

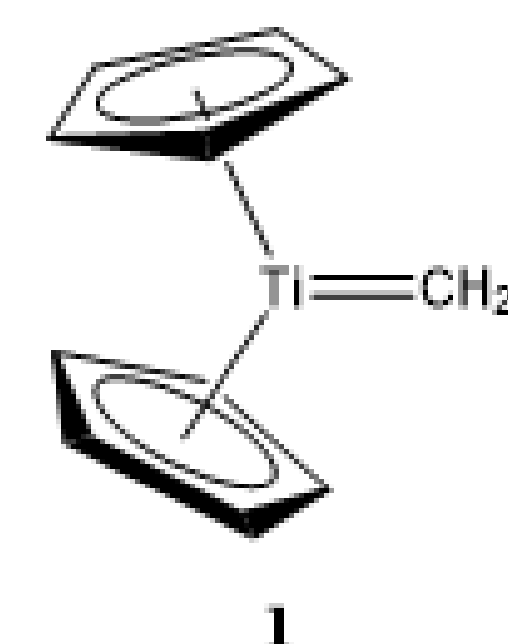
Novel Catalytic use of Titanium Methylidene for Olefin Homologation

Jeremy McAndrew and Daniel Mindiola
Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104



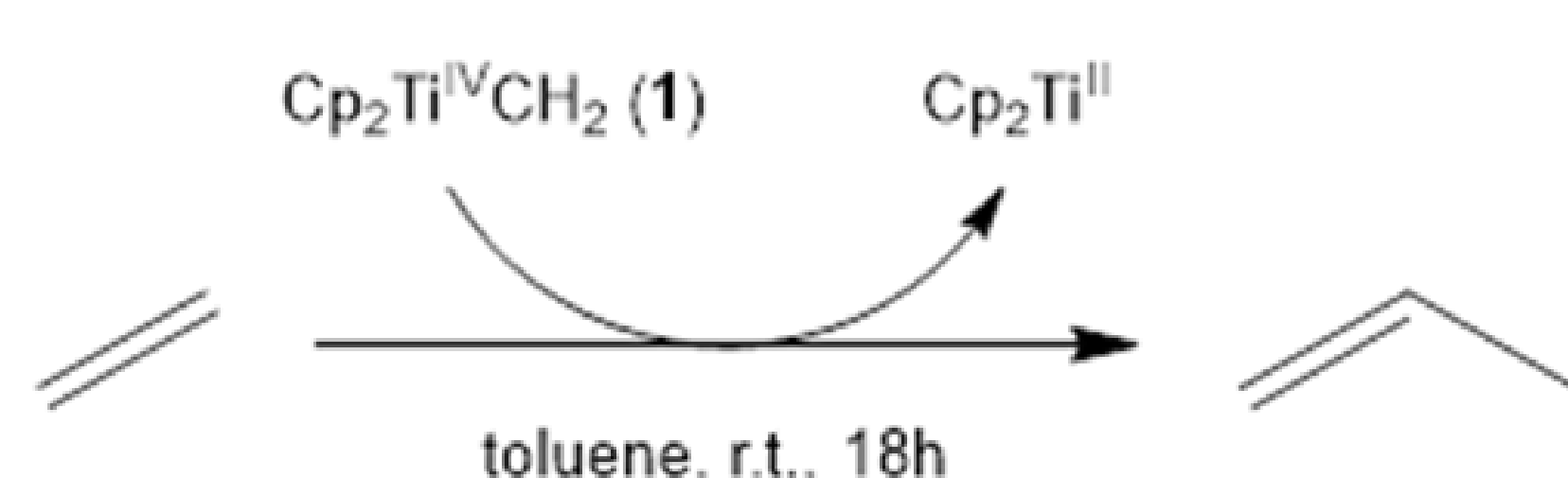
Introduction

Steam cracking is the process by which the petrochemical industry dehydrogenates saturated hydrocarbons into their unsaturated analogs. These unsaturated analogs (e.g. olefins) are utilized to produce products having extensive uses such as in the production of adhesives, elastomers, and polymers all of which make modern life possible. Great disadvantages plague the steam cracking process however, as it is extremely energy intensive (requires extremely high temperatures, > 800 °C) and unselective due to the radical nature of dehydrogenation exacerbating the cost due to separation.¹ This project explores the possibility of converting the stoichiometric homologation of already existing olefins with the transient species dicyclopentadienyltitaniummethylidene [Cp₂TiCH₂], **1** into a catalytic process under mild conditions.

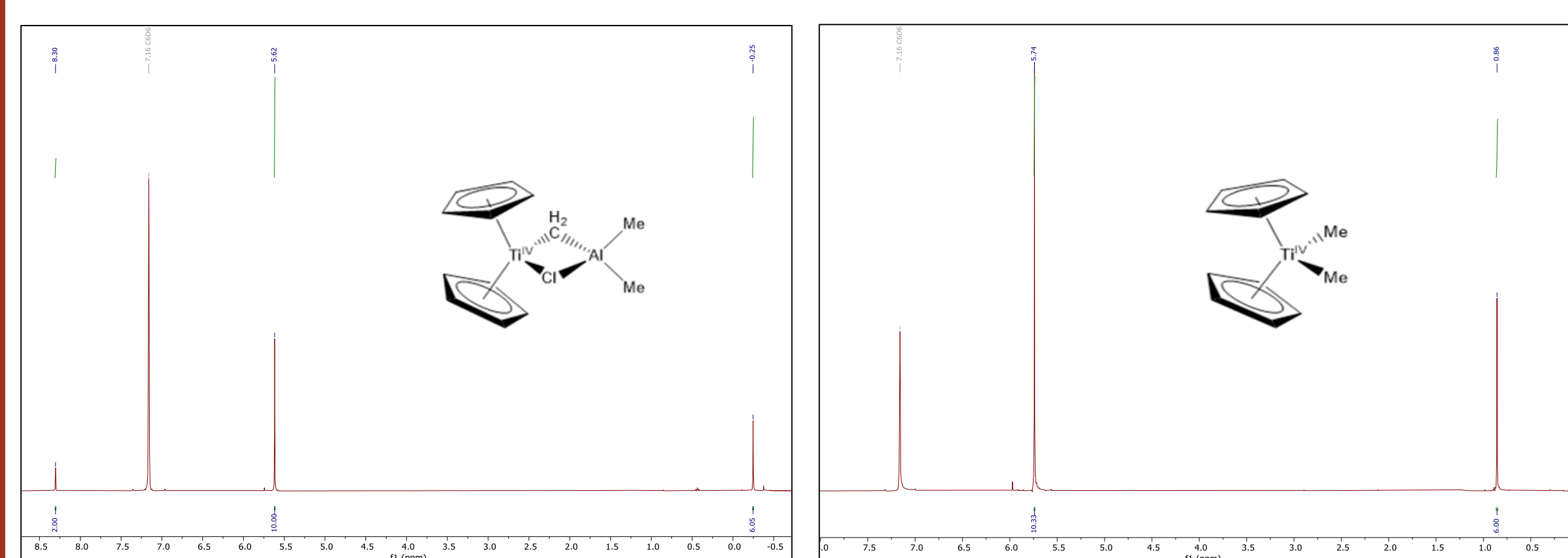
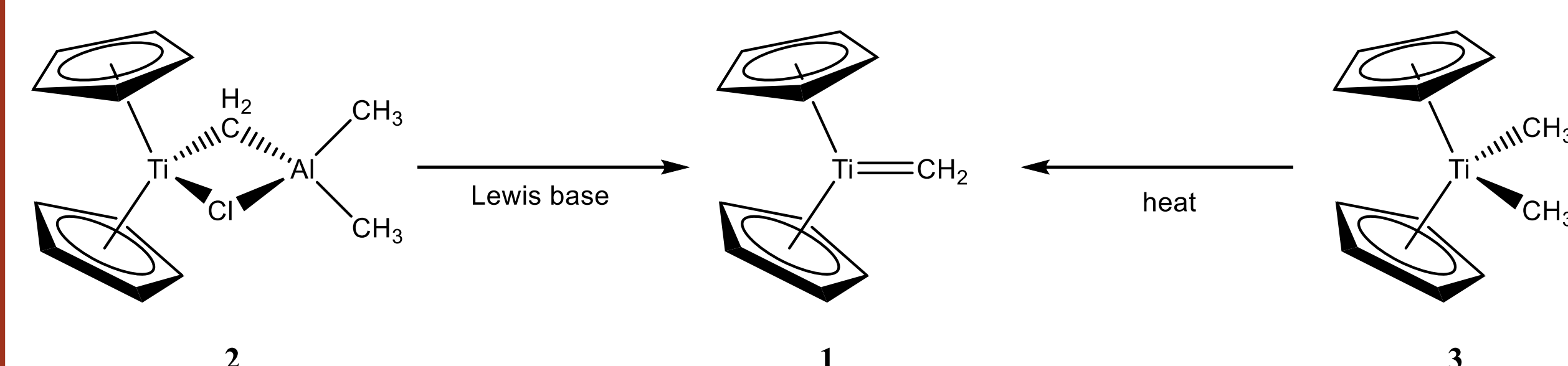


Background

The stoichiometric homologation of ethylene has been demonstrated with the transient species dicyclopentadienyltitaniummethylidene [Cp₂TiCH₂], **1**, to generate propylene at mild conditions.²



Transient species **1** can be generated through two synthetic routes; activation of the Tebbe reagent Cp₂Ti(μ₂-Cl)(μ₂-CH₂)Al(CH₃)₃, **2**, with a Lewis base or heating Petasis reagent, **3**.^{2,3}



When performing stoichiometric homologations 1-octene was used in lieu of ethylene due to its experimental availability, non-volatility at room temperature, and non-toxicity. Therefore the expected product of expected stoichiometric homologation using 1-octene as the olefin source is 2-methyl-1-octene.

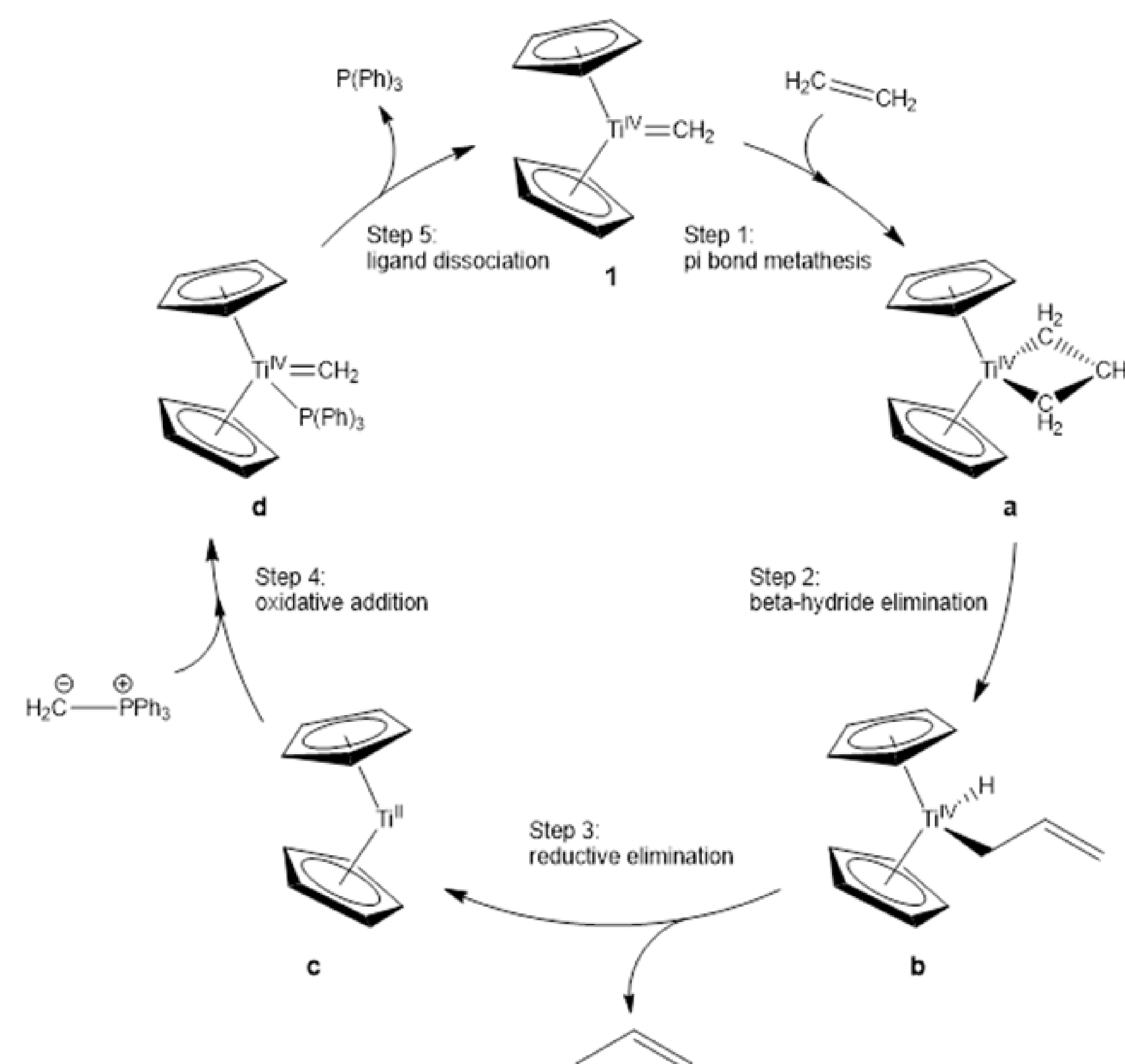
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Proposed Catalytic Cycle

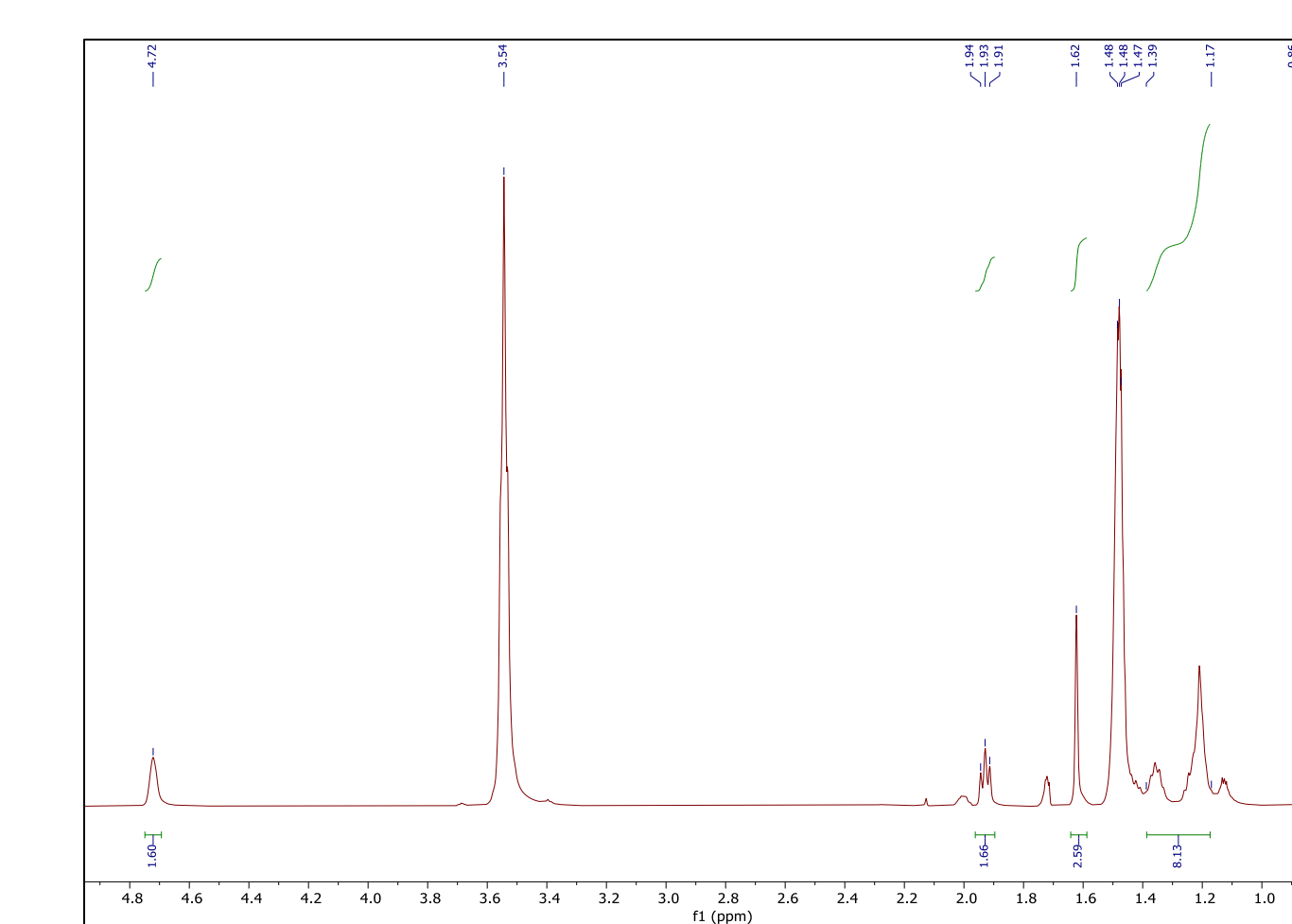
Converting this homologation into a catalytic cycle involves the addition of a triphenylmethylenephosphorane ylide *in situ*. The proposed catalytic cycle is as follows.

Step 1: Transient species **1** undergoes [2+2] cycloaddition with olefin (e.g., ethylene) to form a four membered metallacycle **a**.⁵
Step 2: Intermediate **a** undergoes β-hydride elimination to form allyl-hydride species **b**.
Step 3: Species **b** would then reductively eliminate to form **c** to simultaneously expel the homologation product (e.g., propylene). In this step, the Ti^{IV} ion is reduced to Ti^{II}. Ti^{II} product is expected to decompose, but by adding an ylide [H₂C=PPh₃], it is anticipated that such a species could be recovered.
Step 4: Addition of triphenylmethylenephosphorane ylide [H₂C=PPh₃] oxidatively adds the methylene unit to **c** to form a methylidene-Lewis base adduct **d**. This is the key fundamental step in regenerating the titanium methylidene. This step has literature precedence with divalent Zr and Ti complexes.^{6,7}
Step 5: Ligand dissociation of triphenylphosphine regenerates the active catalyst **1** to close the cycle.



Synthesis of 2-Methyl-1-octene

Product standard 2-methyl-1-octene was synthesized independent of homologation via Wittig chemistry between 2-octanone and triphenylmethylenephosphorane. Separated through fractional distillation.



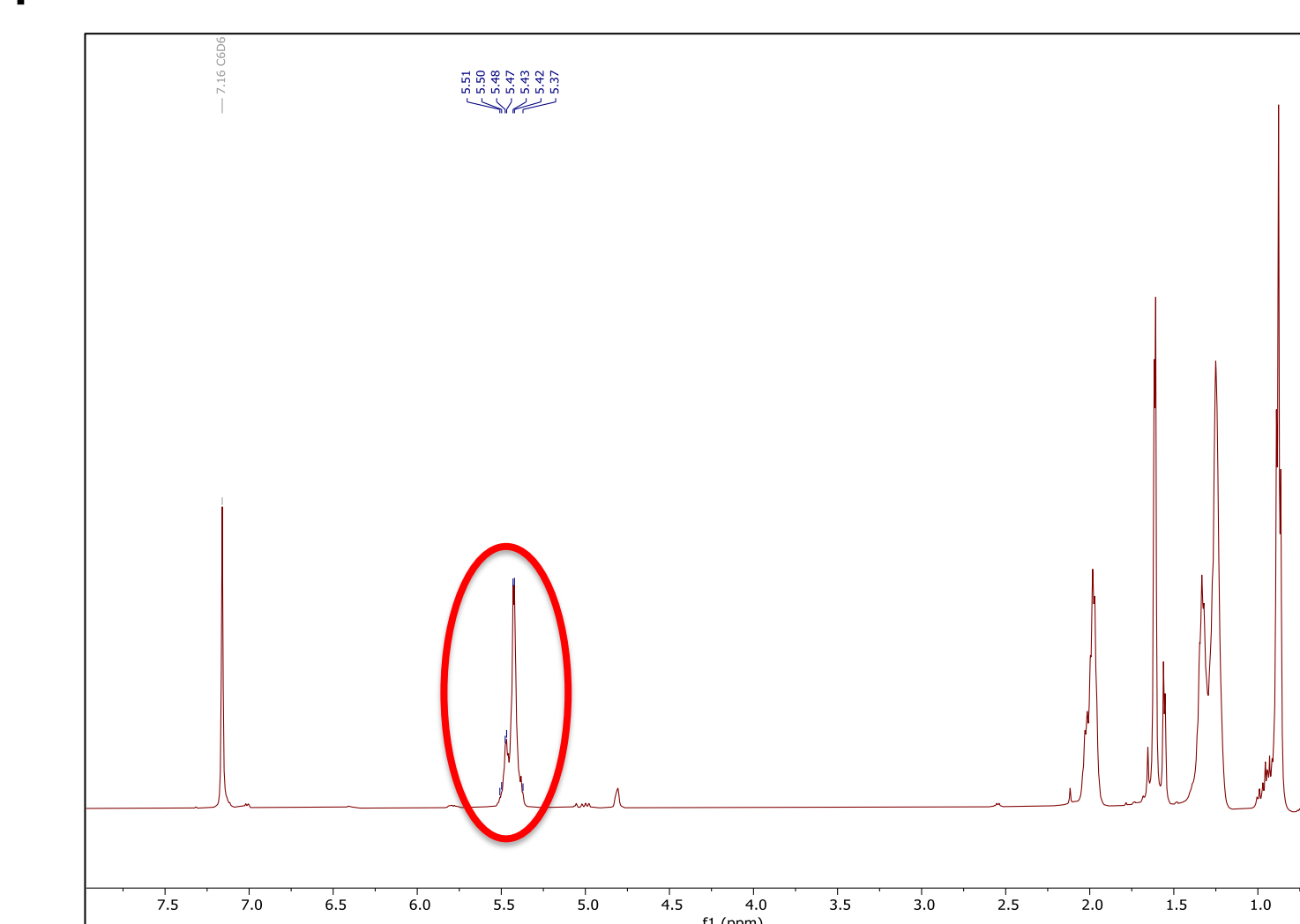
Results

Many attempts to homologate 1-octene to 2-methyl-1-octene via Tebbe and Petasis activation led to no reaction. The following reaction conditions were carried out.

- Tebbe + 1-octene + pyridine (C₆D₆, room temperature, overnight)
- Tebbe + 1-octene + pyridine (C₆D₆, 50 °C, overnight)
- Tebbe + 1-octene + pyridine (C₆D₆, 50 °C, 48h)
- Tebbe + 1-octene + pyridine (C₆D₆, 80 °C, 72h)
- Tebbe + 1-octene (C₆D₆, room temperature, overnight)
- Tebbe + 1-octene (C₆D₆, 80 °C, overnight)
- Tebbe + 1-octene (C₆D₆, 80 °C, 48h)
- Tebbe + 1-octene_{excess} (C₆D₆, 80 °C, 24h)
- Tebbe + 1-octene (C₆D₆, 90 °C, overnight)
- Petasis + 1-octene (C₆D₆, 76 °C, overnight)
- Petasis + 1-octene (C₆D₆, 76 °C, 48h)
- Petasis + 1-octene (C₆D₆, 76 °C, 4 days)
- Petasis + 1-octene (C₆D₆/THF, 75 °C, overnight)

No reaction.

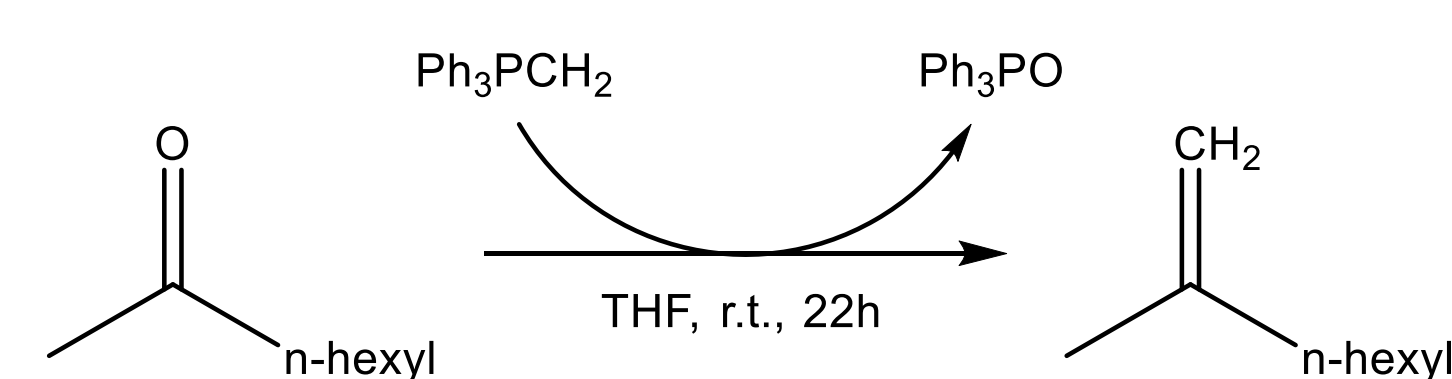
Reaction trials involving Tebbe reagent run at 80 °C or above suggests the dimerization of 1-octene poly(1-octene), multiplet at 5.4 ppm.⁸



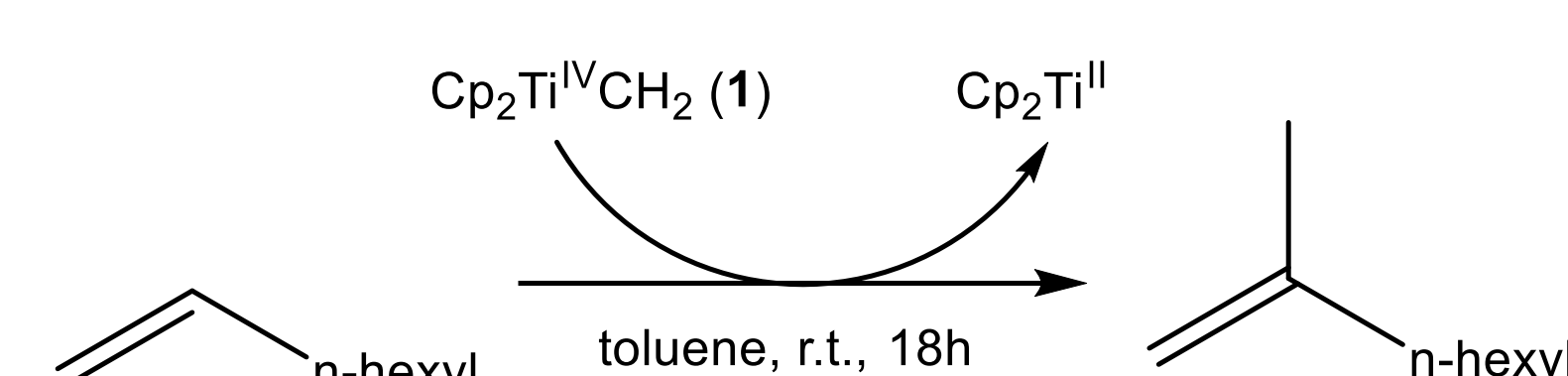
Three Main Goals

This project can be divided into three main objectives.

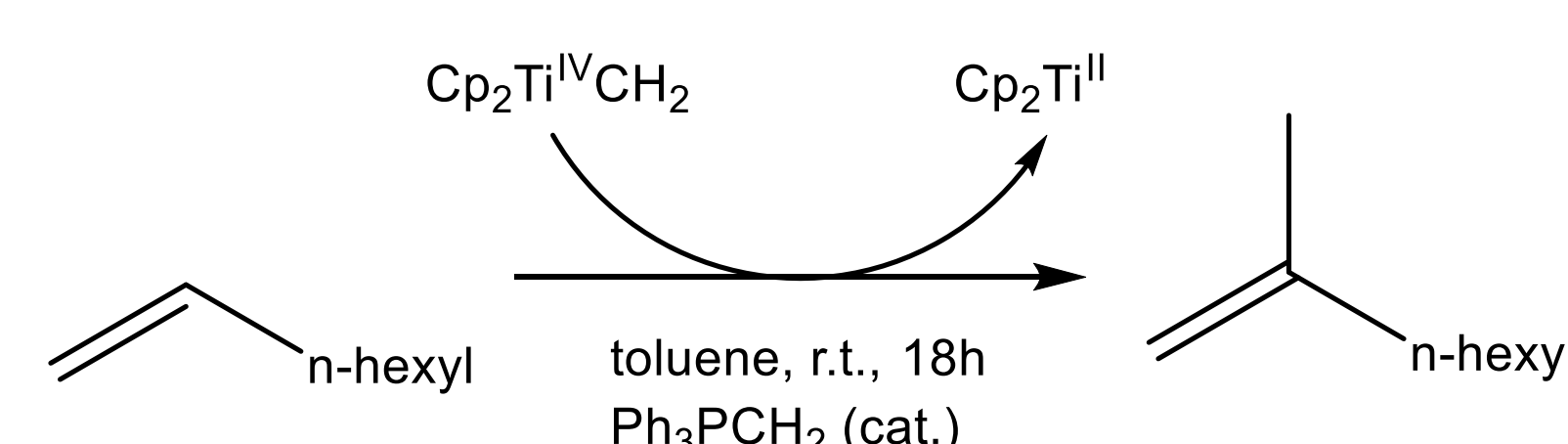
- Synthesis of product standard of 2-methyl-1-octene independent of homologation for reference



- Confirmation of stoichiometric homologation of 1-octene to 2-methyl-1-octene via **1**.



- Attempt catalytic cycle with addition of triphenylmethylenephosphorane ylide.



Future Direction

- Future directions would focus on purifying starting materials. Along with Proton ¹H NMR, crystal structure of both Tebbe reagent and Petasis reagent would be collected to confirm structures.
- To due the possible oligomerization of 1-octene, all reactions would be run sub 80 °C.
- Use ethylene over 1-octene, just as seminal work.
- Alternate titanium complexes would be investigated, including zirconium complexes.