

FACULTY RESEARCH GRANT 2009

FINAL REPORT

PROJECT TITLE

**TRANSITION METAL CARBONYL COMPLEXES CONTAINING POLYAROMATIC
DITHIOLATE LIGANDS**

PRINCIPAL INVESTIGATOR

CHARLES A. MEBI

Department of Physical Sciences

STATEMENT OF PROBLEM

This project was aimed at the preparation of transition metal carbonyl complexes containing polyaromatic dithiolate ligands. These compounds are simple organometallic models for the active site of the efficient hydrogen producing enzyme, [Fe-Fe] hydrogenase (**1**). Hence, the complexes (**2**) are potential catalysts for the reduction of proton to molecular hydrogen, a clean alternative to fossil fuels. The development of inexpensive and efficient catalysts for the production of hydrogen is essential for the realization of the hydrogen economy.

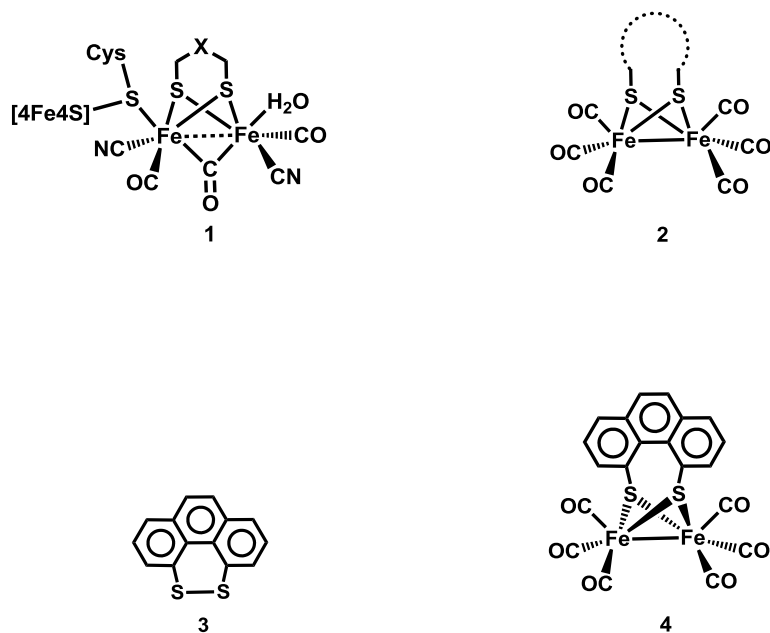
BRIEF REVIEW OF THE RESEARCH PROCEDURE UTILIZED

The preparation of new diironcarbonyl compounds containing polyaromatic dithiolate ligands involved the reaction of polyaromatic disulfide and $\text{Fe}_3(\text{CO})_{12}$ in tetrahydrofuran as solvent using Schlenk line techniques. The structure and electronic properties of the compounds were determined by spectroscopic (Infrared, UV-visible, and Nuclear Magnetic Resonance) methods. The prepared compounds were examined as electrocatalysts for the generation of hydrogen by an electrochemical technique called cyclic voltammetry.

SUMMARY OF FINDINGS

The reaction of phenanthrene-4,5-disulfide (PNT, **3**) with $\text{Fe}_3(\text{CO})_{12}$ have been conducted at room temperature. The product, $[(\text{PNT})\text{Fe}_2(\text{CO})_6]$ **4**, was isolated and characterized by elemental analysis spectroscopic techniques (infrared, UV-visible, and nuclear magnetic resonance), and X-ray crystallography. The Infrared spectrum of $[(\text{PNT})\text{Fe}_2(\text{CO})_6]$ shows three peaks at 2001, 2040 and 2075 cm^{-1} ascribed to terminal metal carbonyl ligands, figure 1. X-ray crystallographic study unequivocally confirms the structure of the complex having a butterfly shape with an Fe-Fe bond distance of 2.5365 Å close to that of the enzyme (2.6 Å). A cyclic voltammetric study on **4** has been

conducted and reveals a reduction peak at -0.9 V and oxidation peak at 1.1 V vs Ag/AgCl. Cyclic voltammograms of **4** in the presence of acetic acid were obtained and indicate the catalytic reduction of proton to molecular hydrogen by **4** at -1.5 V vs Ag/AgCl.



CONCLUSIONS AND RECOMMENDATIONS

The reaction of phenanthrene-4,5-disulfide (PNT) with $\text{Fe}_3(\text{CO})_{12}$ have been accomplished affording the product, $[(\text{PNT})\text{Fe}_2(\text{CO})_6]$. The structure, and electronic properties of $[(\text{PNT})\text{Fe}_2(\text{CO})_6]$ has been examined by spectroscopic techniques and X-ray crystallography. The electrochemical properties of $[(\text{PNT})\text{Fe}_2(\text{CO})_6]$ were determined by cyclic voltammetry in the presence of acetic acid. The results show that $[(\text{PNT})\text{Fe}_2(\text{CO})_6]$ is an effective catalyst for the reduction of proton to molecular hydrogen. With the knowledge gained from this study, we plan to design new molecular systems for more efficient hydrogen production. The results have been submitted for publication in Journal of Inorganic and General Chemistry (see attached article)