

## Narrative Progress Report

1. PRF#57188-ND3
2. Project Title: A Modular, Coordination Chemistry Approach to the Isolation of Metallo-Carbohedrenes ( $\text{Ti}_8\text{C}_{12}$ ,  $\text{V}_8\text{C}_{12}$ ) in Solid Form
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Our goal is the synthesis of macroscopic amounts of the metallo-carbohedrene or metacar,  $\text{Ti}_8\text{C}_{12}$ , which has been detected in the gas phase but has never been isolated in solid form. We expect that isolation of this cluster will require addition of external ligands to protect what we expect are reactive titanium sites. We plan to use titanium acetylide coordination complexes as precursors to the desired cluster. The graduate students in my group are learning the fundamentals of titanium chemistry, since none had any experience making metal complexes of titanium. After several missteps, we have settled upon  $\text{Ti}(\text{CCR})_4$  as our initial target. We are also attempting to use bis(trimethylsilyl)acetylene as a precursor for the formation of short chains containing the  $\text{L}_n\text{Ti}(\text{CCL}_{n-1})_m\text{TiCCTiL}_n$  unit where L may be any of a variety of anionic ligands, chloride, alkoxide, alkyl, etc. In this regard, we have focused on the reaction:  $2 \text{TiCl}_4 + \text{Me}_3\text{Si-CC-SiMe}_3 \longrightarrow \text{Cl}_3\text{Ti-CC-TiCl}_3 + 2 \text{Cl-CC-SiMe}_3$ , but have found the desired coupling difficult to achieve. Additionally, to gain experience in preparing and handling complexes of this sort, the graduate students have been synthesizing complexes of the type  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CCR})_2$ , which have been prepared previously.

While learning the rudiments of titanium coordination chemistry, we had the opportunity to explore another route to make  $\text{Ti}_8\text{C}_{12}$ . We were aware that empty cage fullerenes along with endohedral fullerenes,  $\text{Ti}@C_{2n}$ , could be prepared in the electric arc process that volatilizes graphite in a low-pressure helium atmosphere. Although a number of endohedral fullerenes,  $\text{Ti}@C_{2n}$ , have been detected and even isolated by such a process, the literature does not mention whether metcars like  $\text{Ti}_8\text{C}_{12}$  might also be formed in an electric arc fullerene generator. We had access to a functioning fullerene generator and decided that it would be worthwhile to look for the presence of metcars like  $\text{Ti}_8\text{C}_{12}$  in the carbon soot that is produced. Undertaking this project exposed a graduate student to the complexities of fullerene synthesis and extraction, which were entirely new experiences for her.

Graphite rods were packed with  $\text{TiO}_2$  in a 15:1 C:  $\text{TiO}_2$  ratio. Several three rod-burning conditions were tested. The soot from each of the conditions was dissolved in one of four solvents: two were non-coordinating (*o*-dichlorobenzene and carbon disulfide) the other two could ligate the titanium centers of the clusters (acetone, and dimethylsulfoxide). The literature does not indicate a solvent in which a metcar may be soluble. The suspensions of the carbon soot that formed were sonicated for several hours in the solvents and remained in solvent overnight. MALDI spectra for the crude suspensions were obtained by spotting the suspensions directly on the plate; mass spectra were collected in the positive ion mode of detection. The mass spectra showed that a range of fullerenes, largely empty cages formed. However, the diagnostic peaks expected for  $\text{Ti}_8\text{C}_{12}$  in the 528 m/z region were not detected. Indeed the region from 525 to 690 m/z was entirely devoid of peaks. Consequently, we concluded that any soluble form of  $\text{Ti}_8\text{C}_{12}$  was not created in the carbon arc process.

Literature also supports the existence of a zirconium metcar analog,  $\text{Zr}_8\text{C}_{12}$ . We pursued this product using  $\text{ZrO}_2$  in the place of  $\text{TiO}_2$  in the same stoichiometric amounts, but we again could not detect a mass spectral peak for  $\text{Zr}_8\text{C}_{12}$  in the soluble extracts.

Unfortunately, we concluded that the arc process that generated fullerenes was not producing detectable amounts of soluble metcars. However, if the individual metcar molecules associated to form insoluble materials, we would not have detected them using the procedures available to us.