Narrative Progress Report

1. PRF#57188-ND3
2. Project Title: A Modular, Coordination Chemistry Approach to the Isolation of Metallo-Carbohedrenes (Ti_8C_{12}, V_8C_{12}) in Solid Form
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The project goal is the synthesis of metallo-carbohedrenes, such as Ti_8C_{12}, in macroscopic amounts. The metallo-carbohedrenes M_8C_{12} with M = V, Nb, Mo, W, Ta, Zr, Hf, Fe have been prepared and analyzed in a variety of gas phase studies and examined extensively through computational studies. However, no metallo-carbohedrene has been isolated in a soluble form that would be amenable to classical chemical manipulation and study. Our work is guided by the premises that we may be able to construct such clusters from small molecular precursors using titanium bound to acetylenic units. We also anticipate that addition of ligands to the core metallo-carbohedrene, M_8C_{12}, to form species such as $M_8C_{12}L_8$, should stabilize the cluster by limiting the possibility of self-association of the bare metallo-carbohedrenes through Ti-Ti bond formation.

The graduate students in my group are continuing to learn how to handle titanium compounds. The group had no prior experience in this area of chemistry. They quickly learned new glove box and Schlenk-line techniques for handling reactive chemicals and have gained valuable experience that will benefit them as they develop their careers. They have learned a considerable amount of chemistry that is new to us, but unfortunately previously reported. Nevertheless, they are continuing to learn and to improve their techniques.

We have put considerable effort into synthesizing our initial target molecule, the heretofore unknown "$Ti^{IV}(CCR)_4$" as well as "$Ti^{III}(CCR)_3$". This work has utilized a variety of acetylenes and acetylene-derived Grignard reagents in reactions with several titanium compounds including $Ti^{IV}Cl_4$, $(\eta^5\text{-}C_5H_5)_2Ti^{IV}(Cl)_2$, $Ti^{III}Cl_3(NMe_3)_2$, and $Ti^{III}Cl_3(THF)_3$. As the reviewers of our proposal correctly anticipated, during our attempts at preparing "$Ti^{IV}(CCR)_4$" and/or "$Ti^{III}(CCR)_3$" we have found many routes to the formation of grey to black powders that do not dissolve in organic solvents and are unpromising for further work or characterization. In this regard the project is teaching us about patience and perseverance.

We have also examined the reactivity of the simple reagent, calcium carbide with several titanium starting materials including $Ti^{IV}Cl_4$ and $Ti^{IV}O_2$. Reactions were run in liquid ammonia at -40 °C. No evidence for the formation of metallo-carbohedrenes has been obtained under the conditions utilized and no tractable compound found so far.

During efforts to utilize $(\eta^5\text{-}C_5H_5)_2Ti^{IV}(Cl)_2$ as a starting material in our acetylenic work, we discovered a new hydrolysis product, $(\eta^5\text{-}C_5H_5)_2Ti^{IV}(Cl)OTi^{IV}(Cl)_2(\eta^5\text{-}C_5H_5)$. We have been able to purify and characterize this material, whose molecular structure as determined by single crystal X-ray diffraction is shown in Figure 1. The compound is an unusual di-titanium complex with an unsymmetrical structure built about a nearly linear Ti-O-Ti core. Remarkably, the compound is stable in the gas phase and amenable to analysis by mass spectrometry. Studies of the chemical reactivity of $(\eta^5\text{-}C_5H_5)_2Ti^{IV}(Cl)OTi^{IV}(Cl)_2(\eta^5\text{-}C_5H_5)$ are in progress.

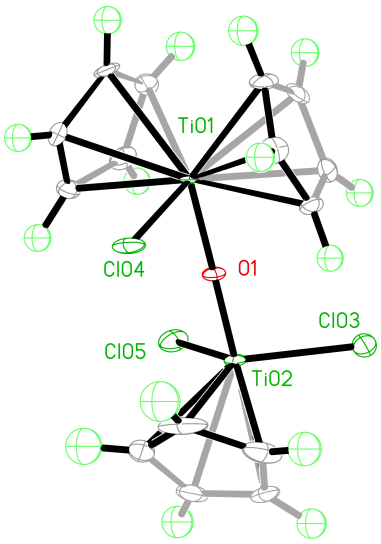

Figure 1. The molecular structure of $(\eta^5\text{-}C_5H_5)_2Ti^{IV}(Cl)OTi^{IV}(Cl)_2(\eta^5\text{-}C_5H_5)$ as determined by single crystal X-ray diffraction.