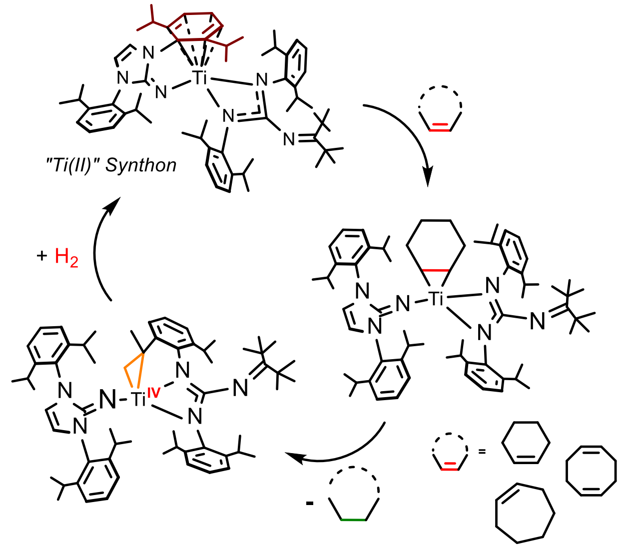
ACS PRF Annual Report
PRF# 57132-DNI3
PI: Skye Fortier, Dept. of Chemistry and Biochemistry, University of Texas at El Paso
Project Title: A Versatile Early-Metal Platform for the Activation and Dehydrogenation of C-H Bonds

Overview: In the realm of organometallic chemistry and catalysis, base metals (e.g., 3d-elements) take a back seat to their precious metal counterparts (e.g., palladium, platinum, ruthenium). This is understandable given the chemical range of the noble metals and their prowess at homogeneous catalysis including cross-coupling, heteroatom transfer, hydrocarbon activation, and oxidative-addition/reductive-elimination chemistries. However, the precious metals suffer from major drawbacks including high cost and toxicity. The latter being a known issue in the synthesis of pharmaceuticals.

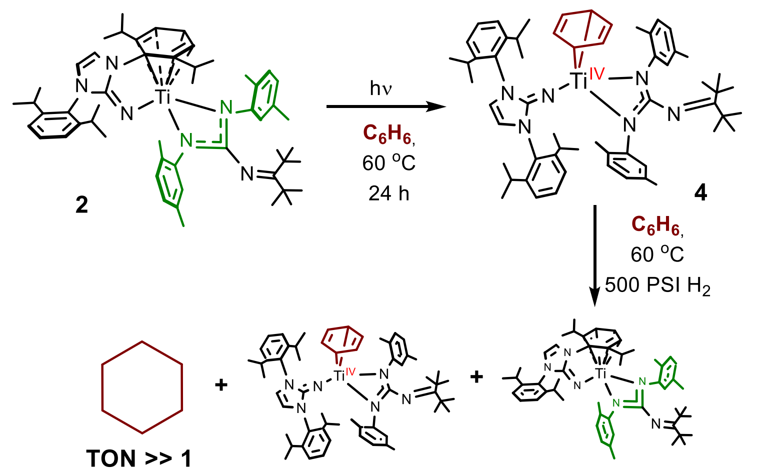
Under this grant, we have been investigating novel routes towards infixing precious-metal type reactivity onto inexpensive base metals for the purpose of C-H activation and hydrogenation chemistry. Our strategy is to synthesize electron-rich complexes with low-valent early metal centers, namely titanium, to facilitate multi-electron transfer chemistry to accomplish challenging hydrocarbon chemical transformations.

Report: We have previously demonstrated that we can access (ketguan)(η^6-Im^{Dipp}N)Ti (**1**) (ketguan = (^{t}Bu$_2$C=N)C(NDipp)$_2$]$^-$; Im^{Dipp}N = 1,3-bis(Dipp)imidazolin-2-iminato) which behaves as a Ti(II) synthon. Complex **1** has been shown capable of performing fully reversible, intramolecular C-H oxidative addition chemistry that can be utilized to perform catalytic transfer hydrogenation reactions (Scheme 1) – the first example of its kind with an early metal system.



Scheme 1. Titanium mediated catalytic transfer hydrogenation.

Recently, our efforts have focused on examining the effect of ligand modifications on the reduction chemistry of our titanium systems. In particular, we have begun to synthesize a series of titanium complexes which differ only at the aryl substituents of the guanidine ligand. For example, we have found that the intramolecularly-capped, xylyl derivative (^{xylyl}ketguan)(η^6-Im^{Dipp}N)Ti (**2**) (^{xylyl}ketguan = (^{t}Bu$_2$C=N)C(2,5-xylyl)$_2$) (Scheme 2) can be readily synthesized and in good yield. On the other hand, the reduction chemistry of the *tert*-butyl derivative (^{tBu}ketguan) (Im^{Dipp}N)TiCl$_2$ (**3**) (^{tBu}ketguan = (^{t}Bu$_2$C=N)C(*p*-C$_6$H$_4$^{t}Bu)$_2$) has proven more challenging as competitive N$_2$ capture and reduction leads to the formation of nitride-bridged titanium species.



Scheme 2. Catalytic arene hydrogenation.

Notably, complex **2** is photosensitive, and upon exposure to ultraviolet radiation binds arenes such as benzene to give the intermolecularly-capped complex (^{xylyl}ketguan)(Im^{Dipp}N) -Ti(C_6H_6) (**4**) in quantitative yield. When solutions of **4** are pressurized with hydrogen and heated to 60 °C, the catalytic hydrogenation of the coordinated benzene to cyclohexane is observed, concomitant with the reformation of **4** (**Scheme 2**). Utilizing either **2** or **4**, the catalytic hydrogenation of aromatic hydrocarbons is observed under the specified conditions. The catalytic efficiency of the observed hydrogenation reactions are low with TON < 10. Yet, we are exploring conditions to enhance this chemistry. Furthermore, we are screening the substrate range and have found our system effective for hydrogenating naphthalene and anthracene. Efforts to optimize and study the mechanistic details of the arene hydrogenation pathway are underway.

As noted above, the reduction of **3** with excess reductant leads to the formation of {K[(^{tBu}ketguan) (Im^{Dipp}N)TiN]}$_2$ (**5**) as a dinuclear, nitride bridged species. This differs significantly from the reduction chemistry of **1**, **2**, and **4** as none of these systems are observed to bind or activate nitrogen when handled under N_2 atmospheres. The isolation of **5** as the reduction product of **3** clearly indicates that minor modifications of the ligand environment can have profound effects on the low-valent chemistry of these titanium systems – an area under investigation in our group.

In addition to providing valuable financial support for the exploration and development of this interesting low-valent early-metal chemistry, the ACS PRF DNI grant has supported the research efforts of students from the undergraduate to graduate level. Namely, this grant has supported the full-time research efforts of one Ph.D. student by providing a research assistantship salary for nearly two years. Moreover, the travel funds provided by the ACS PRF DNI grant facilitated a six-week student visitation for the graduate student at UPenn in the laboratory of a collaborator. At UPenn, the student discovered and was able to develop the arene hydrogenation chemistry detailed above.

We are extremely grateful for the support provided by the ACS PRF as it is giving us the opportunity to continue this new and exciting chemistry which will undoubtedly afford new research pathways.