaH_3 and toluene- d_8 was observed after irradiation at 350 nm for 4 h. Deuterium incorporation into the tantalum complex is readily detected in the hydride region of the ^1H NMR spectrum. Based on growth of residual solvent signal, hydrogen incorporation appears to take place at all positions of toluene- d_8 , including the benzylic position. To confirm this result, we next investigated the reaction of Cp_2TaH_3 with $\text{C}_6\text{H}_5\text{CD}_3$. If H/D exchange is observed, it must originate from activation at toluene's benzylic position because only that position is deuterated. Gratifyingly, H/D exchange was again detected under these conditions, representing the first example of activation of a hydrocarbon $\text{C}(\text{sp}^3)\text{—H}$ bond at a homogeneous Ta(III) center. We are excited about these results for two reasons: (1) together with the calculated activation barriers they provide experimental support that methane activation with tantalum may be within reach, and (2) tantalum-alkyl complexes, such as those that should result from methane activation, are known to undergo α -hydride elimination to generate tantalum alkylidenes. These alkylidenes are well-established to exhibit nucleophilic behavior, which will be required for the second half of our targeted catalytic cycle for methane polymerization (1,2-metallate rearrangement).

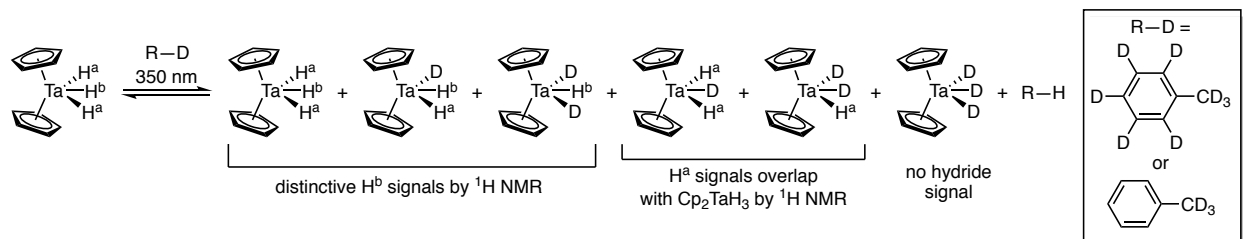


Figure 3. H/D Exchange studies show that Cp_2TaH_3 can activate $\text{C}(\text{sp}^3)\text{—H}$ bonds.

Over the past few months, we have initiated efforts to synthesize novel tantalum hydride analogs of Cp_2TaH_3 (Figure 4). These new complexes are designed to represent varied steric and electronic environments around the metal center. Our immediate goal is to compare the reactivity of these complexes versus Cp_2TaH_3 with liquid hydrocarbons (benzene and toluene). These structure-activity relationship studies will provide insight into how to improve the reactivity of tantalum hydrides with hydrocarbons such as methane.

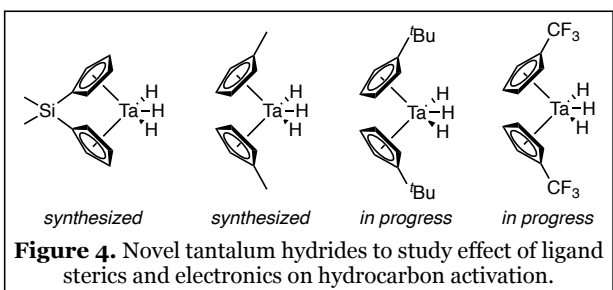


Figure 4. Novel tantalum hydrides to study effect of ligand sterics and electronics on hydrocarbon activation.

Progress Relevant to Aim 2: Boron Homologation. Using DFT calculations at a high level of theory, we conducted further studies on the feasibility of the proposed boron homologation step (1,2-metallate rearrangement). Although the original proposal focused on the use of boranes, our new calculations suggest that alanes are likely to provide much better reactivity with metal methylidenes than boranes (Figure 5). As such, our experimental focus will shift toward aluminum, rather than boron, homologation.

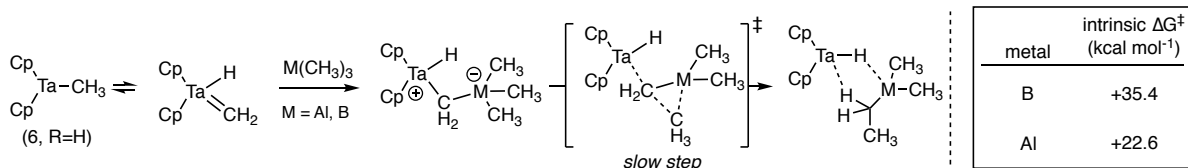


Figure 5. Calculated 1,2-metallate rearrangement mechanism.

Research Impact. Our results from the past year set the stage for our continued progress toward methane polymerization. We anticipate that the demonstrated new reactivity of tantalum hydrides with benzylic C—H bonds will illuminate tantalum as a underdeveloped catalyst for hydrocarbon activation. These studies will provide insight into how to improve our target catalytic system. Additionally, this research has created opportunities for both me and the graduate student primarily involved on this project. Results obtained on this project were instrumental in acquiring an award of computer time from NSF XSEDE in December 2017. One of my graduate students has worked full-time on this project for the past year. He presented his results during his comprehensive exam, and successfully advanced to candidacy on the basis of these studies.