Nitrogen Fixation Utilizing Vanadium Complexes

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Abstract:

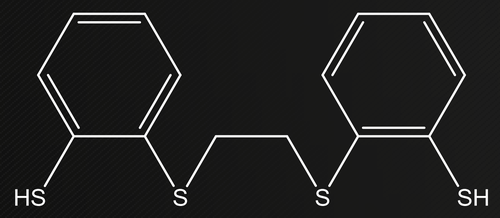
A synthesis of a sulfur supported vanadium complex of (dttd) 2,3,8,9-dibenzo-1,4,7,10-tetrathiadecane(-2) was performed, with complete characterization to follow in the near future. This dttd ligand will be modified to create a more hospitable environment for dinitrogen to react and become reduced to ammonia.

Introduction:

Nitrogen is an important element in the biology of all living things. It is incorporated into DNA, RNA, and proteins, to name a few. However, most of the nitrogen that exists on Earth (and in its atmosphere) is diatomic nitrogen (N_2), which is inert. In order to be used by living creatures, the nitrogen must first be "fixed" into a useable form, such as ammonia. In nature, nitrogen is fixed in the aptly-named nitrogen fixing bacteria, which all contain a variant of the enzyme nitrogenase.

There are four known types of nitrogenase enzymes that are commonly witnessed in bacteria today. Three of these enzymes compose a "classical" trio that are closely related – one based on molybdenum (Mo-nitrogenase), one based on vanadium (V-nitrogenase), and one based on iron only (Fe-only nitrogenase). This experiment focuses on synthetically creating a catalyst which can mimic the effects of V-nitrogenase found in nature.

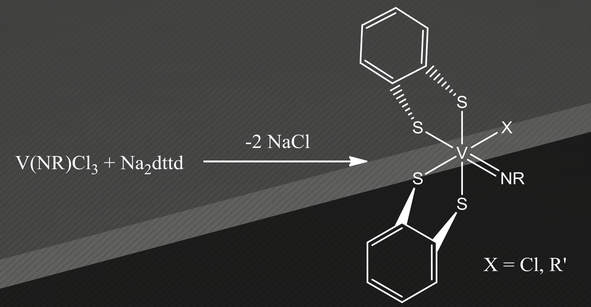
The key to reducing nitrogen using vanadium metal compounds is creating an environment where the vanadium metal atom will be responsive to diatomic nitrogen. The initial ligand used was 2,3,8,9-dibenzo-1,4,7,10-tetrathiadecane(-2), or dttd, shown below.



dttd, the starting ligand

Experimental:

The proposed reaction to create the vanadium catalyst is shown below. This catalyst, once synthesized, will have the coordination environment around the vanadium altered to make it more responsive to diatomic nitrogen.



The starting materials used (Na_2dttd and $VCl_3(THF)_3$) were previously synthesized and stored under nitrogen atmosphere in a Vacuum Atmosphere Company (VAC) dry box. To create the initial complex, 237mg of Na_2dttd and 250mg of $VCl_3(THF)_3$ were added to a flask with a gas adapter and stir bar in the nitrogen dry box. The nitrogen atmosphere in the flask was maintained using nitrogen lines and vacuum lines (for solvents) in a vacuum-gas manifold. Tetrahydrofuran (THF) was added as the solvent for the reaction, and the reaction was kept under ice while it was stirring.

The reaction was run again under similar conditions, except it was run using a two-flask method. The 250mg of $VCl_3(THF)_3$ was added to one flask and dissolved in THF, while 237mg of Na_2dttd was added to a second flask and dissolved in THF. The $VCl_3(THF)_3$ in THF was slowly transferred to the flask containing the Na_2dttd solution while both flasks were under ice. This reaction yielded a brown colored solid, which was characterized by ^{1}H NMR in C_6D_6.

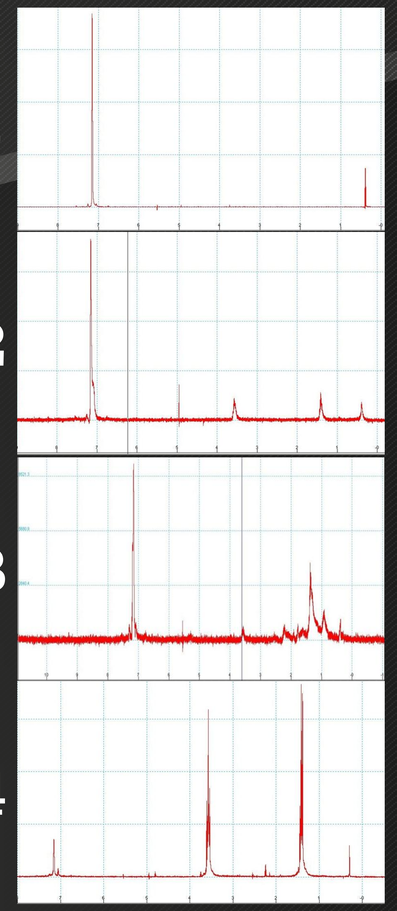
The two-flask method was carried out multiple times, varying the temperature in an attempt to create more product than was indicated during the first run. Multiple ^{1}H NMR spectra were taken of these runs in different solvents to attempt to determine optimum conditions for detection of the product, and the best spectra were selected for use in the results section.

Results:

The ^{1}H NMR spectra on the right correspond to the reactants and products of the one-flask and two-flask reactions.

Spectrum 1 is the ^{1}H NMR of C_6D_6, spectrum 2 is the ^{1}H NMR of $VCl_3(THF)_3$ in C_6D_6, spectrum 3 is the ^{1}H NMR of the one-flask reaction product in C_6D_6, and spectrum 4 is the ^{1}H NMR of the two-flask reaction product in C_6D_6.

The one-flask run did not produce any products that were different from starting materials, as the major peak at δ7.1 was D_6 benzene, and the trio at δ3.5, 1.3, and 0.5 were the result of $VCl_3(THF)_3$. The two-flask reaction showed several small peaks which may indicate the presence of product.



Conclusion:

Although the two-flask reaction ^{1}H NMR spectra indicated the presence of a product in minor peaks, multiple subsequent runs could not reproduce the results. The initial starting materials may have expired in the dry box at some point over the past 16 years if the atmosphere in the box was contaminated, as the bottles containing the dttd and $VCl_3(THF)_3$ were not airtight.

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