

ACS PRF Annual Report

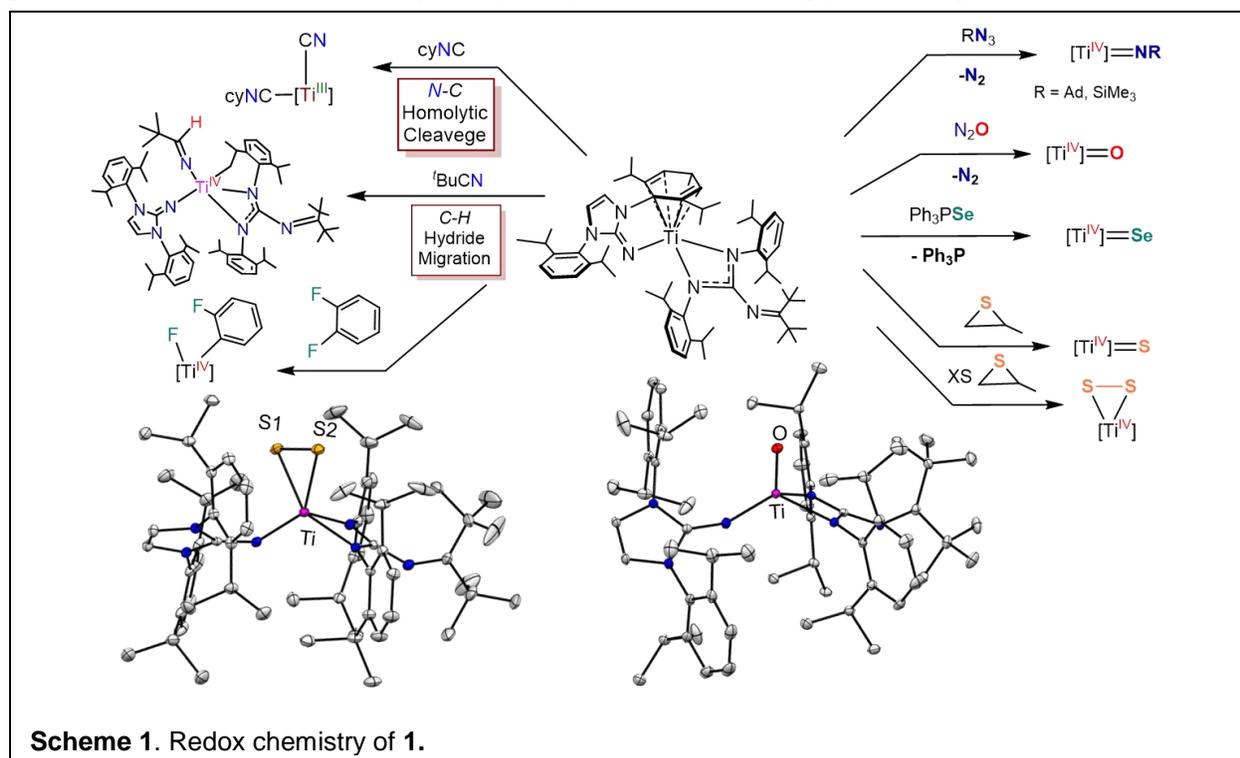
PRF# 57132-DNI3

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Project Title: A Versatile Early-Metal Platform for the Activation and Dehydrogenation of C-H Bonds

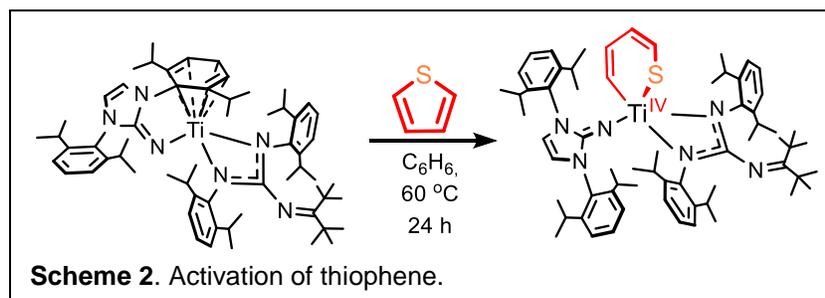
Overview: In our laboratory, we have set forth to explore the chemistry of low-valent early-metal complexes supported by strongly electron donating ligands. In particular, we have designed a 3*N*-ligand manifold consisting of guanidinate and imidazolin-2-iminato ligands to support titanium-centered compounds. We have reported that reduction of the Ti(IV) complex (ketguan)(Im^{Dipp}N)Ti(OTf)₂ (ketguan = (tBu₂C=N)C(NDipp)₂]; Im^{Dipp}N = 1,3-bis(Dipp)imidazolin-2-iminato) generates the intramolecularly masked species (ketguan)(η⁶-Im^{Dipp}N)Ti (**1**) featuring a capping metal-arene interaction as a consequence of two-electron reduction of a peripheral aryl ring. Compound **1** is a potent reducing agent capable of effecting C-H bond activation chemistry and reduction of small molecules. In the time since our last report, we have been thoroughly examining the redox chemistry of **1**.

Report: As outlined in Scheme 1, **1** is highly reactive and gives rise to two-electron chemistry suggestive of Ti(II) redox character. Consequently, **1** can be considered a synthon for Ti(II). For instance, treatment of **1** with organoazides or chalcogen sources (e.g., N₂O) generate the corresponding (ketguan)(Im^{Dipp}N)Ti=E (E = NAd, NSiMe₃, O, S, S₂, and Se) complexes in good yield through the two-electron reduction of these substrates. Attempts to bookend the reduction potential of **1** has been indirectly assayed by its reaction with pyridine to give the Ti(III) dimeric



complex $[(\text{ketguan})(\text{Im}^{\text{DippN}}\text{Ti})_2(\text{NC}_6\text{H}_5)_2]$, formed from reductive coupling of two pyridine molecules. This gives an estimate of a reduction potential for **1** of circa -3.0 V (vs $\text{Fc}^{0/+}$), which suggests that **1** is more reducing than Na/Hg amalgam. In line with this, Scheme 1 clearly shows that **1** is not stabilized by π -acids such as isocyanides or nitriles, but instead reduces these substrates by one-electron leading to C-N bond scission or formal hydride migration reactions. Furthermore, stirring **1** in solutions of *o*-difluorobenzene leads to C-F bond cleavage to give the Ti(IV) organometallic fluoride complex $(\text{ketguan})(\text{Im}^{\text{DippN}}\text{Ti})(\text{F})(\text{C}_6\text{H}_4\text{F})$ (Scheme 1). These reactions and their products have been thoroughly characterized and serves as the basis of a recently submitted manuscript.

Recently, it has come to light that **1** is also reactive to aromatic heterocycles such as thiophene. For instance, addition of thiophene to **1** produces the Ti(IV) thiotitanacycle complex $(\text{ketguan})(\text{Im}^{\text{DippN}}\text{Ti})(\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2)$ (**2**) formed from oxidative addition of titanium across a C-S bond of thiophene (Scheme 2). While this reactivity has been well-studied amongst the late, precious metals, to the best of our knowledge, this is first instance of such chemistry mediated by an early-metal complex.



Thiophene and thiophene-containing molecules in crude petroleum feedstocks are well-known to be more difficult to remove than other sulfur-containing, non-aromatic compounds. Thus, our system

may provide new insights into the improved removal of thiophene from crude oils. Given that **1** has been shown capable of hydrogenating cyclic olefins, and structural derivatives of **1** have demonstrated the ability to catalytically hydrogenate aromatic molecules, it is likely that **2** will prove amenable to such hydrogenation chemistry. Indeed, we envision utilizing our system to effect that catalytic hydrodesulfurization of thiophene.

In addition to our chemical efforts, the ACS PRF DNI award has been utilized to support the training and development of Ph.D. student Rolando Aguilar-Calderon. Because of the resources afforded through this grant, Rolando's research activities were supported via a two-year research assistantship. Through this support, Rolando was able to make significant inroads, including the recent discovery of the titanium-mediated thiophene activation chemistry. In July of 2019, Rolando successfully defended his dissertation and was awarded his Ph.D. in chemistry. Dr. Aguilar-Calderon is a clear beneficiary of the ACS PRF DNI grant and is now continuing his chemical studies as a postdoctoral research associate at the University of Pennsylvania.

We are extremely grateful for the research support that has been provided by the ACS PRF grant. As this award comes to a conclusion, it has enabled exciting new directions into unprecedented base-metal chemistry while providing support for the training and research development of a talented graduate student researcher who is now well-prepared to tackle the next phase of his professional career.