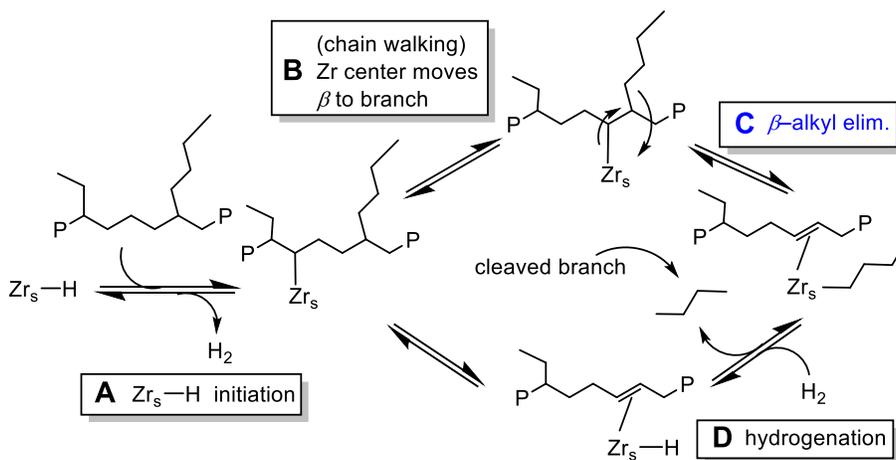


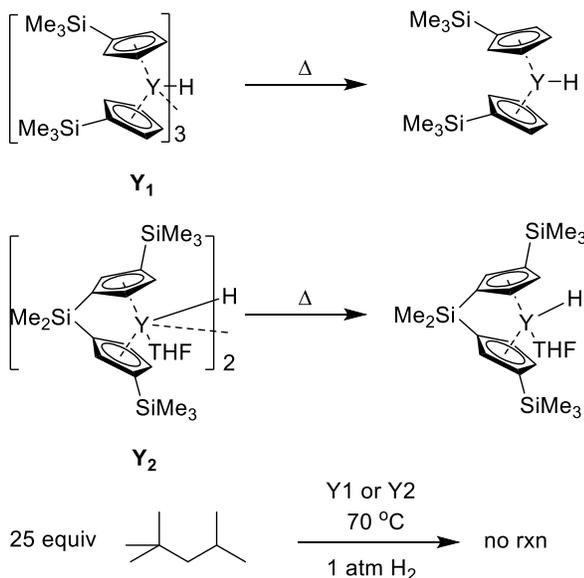
- a. PRF# (58314 ND - 3)  
 b. Homogeneous Catalytic Hydrogenolysis of Polyolefins  
 c. Adam S. Veige

This proposal aims to elucidate fundamental principles of metal-centered  $\beta$ -alkyl elimination reactions and to exploit that understanding to build catalysts for the degradation of polyolefins. The project involves two distinct components: (1) development of structure/activity relationships for group 3 and 4 metal-alkyl and metal-hydride complexes as hydrogenolysis catalysts, and (2) a fundamental study to interrogate  $\beta$ -alkyl elimination.



**Scheme 1.** Proposed mechanism for hydrogenolysis employing a supported  $Zr_s$ -H catalyst:  $\beta$ -alkyl elimination.

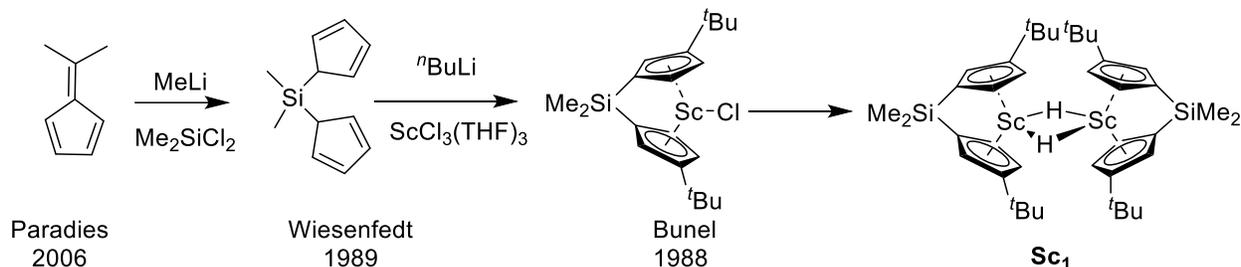
Scheme 1 depicts the proposed mechanism for polymer hydrogenolysis using a supported  $Zr$ -H. One of our first attempts to model the solid state reaction under homogeneous conditions involved testing yttrium hydrides. The test reaction involved combining either complex **Y1** or **Y2** with the model substrate 2,2,4-trimethylpentane in a sealable NMR tube under 1 atm for  $H_2$  pressure (Scheme 2). The trimer (**Y1**) and dimer (**Y2**) dissociate into monomers at elevated temperatures. However, the initial results at 70 °C indicate no reaction occurs. Future work will center on increasing the temperature and pressure within a high pressure reactor followed by GC-MS analysis of the reaction medium. The positive impact on the PI's career comes from expanding the scope of collaborative interactions within the Veige research group. The complexes were provided by Prof. Bill Evans (UCI).



**Scheme 2.** Proposed mechanism for hydrogenolysis employing a supported  $Zr_s$ -H catalyst:  $\beta$ -alkyl elimination.

In a related approach we sought to synthesize  $Cp_2Sc$ -H. This challenging synthesis was undertaken by an undergraduate researcher (Alexander Kane). Positive outcomes from this endeavor include training in various aspects of air sensitive inorganic synthesis including: recrystallizations, distillation, sublimations and data analysis. Work continues to try  $Cp_2ScCl$ ,  $Cp_2ScH$ , or  $Cp_2ScMe$  under hydrogenolysis conditions with the model substrate 2,2,4-trimethylpentane. Another positive impact that emerged from this project and the involvement of an undergraduate student comes in the form of career development for the student. The student trainee working on this project was selected to participate in an NSF sponsored research experience for undergraduates (NSF-REU). The program involves a student exchange between UF and French institutions. The student trainee spent the summer of 2019 in Strasbourg gaining new skills and experiences in the chemistry labs of Prof. Laurent Douce.

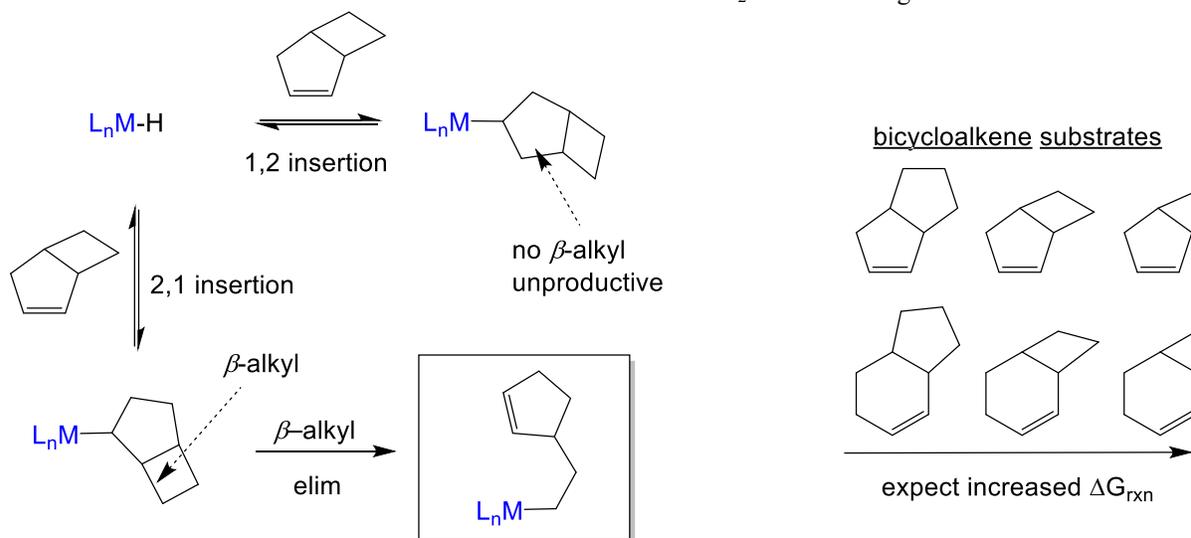
Related to the Cp<sub>2</sub>ScH catalyst work, a student trainee worked on the synthesis of the bridging Sc-H complex **Sc<sub>1</sub>** depicted in Scheme 3. The student trainee gained experience in air sensitive synthesis during the procedure. A significant amount of effort was spent trying to reproduce the literature syntheses. Moving forward, the hydride remains to be isolated and tested for activity in hydrogenolysis.



**Scheme 3.** Synthesis of target complex **Sc<sub>1</sub>** to be tested for hydrogenolysis activity.

Another approach centered on generating a cationic [Zr-H]<sup>+</sup> in situ followed by introduction of substrate. Yang and Marks demonstrated that treating Cp<sub>2</sub>\*ZrMe<sub>2</sub> with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> generates [Cp<sub>2</sub>\*ZrMe][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] and then under H<sub>2</sub> the Zr-hydride [Cp<sub>2</sub>\*ZrH][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] forms. A graduate student trainee synthesized the complexes and reproduced the synthesis [Cp<sub>2</sub>\*ZrH][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]. Instead of generating the cationic species the neutral Cp<sub>2</sub>\*ZrMe<sub>2</sub> complex was tested as a catalyst for the hydrogenolysis of pentane. Treating Cp<sub>2</sub>\*ZrMe<sub>2</sub> with 1 atm of H<sub>2</sub> in a sealable NMR tube generates CH<sub>4</sub> but the resulting Zr-hydride does not react with C-H bonds on pentane used as the substrate. Positive career outcomes from this endeavor come in the form of MS degree granted to the student trainee.

Now that the student trainees are familiar with air-sensitive inorganic synthesis, the complexes synthesized will be interrogated for β-alkyl elimination in a mechanistic investigation. The complexes synthesized will be tested for their ability to insert into a C=C double bond within a strained molecule where β-alkyl elimination will relieve the strain and drive the reaction in the absence of H<sub>2</sub> according to Scheme 4.



**Scheme 4.** Ongoing study to elucidate the mechanism of β-alkyl elimination using strained bicycloalkenes.

Overall, several positive impacts emerged from this first project period. Most important was the training of new students in the art of air-sensitive inorganic/organometallic synthesis. Two student participating in this project will receive MS degrees in 2019. A third Ph.D. student has joined the project and is projected to earn a Ph.D. in 2021. With regard to career development, the undergraduate student participating in this project will apply to Ph.D. programs in the upcoming cycle and was awarded a prestigious opportunity within the UF-France REU program.