Overview of Project Goals and Progress. The original objective of this proposal was to develop a catalytic system for methane polymerization by exploiting metal methyldienes, generated by methane activation, and boron homologation (Figure 1). This goal was inspired in part by literature reports that silica-supported tantalum hydrides are active for the non-oxidative coupling of methane. We hypothesized that homogeneous tantalum hydrides would also be able to activate methane, but perhaps under more mild conditions (homogeneous catalysts typically operate at lower temperatures than heterogeneous analogs). Furthermore, the properties of homogeneous metal complexes can be tuned through ligand variation. However, at the time, there was no precedent for cleavage of unactivated C(sp^3)—H bonds at Ta(III), a step critical to our proposed catalytic cycle. As such, we began our studies by re-examining known activity of tantalocene hydrides toward H/D exchange of arenes (activation of C(sp^3)—H bonds). We next turned to exploring the reaction of these complexes with C(sp^3)—H bonds. These results are summarized below (manuscript in preparation).

Reaction of Cp:TaH₃ with Arene C—H Bonds. Cp:TaH₃ was previously reported to catalyze H/D exchange between H₂ and deuterated arenes. We investigated the mechanism of this H/D exchange using DFT calculations. Our calculations are consistent a mechanism involving (1) reductive elimination of H₂ to give a high-energy Ta(III) intermediate, (2) π complexation between Ta(III) and the arene, and finally (3) arene C—H activation by oxidative addition to give a high-energy Ta(V) aryl species (Figure 2A, gray pathway). Interestingly, the barrier to C—H activation at the benzylic position of toluene (an “activated” C(sp^3)—H bond) is predicted to be similar (Figure 2A, black pathway), suggesting that toluene might be a good initial test substrate for C(sp^3)—H activation.

![Proposed catalytic cycle](image)

Figure 1. Proposed catalytic cycle.

Previous studies on the H/D exchange between Cp₂TaH₃ and arenes analyzed the isotope distribution of either H₂ or the organic arene solvent. In contrast, we used ¹H NMR spectroscopy to detect H/D exchange at the metal center directly (Figure 2B). This exchange can be seen clearly when Cp₂TaH₃ is heated in C₆D₆ or in toluene-d₈. However, when the metal complex is heated in toluene-d₈ (C₆H₆—CD₅), there is no strong evidence of H/D exchange. This result is somewhat surprising in light of the DFT calculations that suggest that the barrier to oxidative addition at the benzyllic position of toluene is only slightly higher than for reaction at the arene C—H bonds. However, π complexation to Cp₂TaH is a favorable step, and arene C—H activation from the π complex is an intramolecular process. As such, it

![DFT calculations](image)

Figure 2. (A) DFT calculations suggest that oxidative addition into the C(sp³)—H bond of toluene should not be much more difficult than reaction with aromatic C(sp²)—H bonds. (B) H/D exchange between Cp₂TaH₃ and toluene-d₈ can be detected by ¹H NMR.
appears that arene C—H activation outcompetes benzylic C—H activation because of the intermediate π complexation step. Based on these results, we reasoned that an intramolecular C(sp³)—H activation might be more feasible.

**Intramolecular C—H Activation of C(sp³)—H Bonds using Cp∗:TaH₃ Complexes.** We next turned to the synthesis of several tantalocene hydrides bearing alkyl-substituted Cp rings. We hypothesized that intramolecular C—H activation could take place to form transient “tuck-in” complexes. Indeed, formation of a tuck-in complex from Cp∗:Ta(III)H (5) has been previously reported (Cp∗ = pentamethylcyclopentadiene); this reaction involves oxidative addition into an activated (pseudo-benzylic) C—H bond on the ligand. Complexes 1–5 were synthesized and characterized, and then subjected to heating in toluene-đ. Gratifyingly, H/D exchange on the alkyl groups of the ligands was observed with complexes 1–4 (toluene-đ serves as the deuterium source). Although the methyl position of 1 and the 2° and 3° positions of 2 and 3 are activated (pseudo-benzylic) C—H bonds, the observed H/D exchange at the 1° positions of 2–4 represent the first examples of oxidative addition of unactivated C(sp³)—H bonds at Ta(III). Notably, no H/D exchange was detected on the methyl groups of 5. However, with this complex, no H/D exchange is detected between the metal hydrides and deuterated arenes (our calculations indicate that this complex is too hindered to react with benzene), so it is not surprising that deuterium is not incorporated into its ligands. The relative rates of H/D exchange at the different alkyl sites of 1–4 are depicted in Figure 3B. The fastest H/D exchange (statistically corrected) takes place at the tertiary C—H bond of 3. This bond is expected to be the weakest C(sp³)—H bond in the series. Our calculations indicate that C—H activation at the 3° site of 3 leads to a fulvene-like “tuck-in” complex.

![Figure 3](image)

**Figure 3.** (A) Substituted Cp∗:TaH₃ complexes that were synthesized and studied for intramolecular H/D exchange. (B) Statistically corrected relative rates of H/D exchange at different C(sp³)—H positions of the ligands in complexes 1–4.

**Intermolecular C—H Activation of C(sp³)—H Bonds.** With results in hand showing that C(sp³)—H activation is feasible in intramolecular systems, we reasoned that intermolecular C—H activation could also be observed in the absence of competing π bonds that can coordinate to transient Ta(III). As such, we next investigated the reaction of Cp∗:TaH₃ with octane-đ. Gratifyingly, upon heating at 120 °C, H/D exchange on tantalum is clearly detected by ¹H NMR. This result represents the first example of intramolecular C—H activation of an unactivated C(sp³)—H bond at Ta(III).

**Research Impact.** Our results from the past year demonstrate that homogeneous tantalum(III) is a competent catalyst for C—H activation of C(sp³)—H bonds. These results set the stage for development of a homogeneous system for methane activation. We are currently writing up our results for publication. 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 2018. One of my graduate students has worked full-time on this project for the past year. He presented his results at the national ACS conference in San Diego in summer 2019.