AN ABSTRACT OF THE THESIS OF

Kriangsak Khownium for the degree of Master of Science in Chemistry presented on August 11, 2003. Title: Direct Atom Transfer vs. Ring Expansion in Reaction of Rhenium Oxo Complexes with Cyclooctene Epoxides and Episulfides.

Redacted for Privacy

Abstract Approved: _____
Kevin P. Gable

The rhenium (V) complex Tp'ReO_2 (Tp' = hydrido-*tris*-(3,5-dimethylpyrazolyl)borate), generated *in situ* from PPh_3 reduction of Tp'ReO_3, reacts with small ring heterocycles such as epoxides and episulfides. The strained *trans*-cyclooctene ring provides an unusual thermodynamic bias against direct atom transfer, but *trans*-cyclooctene oxide still produces substantial amounts of *trans*-cyclooctene. Episulfides also react under the same conditions. These are more reactive than epoxides and show a greater propensity for direct atom transfer; under catalytic conditions the eventual products are dithiolate complexes. The differences in reaction outcome point to important differences in selectivity for O- vs. S-atom transfer.

The rate constant for *trans*-cyclooctene production was obtained using a parallel reaction model since an epoxide coordinated to rhenium as

the intermediated undergoes direct O-atom transfer to give alkene and $Tp'ReO_3$ and ring expansion to give the diolate. The ratio of diolate/alkene is 2:1. The observed rate constant for ring expansion is $(1.24 \pm 0.03)x10^{-5}$ s^{-1} and the rate constant for direct atom transfer is $(6.02\pm0.02)x10^{-6}$ s^{-1}. *cis*-Cyclooctene showed a higher preference to give alkene (24.5:1) than *trans*-cyclooctene. The observed rate constant for direct atom transfer is 5.07 x 10^{-5} s^{-1} and the rate constant for ring expansion is 2.07 x 10^{-6} s^{-1}.

Desulfidation of *trans*- and *cis*-cyclooctene showed the reaction proceeds faster than deoxygenation to give the thermally stable dithiodiolate species and alkene at 75 °C. *cis*-Cyclooctene episulfide gave a higher alkene/diolate ratio (10:1) than *trans*-episulfide (5:1).

However, monothiodiolate formation in a phosphine free system (Tp'ReO(OH)(EtOH) as a $Tp'ReO_2$ source) was observed, in addition to dithiodiolate. Tp'ReOS or $Tp'O_2$ were suggested to serve as S-atom transfer agents. $Tp'ReO_3$ was also detected in the phosphine free system by formation of diolate from excess *trans*-cyclooctene

Combining the kinetic and thermodynamic data, the order of reactivity of substrates is: *cis*-cyclooctene episulfide > *trans*-cyclooctene episulfide > *cis*-cyclooctene oxide> *trans*-cyclooctene oxide.

DIRECT ATOM TRANSFER VS. RING EXPANSION IN REACTION OF RHENIUM OXO COMPLEXES WITH CYCLOOCTENE EPOXIDES AND EPISULFIDES

by
Kriangsak Khownium

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

Presented August 11, 2003
Commencement June 2004

Master of Science thesis of Kriangsak Khownium presented on August 11, 2003.

APPROVED:

Redacted for Privacy

Major Professor, representing Chemistry

Redacted for Privacy

Head of Department of Chemistry

Redacted for Privacy

Dean of Graduate School

I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

Redacted for Privacy

Kriangsak Khownium, Author

ACKNOWLEDGEMENTS

I certify that this thesis, and the research to which it refers, are the product of my own works and that any ideas or quotations from the work of other people, published or otherwise, are fully acknowledge in accordance with the standard referencing practices of the discipline. I deeply acknowledge Prof. Kevin Gable for all his support, guidance and encouragement as my advisor to make this thesis possible. I would like to thank my committee members Prof. Max Deinzer, Prof. Douglas Keszler and Prof. John Wager for their support. I also would like to thank to Rodger Kohnert for his support on NMR works, Dr. Christine Pastorek for her support on GC-MS work, and also Jeff Morre for his support on MS work. I am indebted to Dr. Eric Brown, Pitak Chuwong, Punlop Kuntiyong, and Sorasaree Tonsiengsom for their support and friendship. I also would like to express my gratitude to the Development and Promotion of Science and Technology Talents Project, DPST, of the Royal Thai Government for financial support through DPST scholarship. I also owe much gratitude to the OSU Chemistry Department for financial support through teaching assistantships, my advisor for financial support through research assistantships, and also the National Science Foundation, NSF, for research grant. Finally, I would like to thank my friends and family for their friendship and support.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

LIST OF FIGURES

LIST OF FIGURES (Continued)

Figure Page

LIST OF FIGURES (Continued)

LIST OF TABLES

LIST OF APPENDIX FIGURES

This is dedicated to my family, Khom and Nhoonom Khownium, my sister Nheungruthai Khownium and all of my dear friends.

DIRECT ATOM TRANSFER VS. RING EXPANSION IN REACTION OF RHENIUM OXO COMPLEXES WITH CYCLOOCTENE EPOXIDES AND EPISULFIDES

Chapter 1. Introduction and Literature Review

1.1 Metal Mediated Oxygen- and Sulfur- Atom Transfer

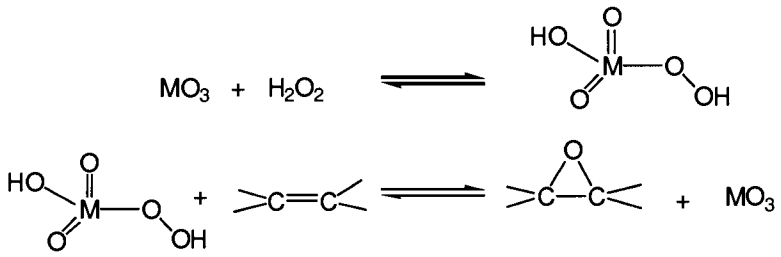
Transition metal catalysts are exquisitely exploited in many applications[1]. For example, products ranging from pharmaceuticals to pesticides are produced catalytically; our bodies are operated by catalysts, many of which are metalloenzymes[2].

The chemistry of O- and S- atom transfers between a metal center and an organic substrate have recently received attention because of their importance in biological systems[3] and in catalytic reactions in the petroleum[4] and commodity chemical industries[5]. Transition metal complexes have been used in the stoichiometric and catalytic oxidation of organic compounds. An important industrial process based on $PdCl_2$ and alkene forming a Pd-alkene complex is the Wacker reaction[6], a catalytic method for conversion of ethylene to acetaldehyde. Water is added to the Pd-activated alkene to give acetaldehyde and Pd. Pd is reoxidized to Pd^{2+} by using the co-reagents $CuCl_2$ and O_2.

Formation of C-O bonds can be achieved by using oxo metal complexes that can utilize a variety of oxygen sources for oxidation processes under mild conditions. High oxidation state oxo compounds, such as V_2O_5[7], RuO_4[8], MnO_2[9], and OsO_4[10] have been used as catalysts for the conversion of olefins to epoxides. This can lead to forming two stereogenic carbons in one step, and the epoxide product can be converted to a variety of other useful compounds.

Vanadium(V)oxide and other acidic metal oxides (Cr, Mo, Nb, Ta, Th, V, W, Zr) catalyze the reactions of hydrogen peroxide via forming oxo or peroxometal complexes (Figure 1.1)[11].

Figure 1.1: Epoxidation Catalytic Cycle

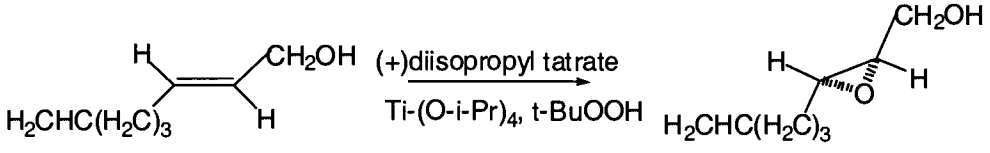


Transition metal complexes can exert the following four possible effects[12]: (1) Activation of reacting species by coordination, which offers alternative pathways with lower Gibbs free energies of activation. Examples are forming oxo or peroxo metal complexes to avoid spin forbidden reactions of dioxygen, (2) structural selectivity effect due to steric and (or)

electronic factors; (3) providing a pathway for inner-sphere or outer-sphere electron transport in the case of 2-centered redox catalysis, as in the catalysis by $PdCl_2$-$CuCl_2$ in oxidation of ethylene to acetaldehyde; and (4) providing a pathway for coupled electron and energy transport. This last effect is important in electro-catalysis and photo-catalysis, as well as in ATP catalysis of some biological redox reactions.

In particular, the Sharpless asymmetric epoxidation[13] provides enantioselective product control through the use of either (+) or (-) tartrate ester. (Figure 1.2)

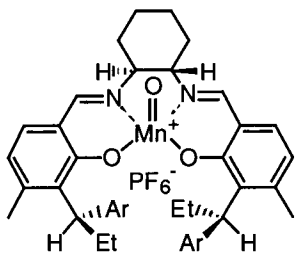
Figure 1.2: Sharpless Asymmetric Epoxidation



The enantioselective oxidation process is believed to involve a titanium complex in which the chirality of the tartrate ester controls the orientation of allylic alcohol. During the transition state, the oxygen atom from peroxide is transferred to the double bond. This reaction can be done with catalytic amounts of titanium isopropoxide and the tartrate ester. In addition, by using molecular sieves to remove water, both the rate and enantioselectivity of the reaction are enhanced.

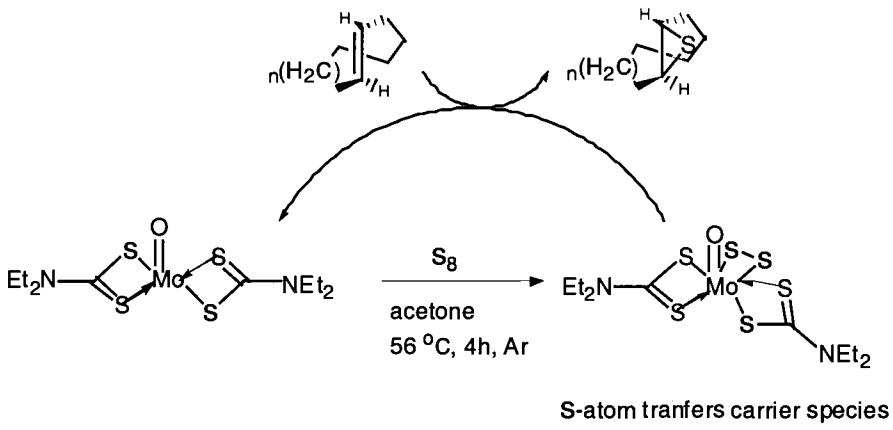
In 1990, Jacobson reported unfunctionalized alkenes could be epoxidized with high enantioselectivities using chiral manganese(III) salens[14] (Figure 1.3) in combination with a stoichiometric amount of a simple oxidant such as aqueous hypochlorite, iodosylarenes and amine *N*-oxides. For example, asymmetric epoxidation of *cis*-β-methylstyrene by commercial bleach (NaOCl) afforded (*R,S*)-*cis*-β-methylstyrene oxide in 87 % yield and 82% ee.

Figure 1.3: Jacobsen-Suzuki asymmetric epoxidation catalyst



For S-atom transfer, to date little is known about how the catalytic S-atom transfer compares to O-atom transfer. Adam[15] and co-workers developed a molybdenum oxo complex that efficiently catalyzes the sulfur atom transfer to alkenes to make their episulfides. Stereoselective reaction of trans-cyclooctene were obtained in high yield from catalytic episulfidation by elemental sulfur catalyzed by $Mo(O)(S_2)(S_2CNEt_2)_2$ as shown in Figure 1.4.

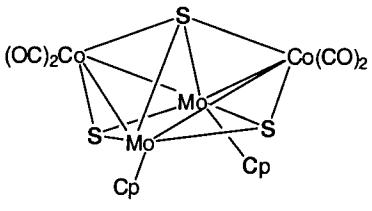
Figure 1.4: Episulfidation Catalyzed by Molybdenum Complex



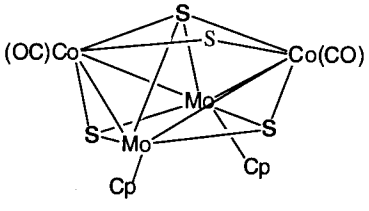
In contrast to forming C-S bonds, molybdenum[16] is used in hydrodesulfurization (HDS) catalysts for treating heavy crude oil in the petroleum industry. The catalyst typically consists of small clusters of molybdenum disulfide with low concentrations of cobalt or nickel additives to promote chemical reaction.

Figure 1.5: Mo/Co/S Cluster and an Desulfurization Reaction

a) Mo/Co/S cluster

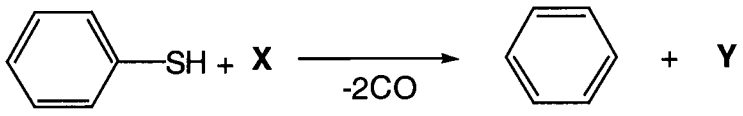


X



Y

b) Desulfurization of ArSH by Mo/Co/S Cluster



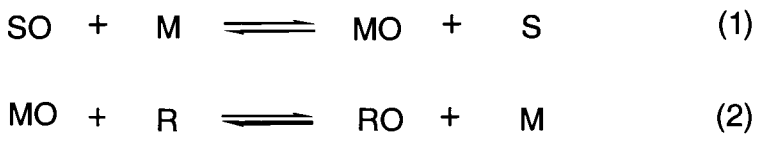
Clusters **X** and **Y** are used as models for the "CoMoS" phase in for study of HDS catalysts. The nature of these complexes is still under investigation and has been the subject of interest for nearly 30 years.

1.2 Electronic Structure of Metal Terminal Oxo Complexes

Many catalytic O-atom transfer reactions can be described[18] by Figure 1.6. Metal oxidation and substrate reduction will be enhanced by a strongly reducing metal center, a strong M-O bond, and an oxygen atom donor with a relatively weak X-O bond. The oxygen atom donor (**SO**), such as O_2, H_2O_2, PhIO, *m*-$ClC_6H_4CO_3H$, *t*-BuOOH, Me_2SO, epoxides or amine *N*-oxides, donates an oxygen atom to the transition metal complex, **M**, forming either an oxo- or peroxometal complex, **MO**. The oxo- or peroxometal complex can either transfer the newly acquired oxygen atom back to **S** or it can transfer the oxygen atom to the oxygen atom acceptor **R**. The most common oxygen atom acceptors are olefins, sulfides, tertiary

phosphines and phosphates whose basicities or nucleophilicities usually increase with the number of alkyl groups.

Figure 1.6: Catalytic O-atom Transfer Reaction Cycle

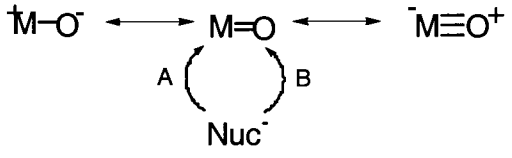


Oxometal groups[18] which have been structurally defined by X-ray diffraction are MO, linear MO_2, bent MO_2 and pyramidal MO_3. In general, metal oxo bonds have length of 1.6-1.8 Å and stretching frequency in the range 850-1100 cm^{-1}, both properties establishing their multiple-bond character. Metal-oxo bonds are usually designated as M=O, with recognition that bond order may vary depending on the d^n configuration.

The reactivity of an oxometal can be described by resonance forms which show that each canonical form will describe different reactivity for the metal and oxygen. Typically for metal oxides the LUMO is localized on the metal, which is subject to attack and coordination by nucleophiles[19]. However, polarization of the oxo group can lead oxygen to be subjected to attack by nucleophiles as well. This can be ascribed to lowering of the

energy of the LUMO orbital, π^*. The LUMO can attain more oxygen character, or the metal can make the oxygen electrophilic[20].

Figure 1.7: Resonance Forms of Metal Oxide



1.3 C-O and C-S Cleavage Mediated By Cp*Rhenium Oxo Complex

Metal oxo complexes mediate cleavage of C-O bonds with concomitant formation of one or more new M=O bonds. This can be used in converting biomass to alkenes with high complexity. Biomass is the most abundant source of carbon but most parts are composed of carbohydrates which are often too oxygen-rich to be of any direct value without extensive modification. In addition, selective removal of oxygen can retain stereocenters while reducing structural complexity[21].

The chemistry of C-S bond cleavage can be exploited in hydrodesulfurization in large scale industrial processes to remove sulfur from petroleum via hydrogenolysis.

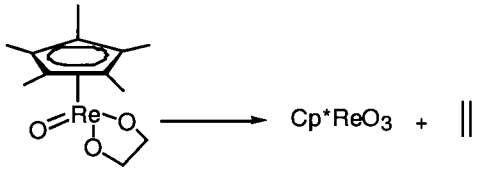
$$R\text{-}S\text{-}R + 2H_2 \xrightarrow{MS_n\ catalyst} 2RH + H_2S$$

Desufurization in this process is catalyzed by metal sulfides, typically MoS_x/CoS_y, but sulfides of rhenium, ruthenium, and other metals are even more active[23]. Both organometallic and inorganic systems have been studied as homogeneous models for HDS. For instance, the complex species Cp^*_2TiS[24], Cp_2MoS_4[25], and $(PR_3)_6Rh_2S_2^{2+}$ [(26)] have been known to activate H_2 in this process.

In principle, molybdenum sulfides are the major HDS catalysts; the reactivity of thiomolydenates such as MoS_4^{2-} have been of particular interest to understand the catalytic cycle. Unfortunately, thiomolybdenates display little or no affinity for alkenes, dihydrogen, or the organosulfur species found in petroleum[27]. In contrast, ReS_4^-, which is isoelectronic and isostructural with MoS_4^{2-}, reacts with alkenes and alkynes to produce the tetrahedral d^2 adducts $ReS_2(S_2alkene)^-$ [(28)]. Recent interest in rhenium oxo chemistry highlights the structural diversity of $LReO_n$ sytems and the practical possibility for adjusting overall thermodynamics through structural modifications of the organorhenium compound.

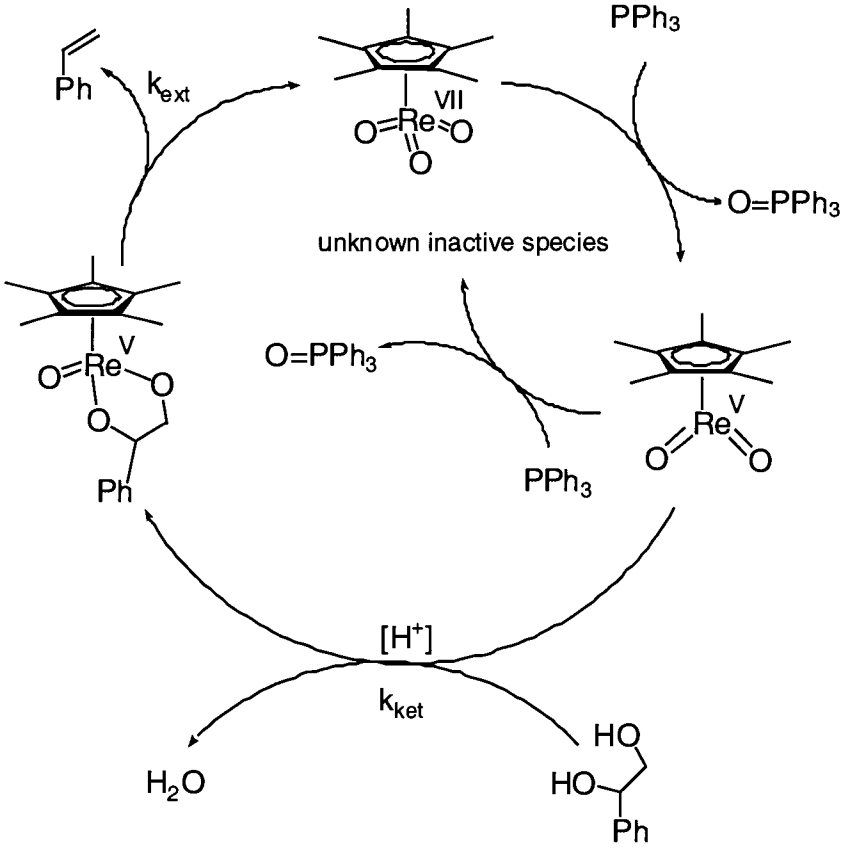
The exploration of catalytic rhenium mediated O-atom transfer from diols and polyols to alkenes and allylic alcohols was recognized after the report of alkene extrusion from rhenium(VII)diolate complexes by Herrmann in 1987[29] (Figure 1.8). The diolate complex was observed to cyclorevert to Cp^*ReO_3 (Cp^* = pentamethylcyclopentadienyl) and ethylene in refluxing toluene.

Figure 1.8: Alkene Extrusion



In particular, catalytic deoxygenation of conversion of vicinal diols or polyols to alkene had been studied by Cook and Andrews in 1996 (Figure1.9)[30].

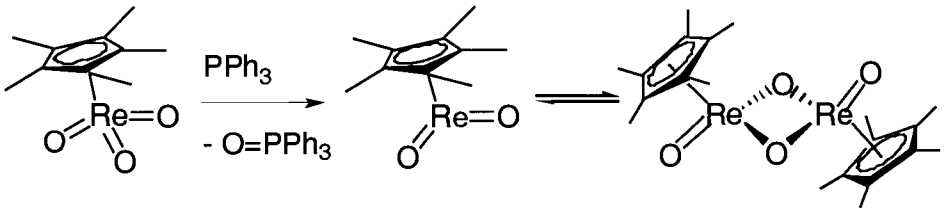
Fig 1.9: Catalytic Cycle of Cp^*ReO_3



The catalytic cycle involves *in situ* reduction of Cp^*ReO_3 with triphenylphosphine. When the rhenium diolate complex cycloreverts it gives alkene and Cp^*ReO_3 which is reduced and returned to the deoxygenation catalytic cycle. However, the catalytic cycle is deactivated by forming an unknown species. The result is low turnover numbers ranging from 1 to 60.

The stoichiometric reduction of Cp^*ReO_3 with oxophilic PPh_3 results in the formation of the bridging oxo dimer $(Cp^*ReO)_2(\mu\text{-}O)_2$ (Figure 1.10)[31]. Fragmentation of the dimer to the reactive monomer, Cp^*ReO_2, was observable by both NMR and UV-vis spectroscopy[32].

Figure 1.10: Dimerization of Cp^*ReO_2

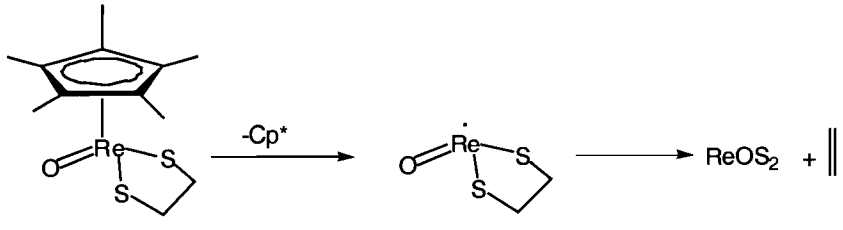


A deoxygenation process for epoxides was developed using catalytic amounts of Cp^*ReO_3[33]. The catalytic cycle is similar to the deoxygenation process for diols. Again, low turnover numbers were observed for each of the epoxides; this was attributed to formation of a tetranuclear cluster that was unreactive to epoxides; This originated from conproportionation of

reduced and oxidized intermediates. The crystal structure of the cluster was elucidated by X-ray crystallography and exhibited a unique IR peak at 736 cm^{-1}. Increasing the concentration of triphenylphosphine led to improved conversion from <5% to 50% by reducing any amount of Cp^*ReO_3 and preventing Cp^*ReO_3 from conproportionating with Cp^*ReO_2.

For a sulfur analog study, cycloreversion of Cp*rhenium(V)ethane dithiodiolate was reported by Herrmann[34]. The dithiodiolate analogs were more stable than diolate; however, on heating to 200 °C over 30 minutes a quantitative production of ethylene was observed (though none of the rhenium species was characterized). There are two possibilities to generate ethylene: (1) in the cycloreversion process or (2) from multi step fragmentation(Figure 1.11).

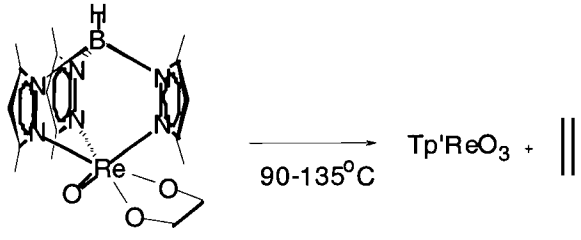
Figure 1.11: Multi Step Fragmentation of Cp*Rhenium Ethanedithidiolate



1.4 C-O and C-S Cleavage Mediated By Tp'Rhenium Oxo Complex

The sterically bulkier Tp' ligand (Tp'=hydrido-tris-(3,4-dimethyl pyrazoyl)borate) was developed and known as a "cyclopentadienyl equivalent because it is anionic, 6 electron donor[35]. Because of its steric bulk, it was predicted to suppress formation of the dimeric bridged oxo compound $[(LReO)_2(\mu\text{-}O)_2]$, but it should have similar chemistry such as cycloreversion. In 1999, Gable and co workers[36] reported that Tp'rhenium(V) diolates also cyclorevert stereoselectively to form $Tp'ReO_3$ and alkenes (Figure 1.12).

Figure 1.12: Cycloreversion of Tp'Rhenium Diolate



In contrast to diolate chemistry, Gable and Chuawong[37] reported the high thermal stability of Tp'Re(V) ethanedithiodiolate which is unlike the corresponding Tp'Re(V)ethanediolate. This dithiodiolate was heated at 120 °C in benzene or toluene for at least one week. No alkene or new rhenium

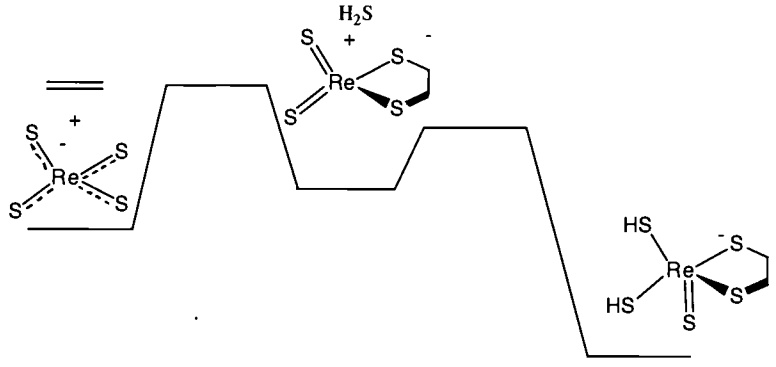
compound was observed. The barrier for cycloreversion was ascribed to thermodynamic stability of Tp'Re(V)ethanedithiodiolate by comparison of calculated reaction energies based on DFT calculations performed at the B3LYP/LACVP** level. The analysis reveals that substitution of each sulfur raises the ΔE_{rxn} for alkene extrusion by about 10 kcal/mol.

1.5 Binding of alkene to Tetrathioperrhenate Anion ($ReS4^-$) and Influenece of Hydrodensulfide and Thiols

Tetrathioperrhenate anion, ReS_4^-, is isoelectronic[38] with OsO_4 or MoS_4^{2-} and it react with alkenes. Rauchfuss reported in 1999 that ReS_4^- reversibly binds with alkenes[39]. Thermodynamic parameters of binding for norbonene was obtained by evaluating K_{eq} over the range of 5-50 °C, ΔH^o= -12.67 kcal-mol^{-1} and ΔS^o= -23.44 cal-mol^{-1}K^{-1}. The binding of ReS_4^- to norbornene appeared to be a favorable process due to high equilibrium constant observed at 23 °C in acetonitile.

The influence of hydrogen sulfide and thiols on the binding of alkenes to ReS_4^- was also measured. The $Re(S)(S_2)(alkene)(SH)_2^-$ derivatives were the product . The qualitative reaction coordinate in which ethylene was used as alkene is shown in Figure 1.13.

Figure 1.13: Qualitative Reaction Coordinate of ReS_4^- , Hydrogen Sulfide, and Ethylene



The first step was reported to be favored with high equilibrium constant. The second step is even more favorable which can explain by the spectator sulfido effect[40]," Addition of RSH across a Re=S bond provides the very highly stabilized $X_4Re{=}S$ species".

1.6 Direct Atom Transfer vs. Ring Expansion

In 1999, Gable and Brown reported epoxides can be subjected to catalytic O-atom transfer[41] by a reduced rhenium species, $Tp'ReO_2$, generating *in situ* by reduction of $Tp'ReO_3$ using triphenylphosphine or triethylphosphite at 75-105 °C. *cis*-Epoxides react faster than *trans*-epoxides, and terminal alkene epoxides proceed faster than internal alkene epoxides suggesting the reaction is governed by steric issues. Alkyl substituents slow the reaction in comparison with aryl groups. The choice of

functional groups also can interfere with the reaction, as in the presence of a nitro group a conversion of epoxide to alkene was low.

A linear free energy relationship study[41] of a series of *para*-substitued styrene oxides, as substrates in a Hammett study, showed electron donors had a $\rho = -1.28$, while electron-withdrawing groups had a $\rho = +0.52$ which results in an upward V-shaped Hammet plot. It indicates of a change in mechanism or at least two competing pathways.

Saturation kinetics were reported[42] in deoxygenation of *cis*-stilbene oxide and styrene oxide with $Tp'ReO_3/PPh_3$. From an observed rate versus concentration plot at a constant concentration of $Tp'ReO_3$, the reaction rate increased with increasing epoxide concentration until a maximum rate was reached. This kinetic behavior was attributed to enzymology model which is described by Michaelis-Menton equation (Figure 1.14).

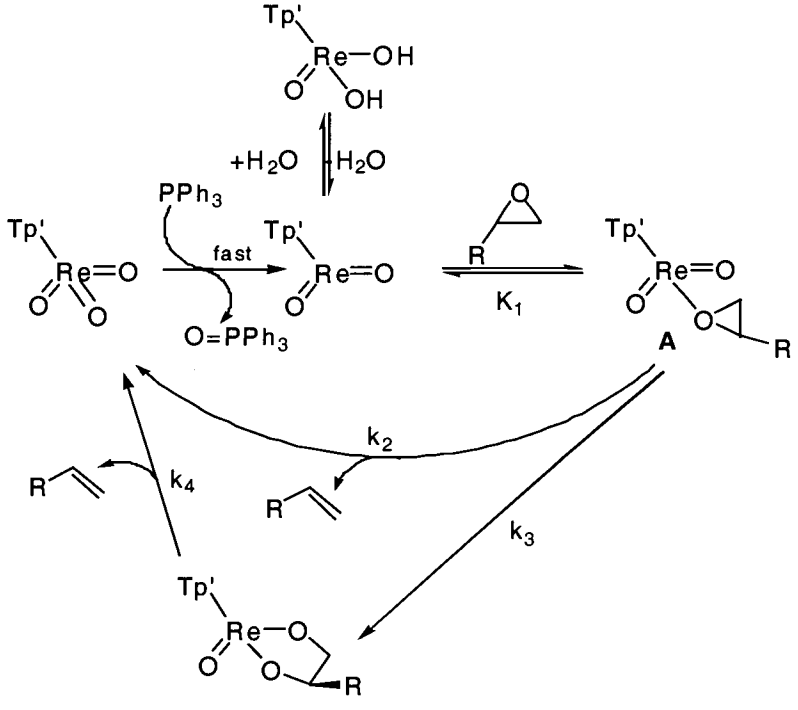
Figure. 1.14: Michaelis-Menton Enzymatic Model

$$E + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} E{\bullet}S \xrightarrow[\text{rate-determining step}]{k_3} E + P$$

$$\frac{d[P]}{dt} = \frac{k_3 [E_o] [S]}{K_m + [S]} \qquad K_m = (k_3 + k_2)/k_1$$

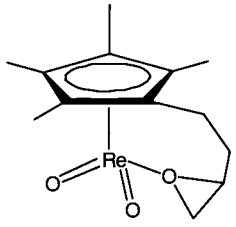
Since metastable diolates were obtained which cyclorevert to $Tp'ReO_3$ and alkene with retention of stereochemistry, a ring expansion needs to part of mechanism. In the meantime, an initial "burst" for *cis*-stilbene formation was also observed. The alkene/diolate ratio was 4.4 after six minutes at 75°C; even though cycloreversion of diolate is slow, k= 4.62×10^{-7} M/s. This rate constant was too slow to explain the observed rate of alkene production under catalytic conditions. Thus another pathway must be direct O-atom transfer. Deoxygenation was proposed[43] as shown in Figure 1.15.

Figure 1.15: Deoxygenation Catalytic Cycle



A coordinated tethered epoxide rhenium complex, 3,4-epoxy-1-butyltetramethylcyclopentadienyltrioxorhenium(VII)[44], was synthesized by the Gable group in 2003. This compound confirms the existence of **A** during the reaction.

Figure 1.16: Coordinated Tethered Epoxide Rhenium Complex

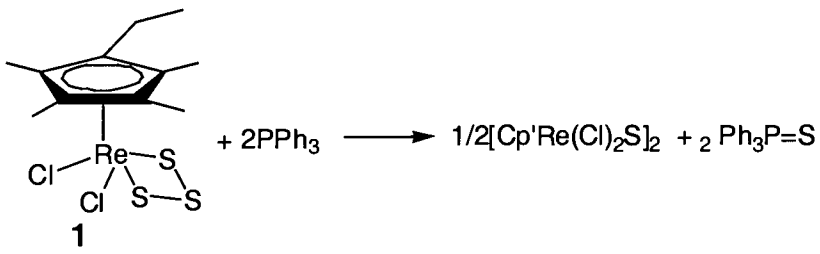


1.7 Rhenium Terminal-Sulfido Complexs

The rhenium terminal sulfido group is of particular interest because of the potential for comparing reactivity and electronic structures with a range of multiply bonded terminal ligands from group 14 through 16. Rakowski-Dubois[45] and coworkers reported the synthesis and reactivity of Cp'Re=S (Cp* = 1-ethyl-tetaramethylcyclopentadienyl) derivatives including reactivity of each species in 2003. Rapid abstraction of two sulfur atoms with only half of the rhenium starting material consumed to gave η^2-disulfide ligand $Cp'ReCl_2(S_2)$ from $Cp'Re(\eta^2\text{-}S_3)Cl_2$ and 1 equivalent of triphenylphosphine. A sulfur-free complex, $Cp'ReCl_2$, was obtained when

more than 2 equivalent of phosphine reagent were used. The dimer $[Cp'ReCl_2S]_2$ was obtained with 1.8 equiv of PPh_3 as shown in Figure 1.17.

Figure 1.17 Reaction of $Cp'Re(\eta^2\text{-}S_3)Cl_2$ with PPh_3



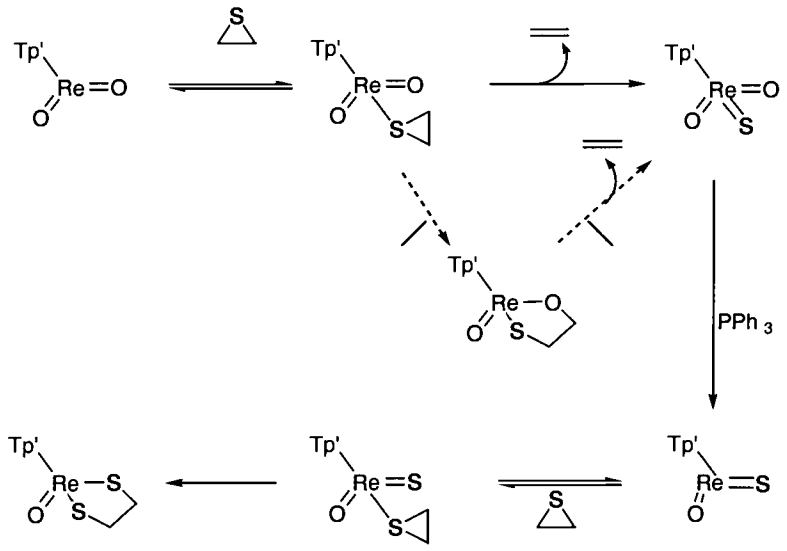
1

In a similar manner, a terminal sulfido ligand complex, $Cp'Re(S)(S_2)$ **2** ,was obtained 30 % yield by reacting **1** with bis(trimethylsilyl)sulfide. In addition, $Cp'Re(S_3)(S_2)$, **3** was formed in this reaction. The reaction of **3** with 2 equivalent of PPh_3 gave **2** and $Ph_3P{=}S$ in a rapid reaction. Complex **2** was used to compare the relative reactivities and electrochemical behavior with the oxo analogue, $Cp'Re(O)(SC_2H_4S)$, **4**. Both compounds are stable in air, when **2** was reacted with 5-6 equivalent of water in toluene-d_8 at 60 °C for 24 h, 40% of **2** was converted to **4**. The cyclic voltammograms of these oxo and sulfido species showed the sulfido complex is both easier to reduce and easier to oxidized than the oxo analog. This results are consistent with Parkin's report[46] that the M=S group is more reactive than M=O due to the weaker π-donor ability of S^{-2}.

1.8 Desulfidation Catalytic Cycle Mediated by Rhenium Oxo Complex

Desulfidation of an episulfide mediated by a Tp'rhenium oxo complex is analogous to deoxygenation of epoxide. Chuawong reported a 30% yield of Tp'Re(V)ethanedithiodiolate was obtained as a product from reaction of ethylene episulfide with $Tp'ReO_3/PPh_3$ at room temperature[47]. Since mono- and dithiodiolate complexes were shown to be thermally stable (no cycloreversion to alkene) for more than a week at 120°C, then the direct S-atom transfer from the episulfide must occur at some point to get to the observed dithiodiolate. The proposed mechanism[47] is shown in Figure 1.18.

Figure 1.18: Catalytic Cycle of Desulfurization



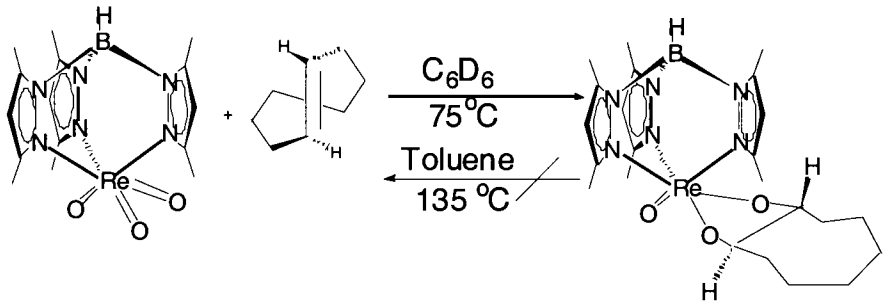
However, it seems unusual that the system switches from selective S-atom transfer (first step) to selective ring expansion (last step). This mechanism also requires selectivity in atom transfer to PPh_3.

1.9 Conclusion of the Literature Review and Research Goals

A number of O- and S- atom transfer catalysts were developed for industry and academic purposes. $Tp'ReO_3$ was developed to be used in the deoxygenation process for epoxides leading to retention of the stereochemistry in the alkene product. The catalytic cycle was reported by Gable and Brown showed that direct atom transfer and ring expansion are competing in this deoxygenation cycle mediated by $Tp'ReO_3$; however, there is some need to get more insight the proposed mechanism.

In this study we first attempted to determine whether a strained epoxide could allow measurement of rate constants for individual processes involved in deoxygenation mediated by rhenium oxo complexes. Early indications of Gable's work appeared to lend weight to our hypothesis that *trans*-cyclooctene, a strained alkene, thermodynamically favors formation of a *trans*-cyclooctane diolate[48] which is stable to a cycloreversion in toluene at 135 °C.

Figure 1.19: Thermodynamically Favored of *trans*-Cyclooctane Diolate



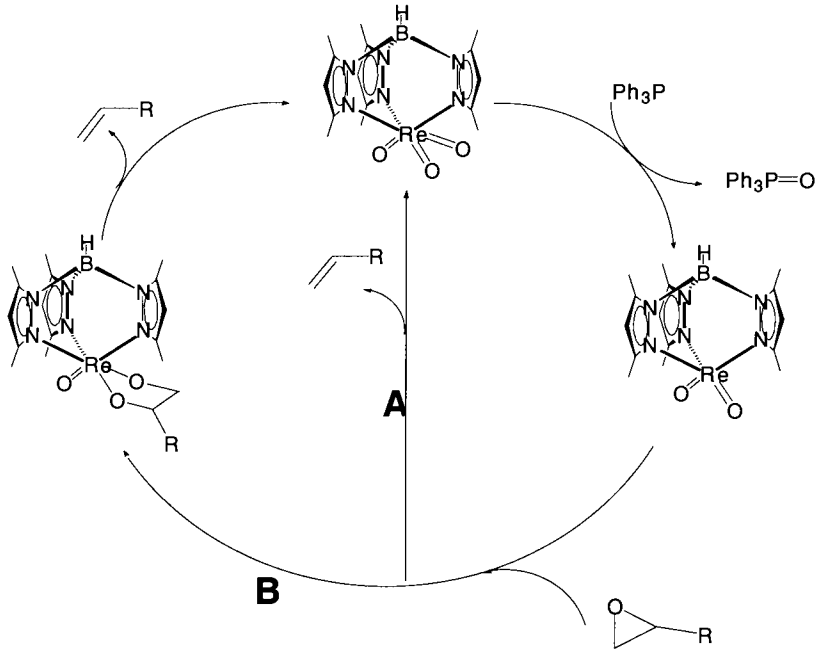
A second challenge was based on the first, to see the impact of sulfur for oxygen substitution on product, rate and selectivity. We expected to observe similar chemistry by using cyclooctene episulfide, as using ethylene episulfide. We expected that the *trans*-cyclooctene episulfide in particular could illustrate atom transfer versus ring expansion selectivity for the sulfur analogs.

Chapter 2. Results and Discussion

Given the interest in developing deoxygenation catalysts, numerous reagents are known to deoxygenate epoxides[49]. One example, the low valent tungsten halide derived from WCl_6, is used to convert epoxides to olefins; in some cases chlorohydrins are formed as by-products and limited stereoselectivity for acyclic di- and tri-substitued epoxides is seen[50]. Stoichiometric amounts of tungsten are required. The development of a catalytically deoxygenating species would be attractive.

A deoxygenation process mediated by rhenium oxo complexes was developed by the Gable group. A catalytic cycle for deoxygenation was proposed in the system by which Tp'ReO_3/PPh_3 (Tp'= hydrido-*tris*-(3,5-dimethyl pyrazoyl)borate) reacts with epoxides (Figure 2.1). O-atom transfer was observed to occur via two distinct processes: (1) a ring expansion mechanism to form a metastable diolate intermediate which cycloreverts to alkene and Tp'ReO_3, and (2) a direct atom transfer mechanism to form alkene and Tp'ReO_3.

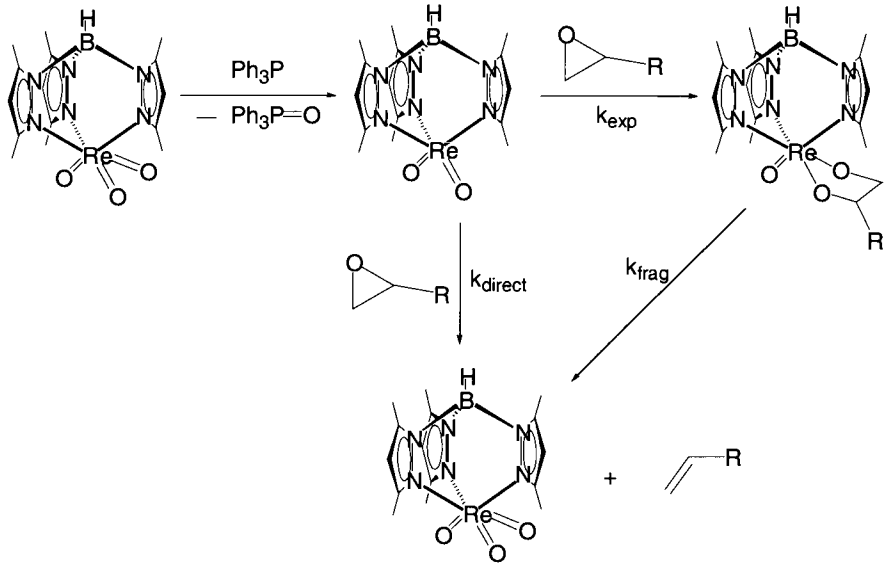
Figure 2.1: Catalytic Cycle of Deoxygenation



2.1 Independent Kinetic Measurement

To answer questions on the selectivity for each process, we need to know reaction rates of these processes (Figure 2.2).

Figure 2.2: Direct Atom Transfer VS Ring Expansion



If we can measure the rate of ring expansion directly, then we could infer from selectivity ratios the rate of direct atom transfer. It was previously known that Tp'Re(O)(*trans*-cyclooctane-1,2-diolate) is thermodynamically favored and would not cyclorevert to give *trans*-cyclooctene (Figure 1.19).

Therefore, we set out to discover whether thermodynamically blocking the diolate-to-alkene reaction allows measurement of k_{exp}, k_{frag}, and k_{direct}.

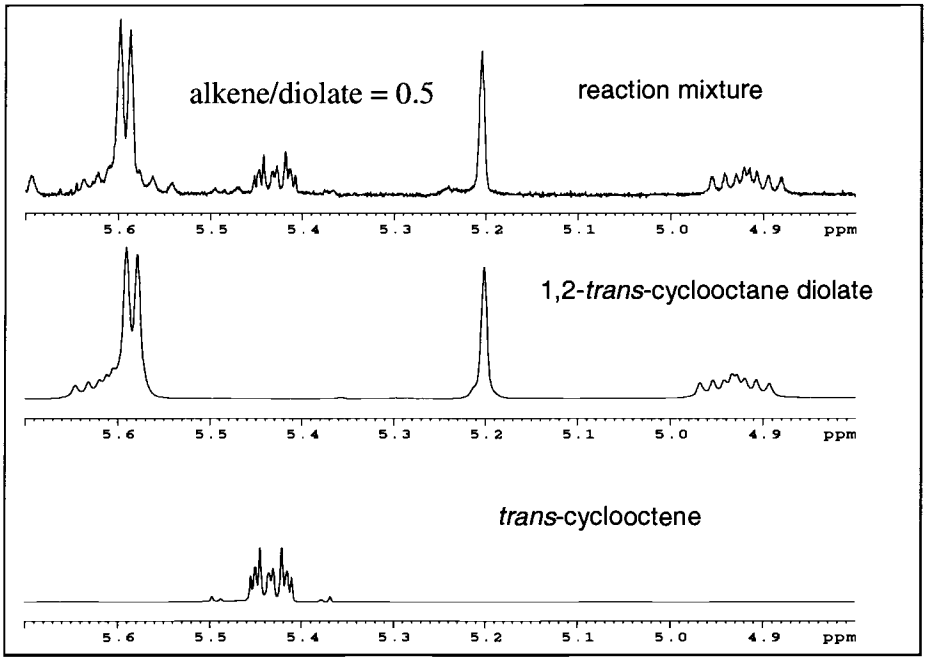
Reaction of insoluble solid $Tp'ReO_3$ with PPh_3 in C_6D_6 at 75 °C leads to formation of soluble $Tp'ReO_2$. This reacts with *trans*-cyclooctene oxide to form thermally stable *trans*-cyclooctane diolate with C_1 symmetry. Stereoselective formation of *trans*-cyclooctene was also observed (alkene/diolate = 0.5) although 1,2-diolate is thermodynamically favored.

$Tp'ReO_3$ was previously shown to react with *trans*-cyclooctene to form the diolate[48].

Deoxygenation of *trans*-cyclooctene oxide was followed in deuterated benzene at 75 °C by ^1H NMR under pseudo-first order kinetic conditions: epoxide:PPh_3:$Tp'ReO_3$ = 5:3:1. Anisole or tetramethylsilane were used as internal integration standards. The sample tube was periodically removed and cooled to 25°C and the ^1H NMR spectrum was collected. The rate of ring expansion was estimated at different concentrations of $Tp'ReO_3$.

The ^1H NMR spectrum of 1,2-diolate shows characteristic peaks of carbinolic protons on the cyclooctane ring at 4.97 ppm and 5.68 ppm in d_6-benzene(Figure 2.3). *trans*-Cyclooctene has a distinct multiplet at 5.43 ppm.

Figure 2.3: Spectra of Pure *trans*-cyclooctane diolate and reaction mixture



Product diolate formation was observed after heating a sample for 6h at 75 °C. The pseudo-first order rate constants for *trans*-cyclooctene oxide deoxygenation at 75 °C were obtained at different epoxide concentrations: 0.0573 mM, 0.1146 mM, 0.1688 mM, 0.2256mM, and 0.6783 mM which ratio to 0.009 or 0.011 mM Tp'ReO_3 at 1:5, 1:10, 1:15, 1:20, and 1:60 in order. The psuedo-first order rate law is given by:

For reaction $A \longrightarrow P$

Rate law $-d[A]/dt = k_{obs}[A]$; Integrated rate law $\ln[A]_t - \ln[A]_0 = -k_{obs}t$

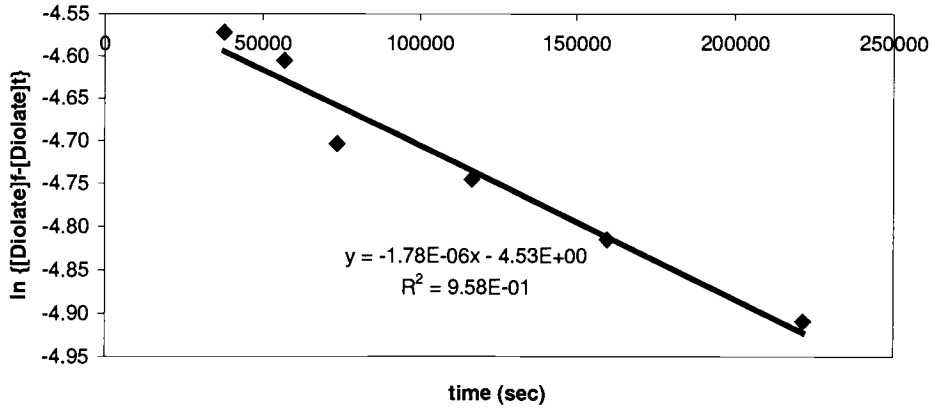
And $k_{obs} = k[\text{epoxide}]$

The concentration of $Tp'ReO_3$, $[A]_t$, is followed indirectly by measurement of the diolate signal at 4.97 ppm vs. anisole signal at 3.30 ppm. We assume $[Tp'ReO_3] = [Re]_{Total}$- [Diolate] and actually, the reactant we worry about is $Tp'ReO_2$; if the reduction is fast, $[Tp'ReO_2]_t = [Re]_{Total}$- [Diolate]. The data did not show a good linear behavior as indicated by a low r^2 value (Figure 2.4).

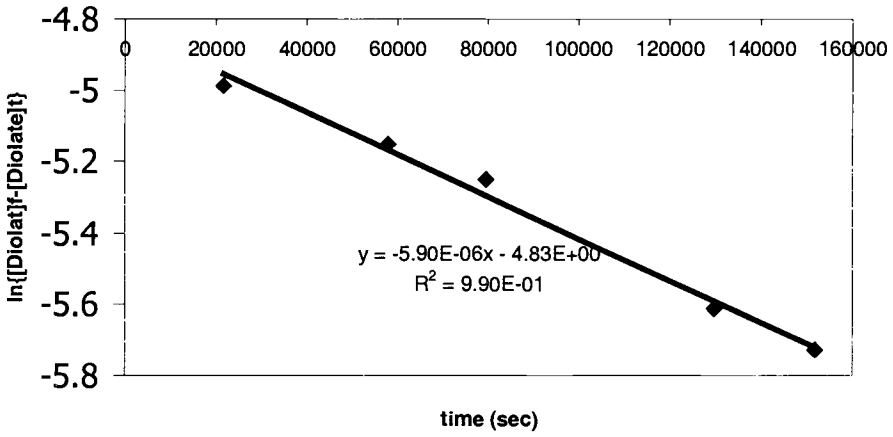
However, several attempts were performed to get a better pseudo-first order plot. The phase change that occurs as insoluble $Tp'ReO_3$ is reduced by of PPh_3 to form $Tp'ReO_2$ might affect the k_{obs}. By changing the amount of $Tp'ReO_3$ from 3.0 mg to 2.4 mg, the disappearance of insoluble $Tp'ReO_3$ was observed after 3 hours while a large amount of $Tp'ReO_3$ still left after 6 hours passed for the larger scale.

Figure 2.4: Selected Pseudo-first Order Plots

a) 5:1 of trans-cyclooctene oxide : $Tp'ReO_3$; $Tp'ReO_3$ 3.0 mg



b) 5:1 of *trans*-cyclooctene oxide: $Tp'ReO_3$;$Tp'ReO_3$ 2.4 mg



Although the r^2 value was better at low concentrations of epoxide, high concentrations led to low r^2 values again. Selected k_{obs} values are shown in table 2.1.

Table 2.1: k_{obs} and half life of ring expansion for *trans*-cyclooctene oxide at different $Tp'ReO_3$ amount

a) $Tp'ReO_3$ = 2.4 mg

Epoxide: $TpRe_3$	[Epoxide] (M)	r^2	Half-Life $10^4(sec^{-1})$	k_{obs} $10^{-6}(sec^{-1})$
5	0.0573	0.990	11.70	5.90
10	0.1146	0.983	7.80	8.89
15	0.1688	0.860	5.73	12.10

b) $Tp'ReO_3$ = 3.0 mg

Epoxide: $TpRe_3$	[Epoxide] (M)	r^2	Half-Life $10^4(sec^{-1})$	k_{obs} $10^{-6}(sec^{-1})$
5	0.0573	0.958	38.94	1.78
20	0.2256	0.942	23.58	2.94
60	0.6783	0.979	16.08	4.31

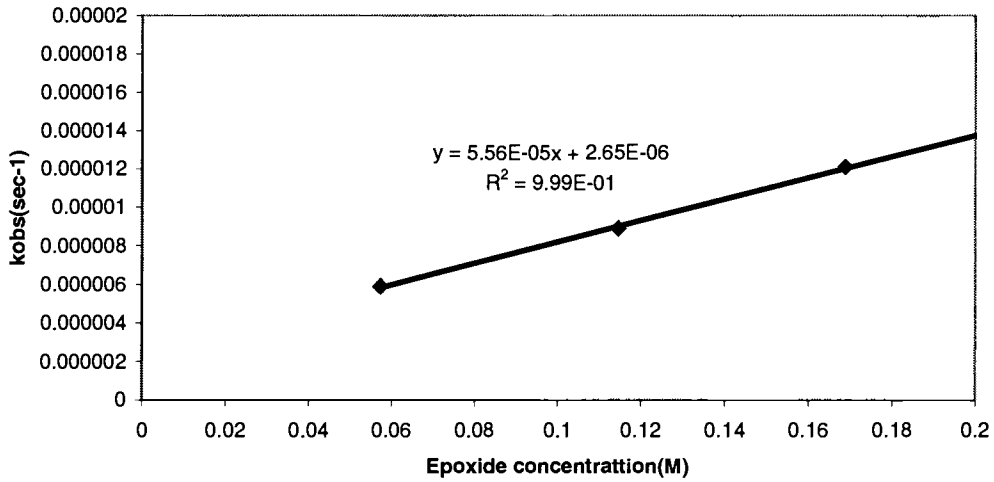
The ring expansion rate constant is given by:

Rate of ring expansion = k_{exp}[epoxide][$Tp'ReO_3$]

where $k_{obs} = k_{exp}$[epoxide]

Thus k_{exp} is a slope of linear plot between k_{obs} and concentration of epoxide. (Figure 2.5)

Figure 2.5: Ring expansion rate constant, k_{exp}, Tp'ReO_3 2.4 mg, Tp'ReO_3 concentration = 9.0 mM



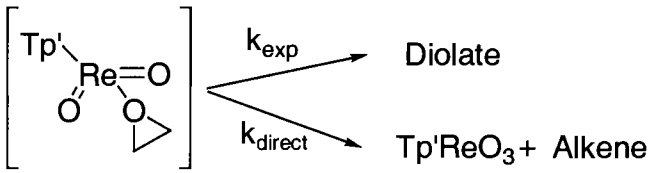
k_{exp} is $(5.56\pm3.97)x10^{-5}$ $M^{-1}s^{-1}$.

We observed a substantial amount of *trans*-cyclooctene in the reaction as confirmed by a characteristic peak of the vinylic proton of *trans*-cyclooctene at 5.43 ppm. The cyclooctene/diolate ratio in the products was 0.5:1. The GC-MS spectrum was conclusive in establishing *trans*-cyclooctene with a major peak at m/z = 110. Since *trans*-cyclooctane diolate is thermodynamically favored and would not cyclorevert to give alkene, *trans*-cyclooctene must form by direct O-atom transfer as noted previously. Alkene also underwent cyclocondensation with Tp'ReO_3 to give diolate. Therefore diolate is not generated exclusively from ring expansion, and treatment of diolate formation as first order is not valid.

2.2 Parallel First-order Reactions

Formation of alkene competing with ring expansion for *trans*-cyclooctene oxide deoxygenation led us to new methodology to obtain k_{exp} and k_{direct}. As proposed by Gable[43], an epoxide coordinated to rhenium is an intermediate to give either diolate or alkene (Figure 2.6).

Figure 2.6: Epoxide Coordinated to Re as an Intermediate



Direct O-atom transfer and ring expansion rate constants were recalculated on the basis that under pseudo first-order conditions the coordinated epoxide concentration over time was equal to $Tp'ReO_2$ concentration. Provided equilibrium formation of epoxide complex is fast, k_{exp}/k_{direct} is equal to [diolate]/[alkene]. The amount of diolate and alkene at any time are given by:

$$[\text{diolate}] = k_{exp}[Tp'ReO_3]_o/(k_{exp}+k_{direct})\{1-\exp[-(k_{exp}+k_{direct})t\}$$

$$[\text{alkene}] = k_{direct}[Tp'ReO_3]_o/(k_{exp}+k_{direct})\{1-\exp[-(k_{exp}+k_{direct})t\}$$

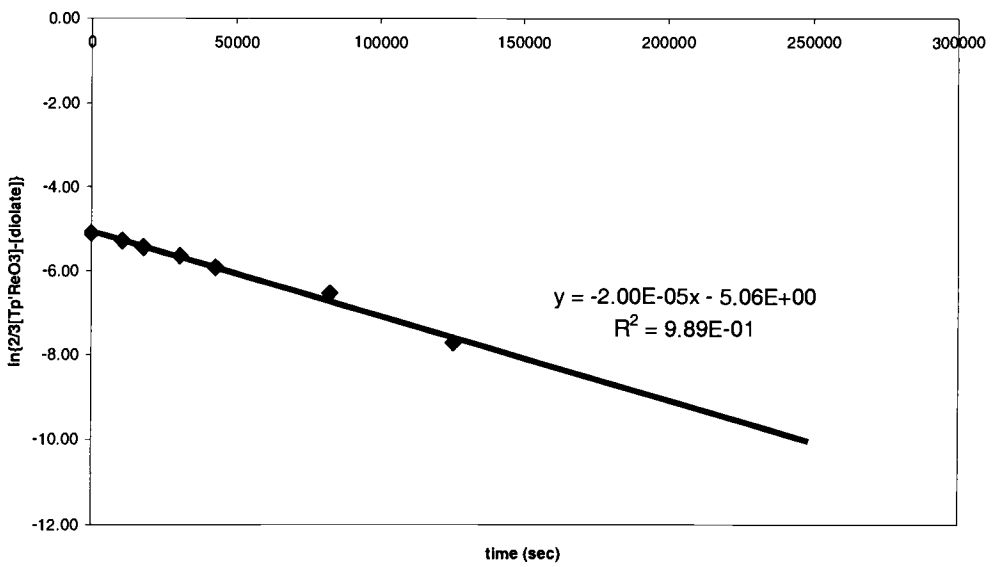
$$[diolate]/[alkene] = k_{exp}/k_{direct} = 2/1$$

$$\therefore [diolate] = 2/3[Tp'ReO_3]_o\{1-exp[-3/2(k_{exp})t\}$$

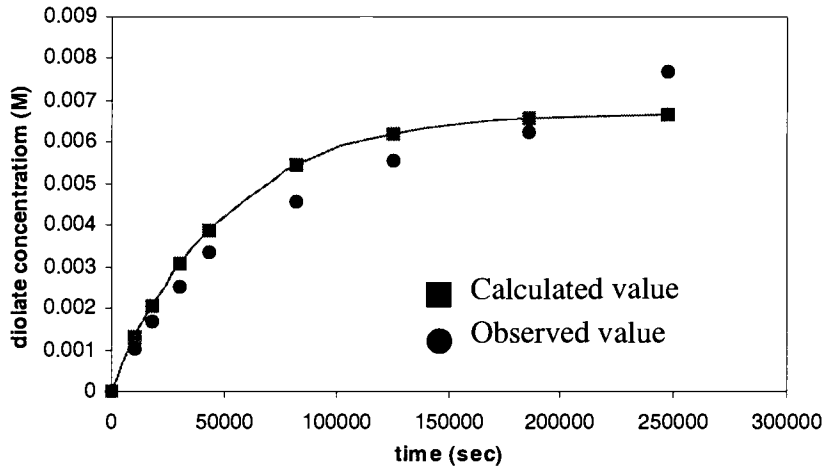
By plotting $ln\{(2/3)[Tp'ReO_3]_o-[diolate]_t\}$ vs. t, k_{exp} is equal to -2/3*slope. The k_{exp} then was used to simulate the diolate concentration over time comparing with the observed value (Figure 2.7).

Fig 2.7: Competition Reaction Model Plot

a) 60:1 epoxide:$Tp'ReO_3$ $k_{exp} = (1.33 \pm 0.002)x10^{-5}$ sec^{-1} and $k_{direct} = (6.67 \pm 0.001)x10^{-6}$ sec^{-1}



b) Comparing calculated value with observed value, standard deviation = 0.0024



The k_{direct} and k_{exp} measurement at different concentration ratios of epoxide to diolate were calculated by the same methodology. All measurements gave the result in the same magnitude as shown in Table 2.2.

Table 2.2: Summarized k_{direct} and k_{exp}

Epoxide: $TpReO_3$	[Epoxide] (M)	k_{exp} 10^{-5}(sec-1)	k_{direct} 10^{-6}(sec-1)	r^2
5	0.0573	1.31	6.55	0.939
15	0.1688	1.09	5.45	0.941
20	0.2256	1.23	6.15	0.986
60	0.6783	1.33	6.65	0.989

From Table 2.2, the average of k_{exp} is $(1.24\pm0.03)\times10^{-5}$ sec-1 and k_{direct} is $(6.20\pm0.02)\times10^{-6}$ sec^{-1}.

2.3 Kinetic Measurement of 1,2-*cis*-Cyclooctene Oxide

cis-Cyclooctene oxide prefers to give more alkene, and also it was known that at temperatures above 105 °C 1,2-*cis*-cyclooctanediolate cycloreverts[35] to give an alkene and $Tp'ReO_3$, not like 1,2-*trans*-cyclooctane diolate. A control experiment was done to estimate the thermal stability range of diolate for this diolate at 75 °C.

1,2-*cis*-Cyclooctanediolate (3.0 mg) was dissolved in C_6D_6 and anisole was used as an internal standard. The sample tube was periodically removed from a thermostatted water bath at 75 °C and cooled to 25°C and the ^1H NMR spectrum was collected. No alkene formation was observed although the reaction was heated for 19 hours.

To estimate k_{exp} and k_{direct}, the same methodology as for *trans*-cyclooctene oxide was applied to a 45.16 mM mixture of *cis*-cyclooctene oxide of (5:1:3 epoxide:$Tp'ReO_3$:PPh_3). *cis*-Cyclooctene, 0.33 mM, was observed initially after 3 hours at room temperature. After 5 minutes at 75 °C, 0.59 mM of cis-cyclooctene was formed and also there was no diolate.

After 24 hours 1.37 mM of alkene was observed, and the ratio of cis-cyclooctene/diolate was 24.5:1 at 75 °C. Thus, k_{direct} is 5.07 x 10^{-5} s^{-1}, r^2 = 0.993. k_{exp} must then be approximately 2.07x10^{-6} s^{-1}.

Direct O-atom transfer dominates ring expansion for *cis*-cyclooctene oxide deoxygenation by observing alkene formation even at room temperature and slow rate of diolate formation.

2.4 Sulfur Analog Study

Metal sulfur chemistry has been investigated in catalysis of hydrodesulfurization systems (HDS), such as clusters of MoS_x/CoS_y. Sulfides of rhenium, ruthenium, and other metals are even more active[23]. Desulfurization of episulfides and dithiols mediated by rhenium oxo complex has been explored by the Gable group. A desulfidation catalytic cycle was proposed in 2001 but some issues on S-atom transfer selectivity and activity of each species involved in the reaction including some parts of proposed catalytic cycle needed more study.

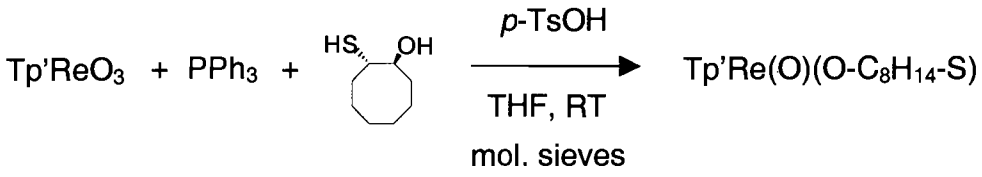
As previously mentioned in section 1.4, the thermally stable compound 1,2-ethanedithiodiolate was claimed as a major product from ethylene sulfide reacting with $Tp'ReO_3/PPh_3$. At least one mole of episulfide needs to transfer its S-atom via direct atom transfer. By changing from ethylene episulfide to cyclooctene episulfide, the same chemistry behavior

should be observed. Strain in trans-cyclooctene episulfide would add another variable with which to probe the system.

2.4.1 Independent Synthesis and Characterization of Hydrido-*tris*-(3,5-dimethyl-1-pyrazoyl)borato(*trans*-cyclooctane-1,2-monothio diolato)(oxo)rhenium(V) (1)

trans-Cyclooctanemonothiodiolate, **1**, was synthesized according to a one pot procedure[58] as shown in Figure 2.8. Cyclocondensation of *trans*-mercaptocyclooctanol with $Tp'ReO_3/PPh_3$ in dry THF under Ar gave a light blue-green compound. After filtration, solvent was removed in vacuo. The crude product was then purified by column chromatography. The light blue-green product was characterized by means of ^{1}H NMR, ^{13}C NMR, IR, and mass spectrometry. The integration ratio of 1:1:1 for vinylic protons and 3:3:3:3:3:3 for methyl protons from Tp' showed the C_1 symmetry of this complex. An infrared band at 949.64 cm^{-1} belonged to the Re=O stretch, and the mass spectrometry using FAB ionization showed the M^+ ion (^{187}Re) at 658.6 m/z .

Figure 2.8: 1,2-*trans*-Monothiodiolate Synthesis



COSY and HSQC spectra in Figure 2.10 allowed for the assignment of protons on Tp' and *trans*-cyclooctane ring. Table 2.3 shows the correlations used to make assignments. The *J* coupling constant between carbinol and thiocarbinol protons, 13.90 Hz, suggested the cyclooctane ring should be the *trans*-isomer. NOESY and nOe experiments on Tp'Re(O)*trans*-1,2-cyclooctane monothiodiolate were done in order to confirm the *trans*-stereochemistry and assign which of two possible diastreomers formed: these give definitive assignments for the two diolate signals at, 3.95 ppm and 4.89 ppm.

Figure 2.9: Diastreomers of **1**

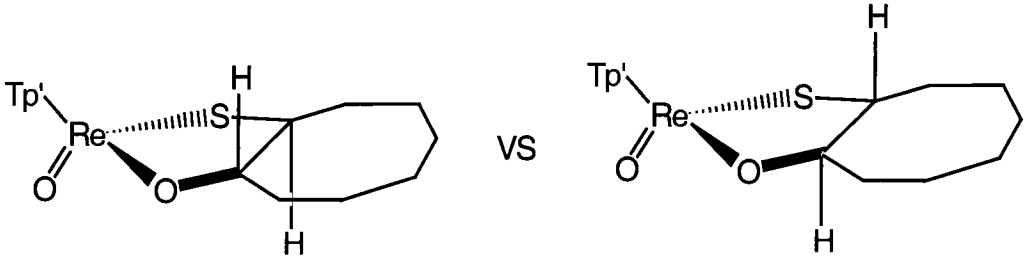
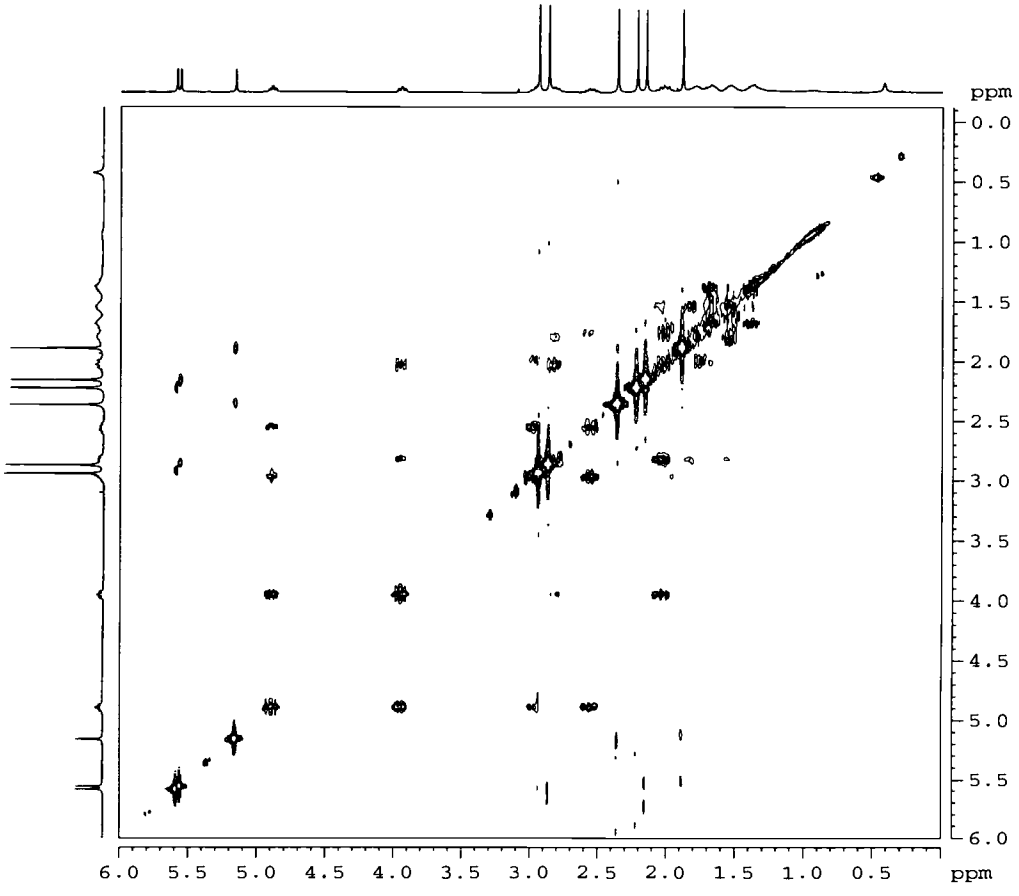


Figure 2.10: COSY and HSQC of **1**

a) COSY



b) HSQC

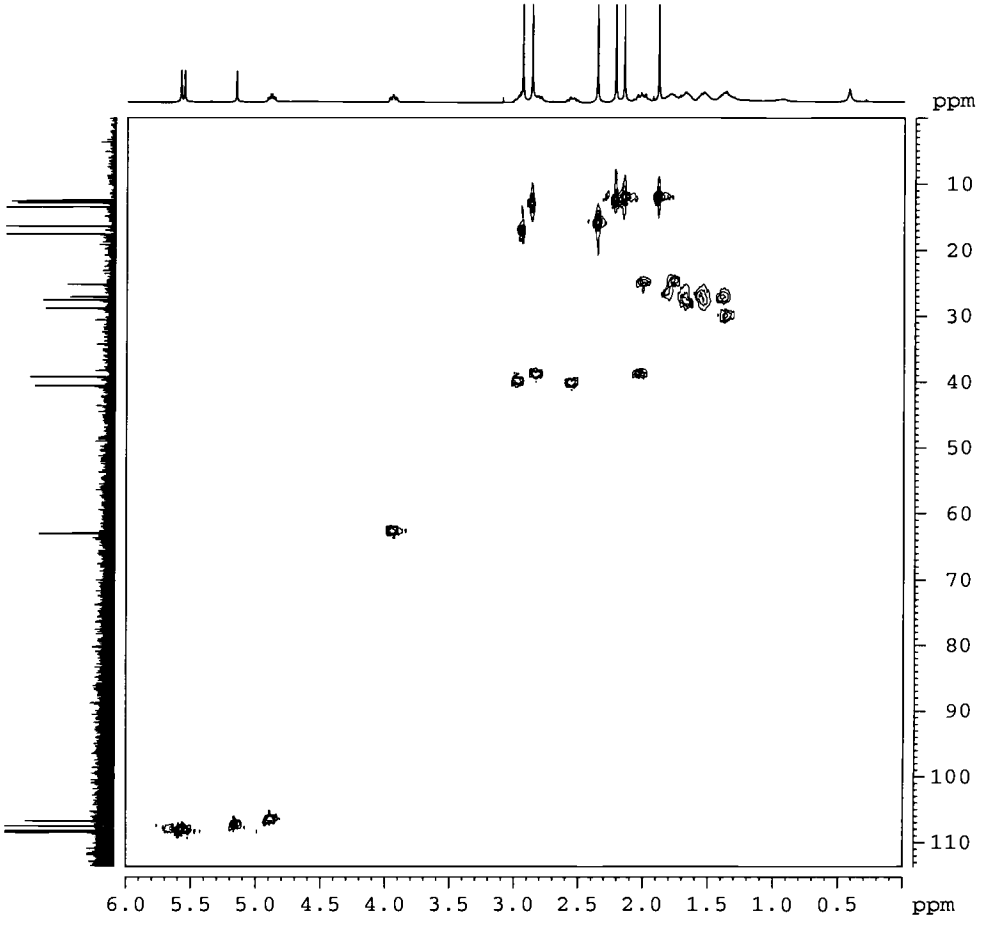
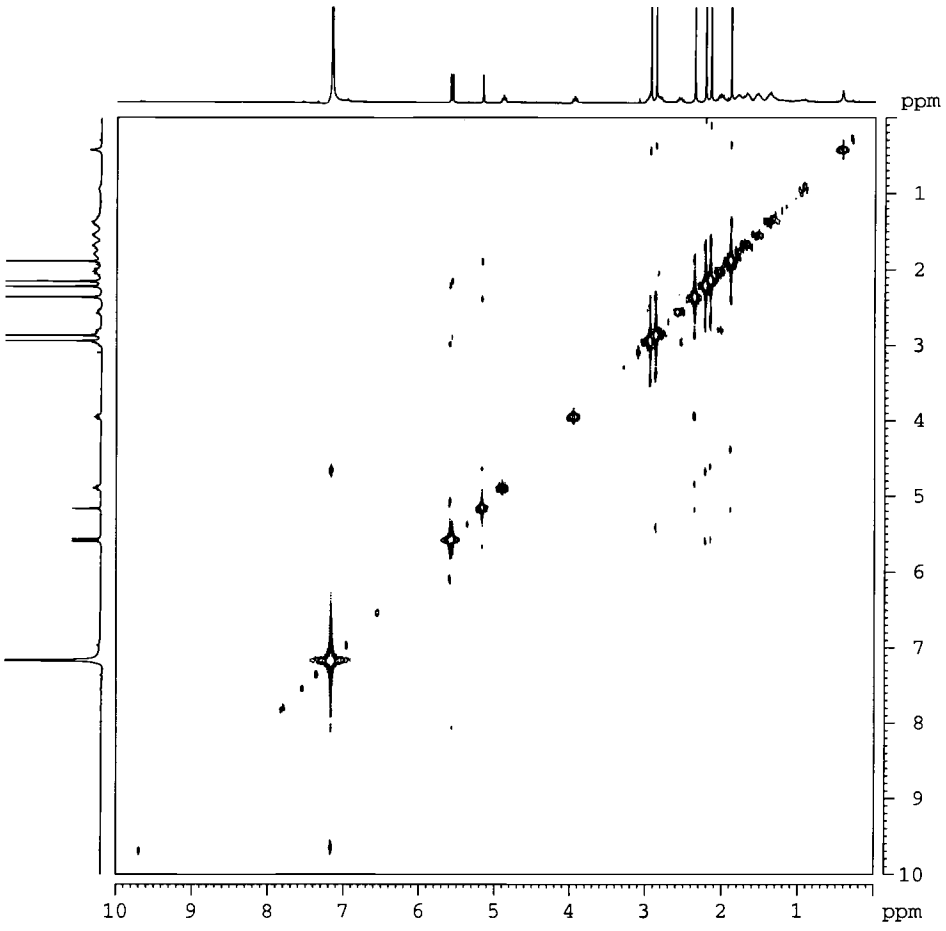

ppm
10
20
30
40
50
60
70
80
90
100
110
6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

Table 2.3: NMR Results from 2D COSY and HSQC experiments of **1**

^{1}H NMR shifts, ppm	Coupled protons	Coupled carbons
Tp'		
1.88(s, 3H)		12.13
2.15(s, 3H)		12.13
2.22(s, 3H)		12.13
2.35(s, 3H)		15.84
2.87(s, 3H)		12.52
2.94(s, 3H)		17.02
5.16(s, 1H)		107.17
5.56(s, 1H)		107.95
5.59(s, 1H)		108.29
Cyclooctane ring		
1.38(m, 1H)	*	26.70
1.53(m ,2H)	1.82, *	27.15
1.68(m, 2H)	*	27.56
1.77(m, 1H)	*	24.95
1.82(m,1H)	1.53, *	26.70
1.99(m, 1H)	2.96, 2.56, 1.77	24.95
2.02(m, 1H)	2.83, 3.95, 1.82	38.90
2.55(m, 1H)	2.96, 4.89, 1.99	40.26
2.82(m, 1H)	3.95, 2.02, 1.82	38.90
2.96(m, 1H)	2.55, 4.89, 1.99	40.26
3.95(ddd, J= 4.85, 9.15,13.90, 1H)	4.89, 2.83, 2.02	62.69
4.89(ddd, J= 4.76,10.70, 13.90, 1H)	3.95, 2.96, 2.55	106.47

*** Not Clearly identified**

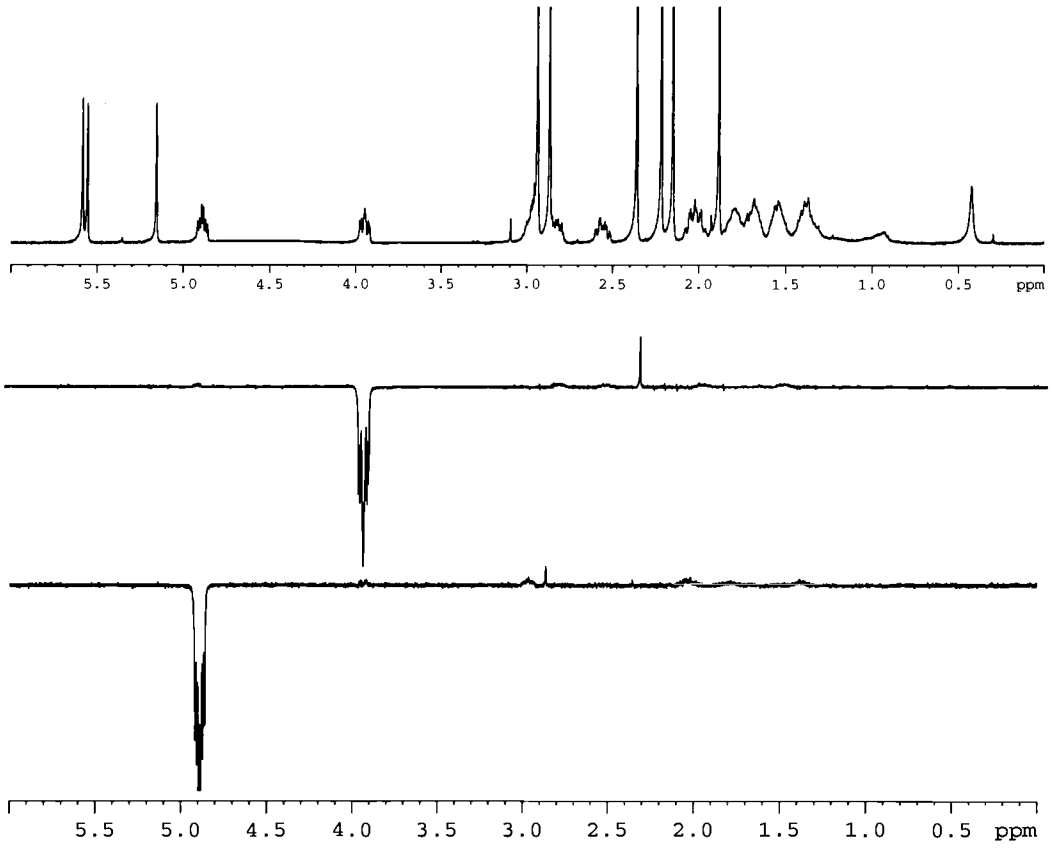
Figure 2.11: NOESY of **1**



The cross peak in the NOESY spectrum between the thiocarbinolic signal at 3.95 ppm and the methyl signals at 2.36 ppm allowed assignment of this proton adjacent to S-atom as being in the *syn* position vs. the Tp' ligand while the the carbinolic proton adjacent to O-atom shows no nOe and thus must be in the *anti* position. Strong correlations among vinylic protons

and methyl groups confirmed the COSY experiment as shown in Figure 2.10.

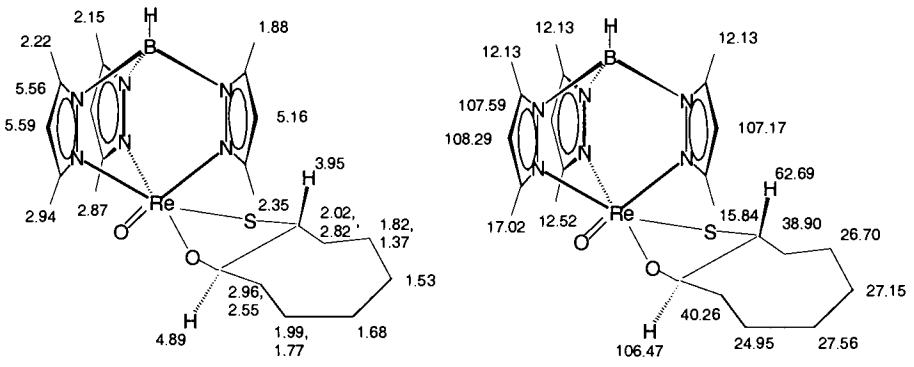
Figure 2.12: nOe of **1**



A 1-D nOe (nuclear Overhauser enhancement) experiment illustrates this conclusively. Irradiation of the signal at 3.95 ppm gave a 4.98% nOe at 2.36 ppm while irradiation of the signal at 4.89 ppm signal gave 1.17% effect at the 2.87 ppm signal as shown in figure 2.12.

The proton and carbon assignments of *trans*-cyclooctanemonothiodiolate were done as shown in figure 2.13.

Figure 2.13: Proton and Carbon Assignments for **1**



^{1}H **^{13}C**

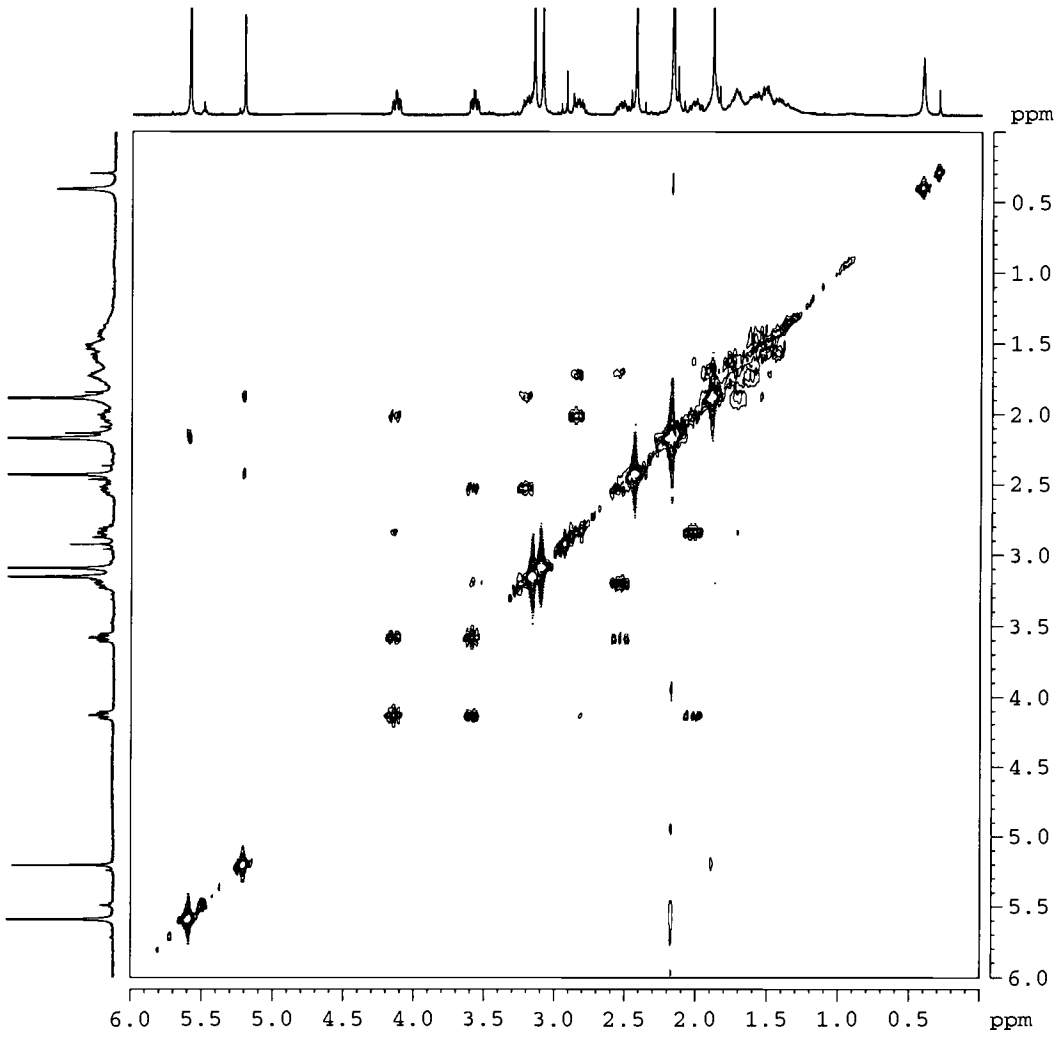
2.4.2 Synthesis and Characterization of Hydrido-*tris*-(3,5-dimethyl-1-pyrazoyl)borato(*trans*-cyclooctane-1,2-dithiodiolato)(oxo)rhenium(V) (2)

trans-Cyclooctene episulfide was allowed to react with $Tp'ReO_3/PPh_3$ in dry C_6D_6 under Ar at 75 °C to give a dark brown compound. After filtration, solvent was removed by in vacuo. The crude product was then purified by column chromatography. The dark blue product, **2**, was characterized by means of ^1H NMR, ^{13}C NMR, IR, and mass spectrometry. The integration ratio of 1:1:1 for vinylic protons and 3:3:3:3:3:3 for methyl protons from Tp' showed the C_1 symmetry of this complex. An infrared band at 940.96 cm^{-1} belonged to the Re=O stretch, and the mass spectrometry using FAB technique showed the M^+ ion (Re 187) at 674.1 m/z.

COSY and HSQC spectra in Figure 2.14 allowed for the assignment of protons and carbons on Tp' and *trans*-cyclooctane rings.

Figure 2.14: COSY and HSQC Spectra of **2**

a) COSY



b) HSQC

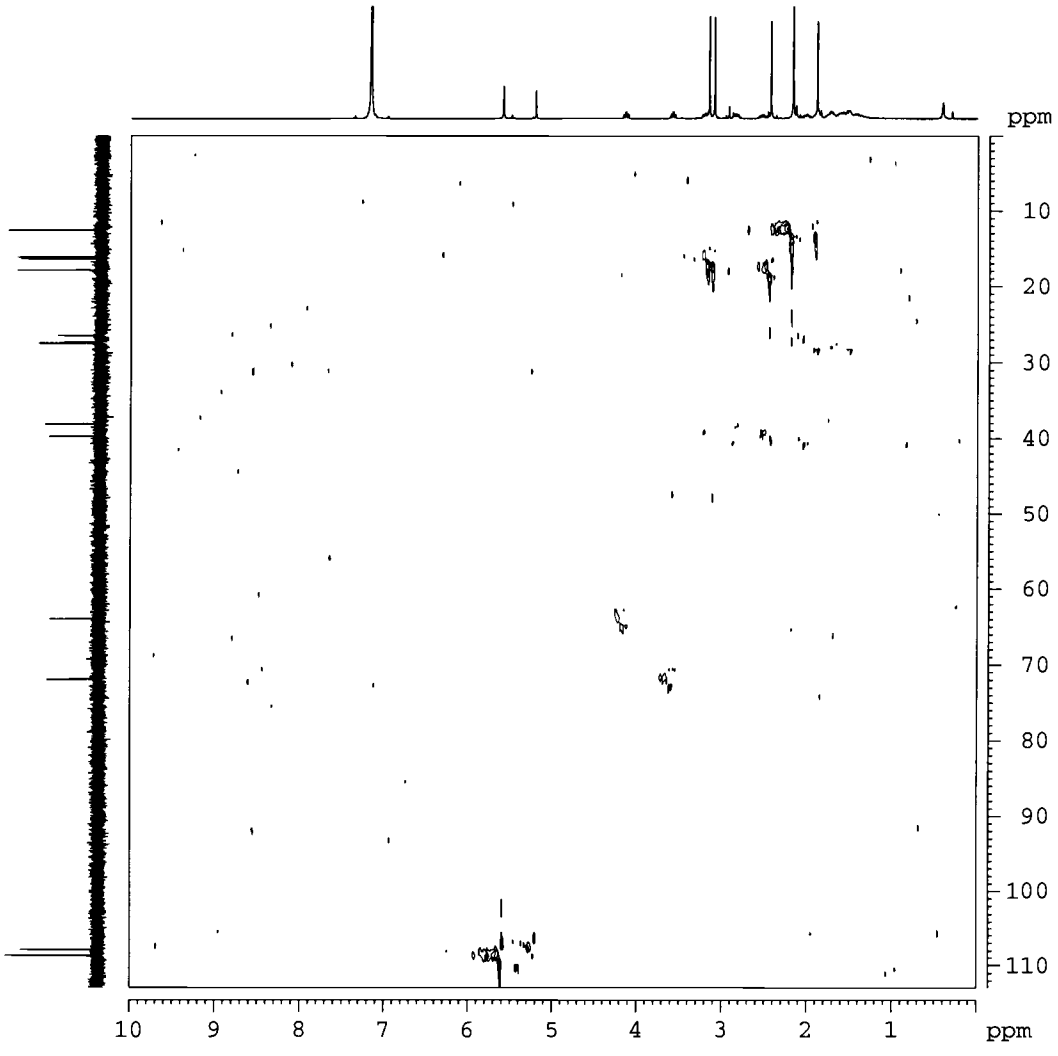


Table 2.4: NMR Results from 2D COSY and HSQC experiments

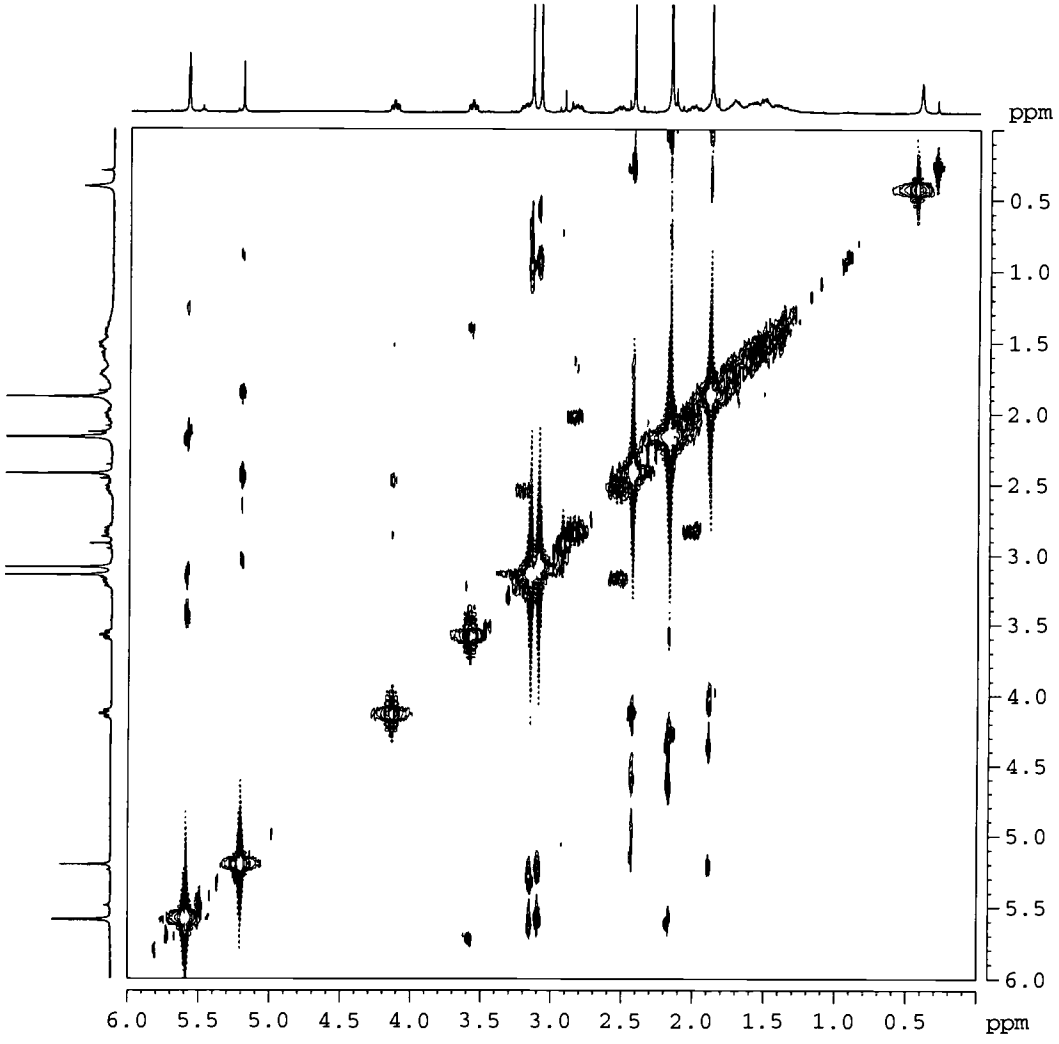
^{1}H NMR shifts, ppm	Coupled protons	Coupled carbons
Tp'		
1.89(s, 3H)		12.17
2.17(s, 3H)		12.37
2.17(s, 3H)		12.37
2.43(s, 3H)		17.47
3.06(s, 3H)		16.10
3.16(s, 3H)		15.95
5.20(s, 1H)		107.84
5.58(s, 1H)		108.58
5.59(s,1H)		108.60
Cyclooctane ring		
1.54(m, 2H)	1.74, *	27.17
1.63(m, 1H)	2.86, *	26.39
1.73(m, 2H)	1.92, *	26.96
1.74(m, 1H)	1.53, *	26.39
1.86(m,1H)	2.52,1.92	27.20
1.92(m, 1H)	1.73, *	27.20
2.01(m, 1H)	1.63, 2.86, 4.13	39.57
2.52(m, 1H)	3.20, 3.58, 1.86	38.02
2.86(m, 1H)	2.01, 1.74, 4.13	39.57
3.20(m, 1H)	3.58, 2.52,1.86	38.02
3.58(ddd, J= 3.38, 9.70, 13.45, 1H)	4.13, 3.20, 2.52	71.77
4.13(ddd, J= 3.48, 9.61, 13.45, 1H)	3.58, 2.86, 2.01	63.88

*** Not clearly identified**

NOESY and nOe experiments on the dithiodiolate **2** were done in order to give definitive assignments for the two diolate position hydrogens at 3.58 ppm and 4.14 ppm.

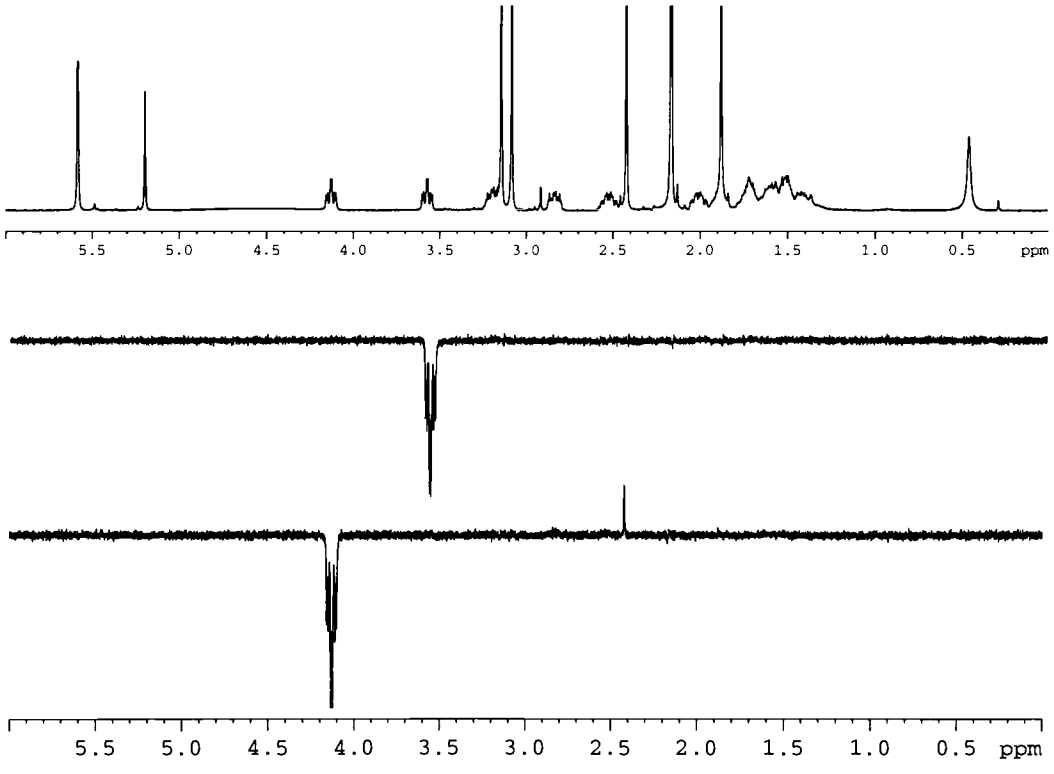
Figure 2.15: NOESY of **2**

a) NOESY



The cross peaks in the NOESY spectrum correlating the 4.13 ppm carbinolic signal and the 2.43 ppm methyl signal on the pyrazole ring allowed assignment of the carbinolic proton adjacent to that S-atom in the *syn* position vs. Tp' while the carbinolic proton adjacent to the other S-atom is in the *anti* position vs. Tp'. Strong correlations among vinylic protons and methyl groups confirmed the COSY experiment as shown in Figure 2.15.

Figure 2.16: nOe of **2**

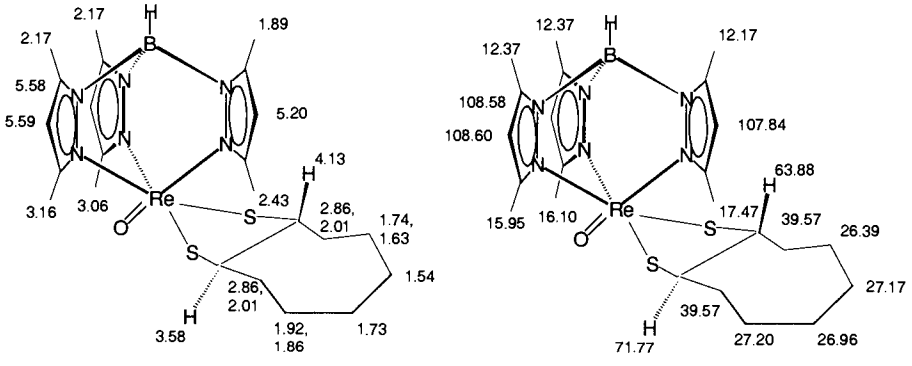


An nOe experiment was performed to confirm the position of carbinolic protons suggested by the NOESY spectrum. Irradiation of the

signal at 4.13 ppm gave a 5.68% nOe effect at the 2.43 ppm signal while irradiation of the signal at 3.58 ppm signal gave 0% nOe effect as shown in Figure 2.16.

The proton and carbon assignments of *trans*-cyclooctane dithiodiolate were made as shown in Figure 2.17.

Figure 2.17 : Proton and Carbon Assignments for **2**



^{1}H **^{13}C**

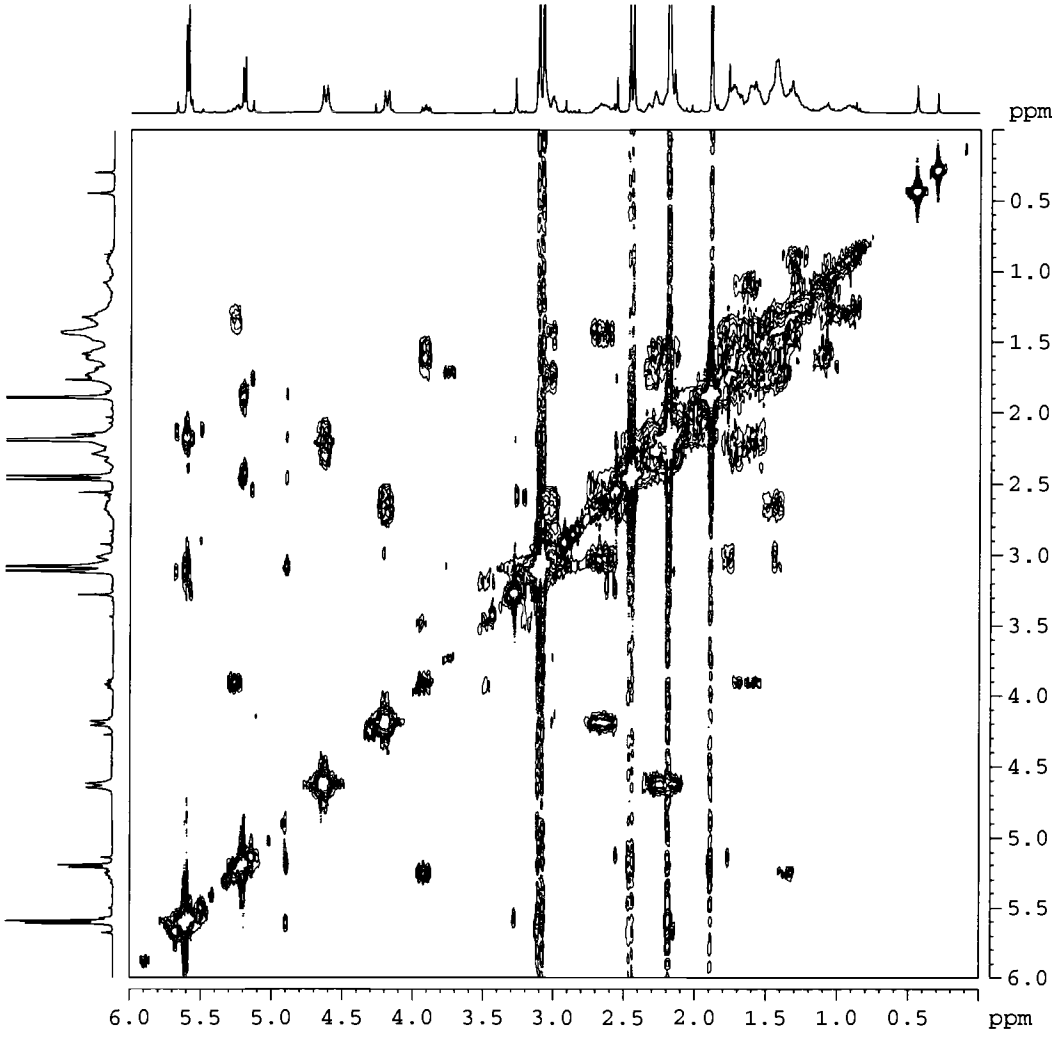
2.4.3 Synthesis and Characterization of Hydrido-*tris*-(3,5-dimethyl-1-pyrazoyl)borato(*cis*-cyclooctane-1,2-dithiodiolato)(oxo)rhenium(V) (3)

By the same manner as for **2**, *cis*-cyclooctene episulfide was allowed to react with $Tp'ReO_3/PPh_3$ in dry C_6D_6 at room temperature under Ar to give a dark brown compound. After filtration, solvent was removed in vacuo. The crude product was then purified by column chromatography. The dark brown product, **3** was characterized by means of ^1H NMR, ^{13}C NMR, IR, and mass spectrometry. An infrared band at 941.18 cm^{-1} belonged to the Re=O stretch, and the mass spectrometry using FAB technique shown a M^+ ion (Re 187) at 674.6 m/z.

The ^1H NMR spectrum showed *syn* and *anti* isomers in the product mixture at a 1:0.7 ratio. The product could not be purified by column chromatography (CH_2Cl_2/hexane). The COSY and HSQC spectrum in Figure 2.18 allowed for the assignment of the mixture of isomers.

Figure 2.18: COSY and HSQC of mixture *syn-* and *anti-* isomer of **3**

a) COSY



From the correlation peaks in this COSY spectrum, the proton signals at 4.19, 3.03, 2.64, 1.71, and 1.60 ppm came from one isomer. The signals at 4.63, 2.29, 2.20, 1.60 and 1.43 ppm came from the other isomer.

b) HSQC

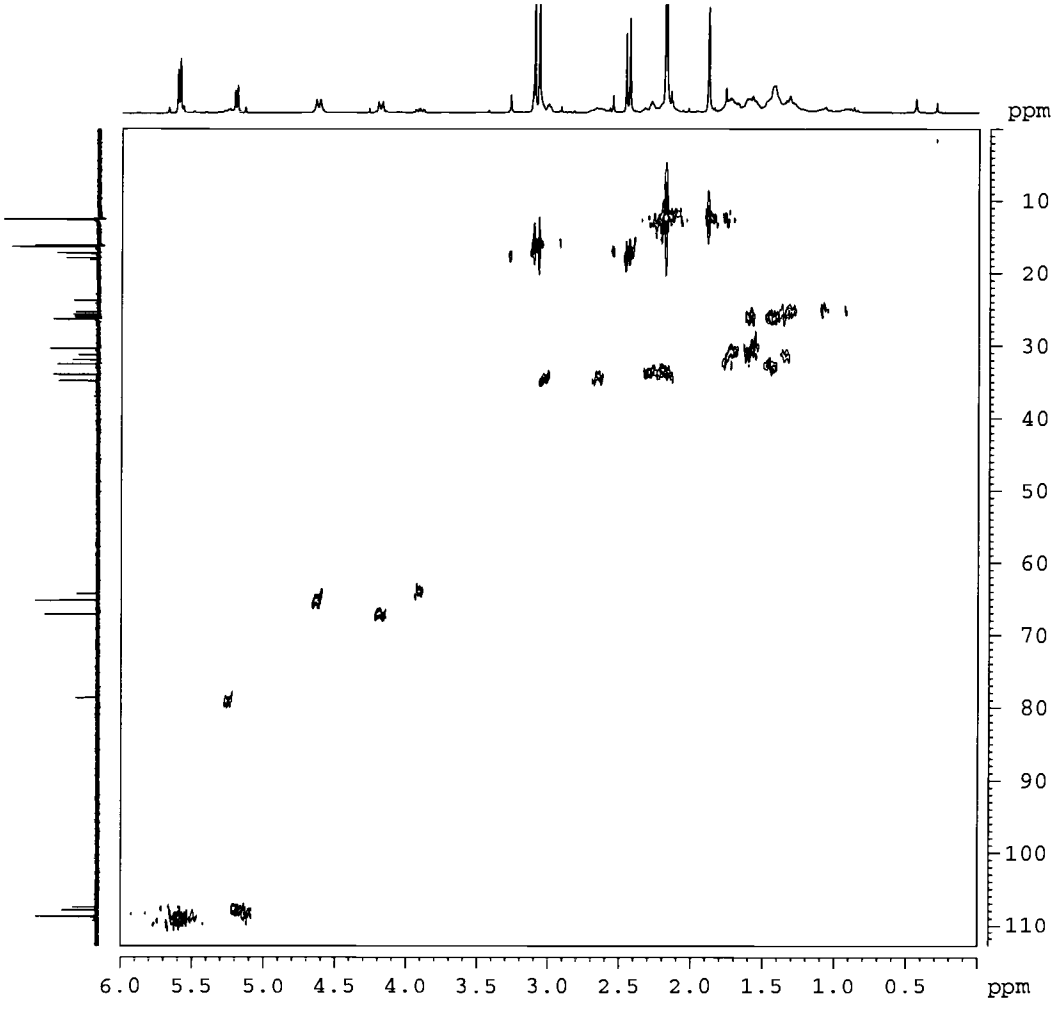

ppm
10
20
30
40
50
60
70
80
90
100
110
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

Table 2.5: NMR Results from 2D COSY and HSQC experiments of **3**

a) *anti-* isomer

^{1}H NMR shifts, ppm	**Coupled protons**	**Coupled carbons**
Tp'		
1.88(s, 3H)		12.62
2.18(s, 6H)		12.18
2.43(s, 3H)		17.07
3.07(s, 6H)		16.48
5.20(s, 1H)		107.62
5.59(s, 2H)		108.68
Cyclooctane ring		
1.43(m, 1H) x 2	1.60, 4.63	26.27
1.60(m, 1H) x 2	1.43, 4.63	26.27
2.20(m, 1H) x 2	2.29, 4.63	33.98
2.29(m, 1H) x 2	2.20, 4.63	33.98
4.63(m, 1H) x 2	1.43, 1.60, 2.20, 2.29	65.32

The integration ratio of 2:1 for vinylic protons and 2:2:1:1 for methyl protons from the Tp' ligand showed the C_s symmetry of this complex.

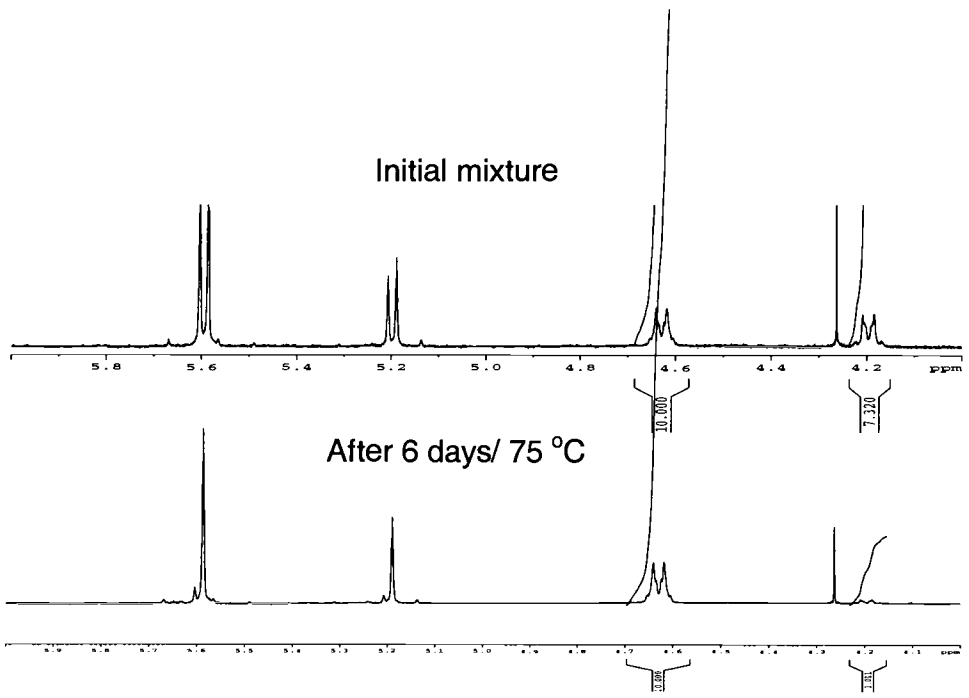
b) *syn*- isomer

Syn-Isomer		
^{1}H NMR shifts, ppm	**Coupled protons**	**Coupled carbons**
Tp'		
1.89(s, 3H)		12.65
2.19(s, 6H)		12.19
2.46(s, 3H)		17.84
3.10(s, 6H)		16.48
5.21(s, 1H)		107.95
5.61(s, 2H)		108.80
Cyclooctane ring		
1.60(m, 1H) x 2	1.71, 4.19,	30.39
1.71(m, 1H) x 2	1.60, 4.63	30.39
2.64(m, 1H) x 2	3.03, 4.63	34.83
3.03(m, 1H) x 2	2.64, 4.63	34.83
4.19(m, 1H) x 2	1.60, 1.71, 2.64, 3.03	67.20

Isomerization of this isomeric mixture was observed at 75 °C in C_6D_6. After a sealed NMR sample was heated for 6 days, the ratio of carbinolic signals at 4.63 ppm and 4.19 was changed from 1:0.7 to 10:1 without any alkene formation (no cycloreversion to give an alkene, and also no change of total rhenium of this **3**, vs. anisole as an internal standard) as shown in Figure 2.19. The increasing amount of the major species vs. the minor was

attributed to the thermodynamic stability of the isomerized species. The thermally stable isomer was then assigned as the *anti* isomer by NOESY and 1-D nOe experiments.

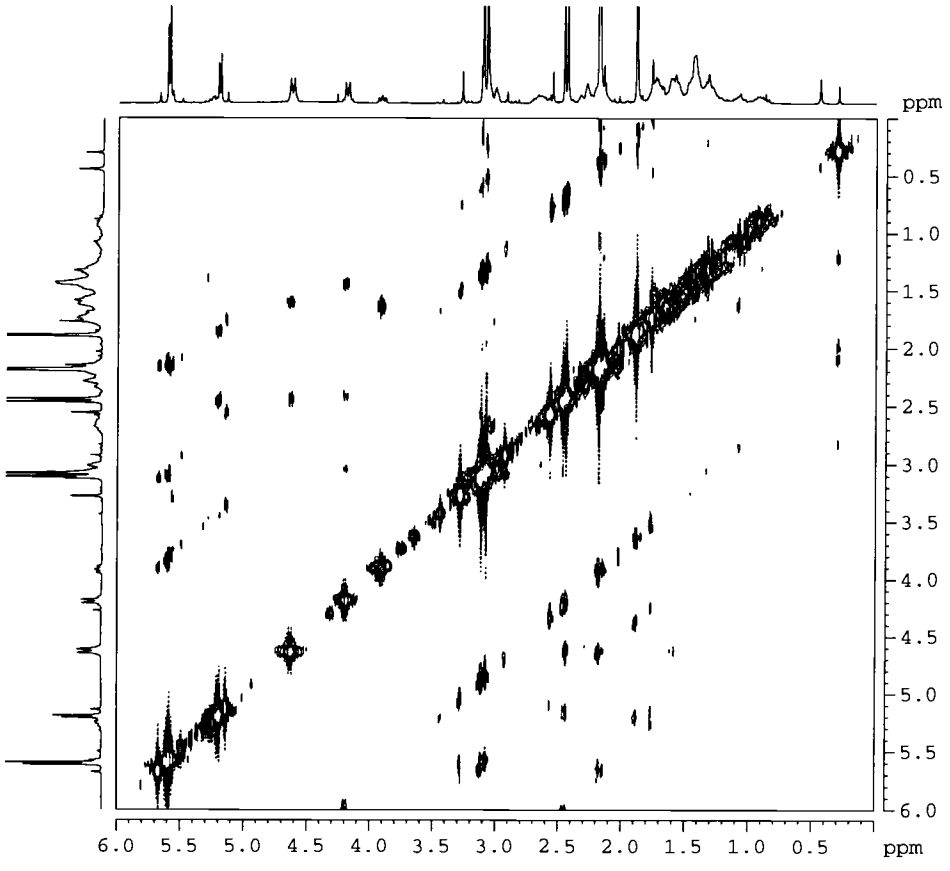
Figure 2.19: Different Thermal Stability of *syn-* and *anti-* isomers



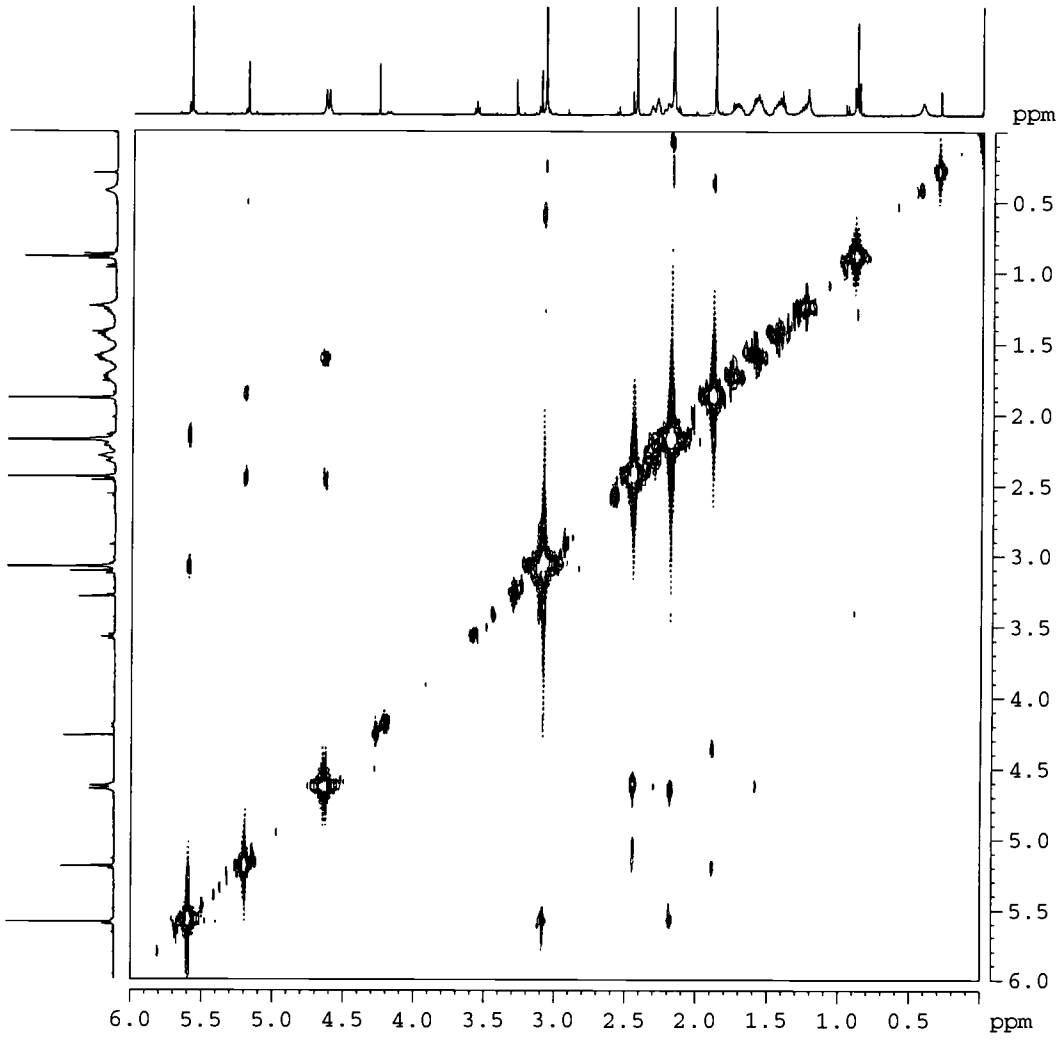
The NOESY spectrum of this 10:1 mixture showed a strong correlation between signals at 4.63 and 2.43 ppm. This result confirms the provisional assignment based on the presumed thermodynamic preference for the *anti-* isomer.

Figure 2.20: Comparing the NOESY from 10:7 and 10:1 mixture

a) 10:7



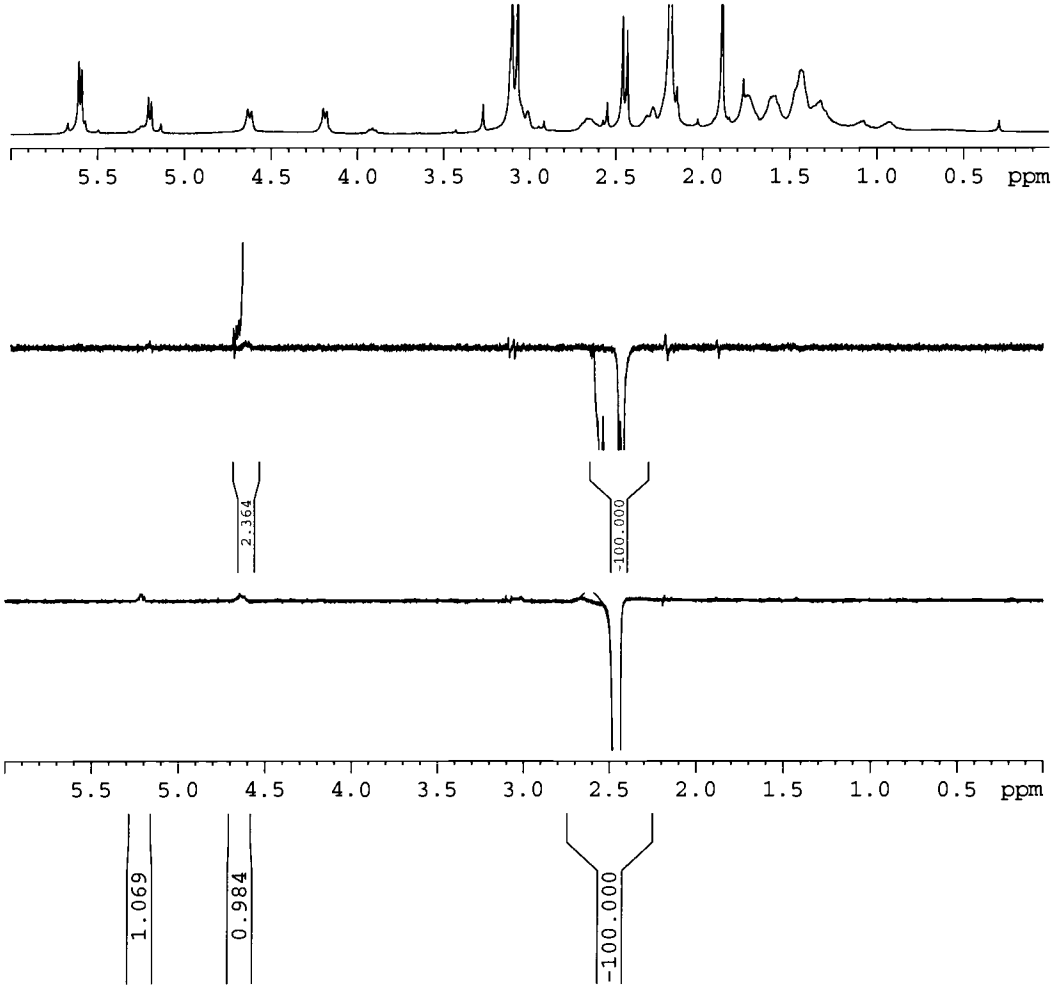
b) 10:1



A 1-D nOe experiment was performed to confirm the position of carbinolic protons suggested by NOESY. Irradiation of the signal at 2.43 ppm gave a 2.36% nOe effect at the 4.63 ppm signal while irradiation of the signal at 2.46 ppm signal gave 1.07% nOe effect at the 5.21 ppm and

0.98% nOe effect at the 4.63 ppm. The enhancement at 4.63 ppm was ascribed to the likely irradiation of the nearby peak at 2.36 ppm as shown in Figure 2.21. This result allowed conclusively establishing the stable isomer is the *anti*-isomer.

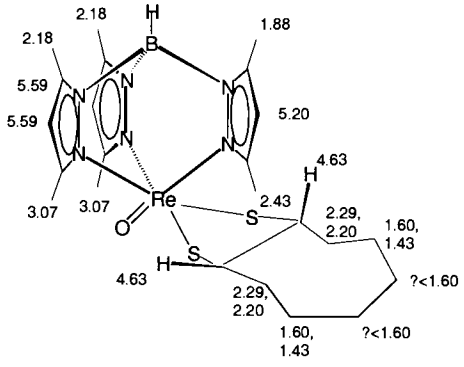
Figure 2.21: nOe of **3**



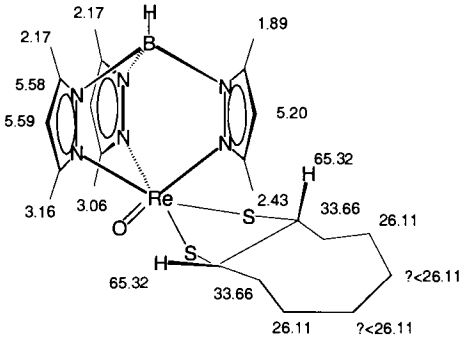
The proton and carbon assignments of *syn*- and *anti*-cyclooctane dithiodiolate were done as shown in Figure 2.22.

Figure 2.22: Proton and Carbon Assignments for *syn*-Cyclooctane dithiodiolate

a) *anti*-isomer

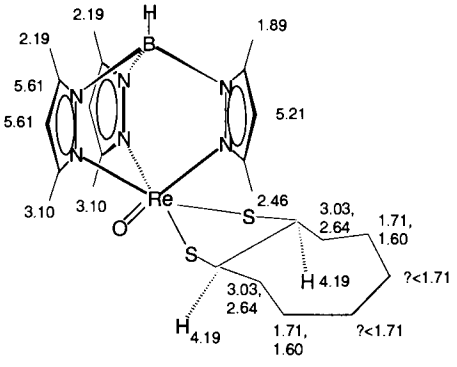


^{1}H

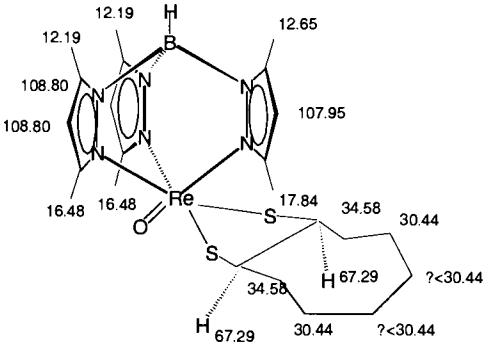


^{13}C

b) *syn*-isomer



^{1}H



^{13}C

2.4.4 Selectivity and Desulfidation Product of Cyclooctene Episulfide

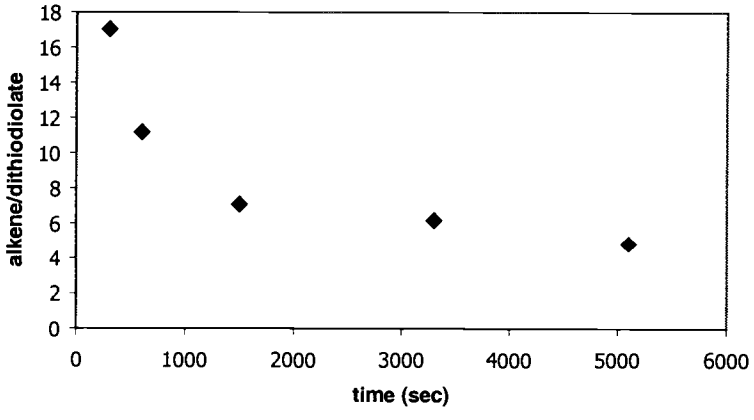
Cyclooctene episulfide was reacted with $Tp'ReO_3/PPh_3$ under the same conditions as with cyclooctene oxide. In an NMR tube, desulfidation of *trans*-cyclooctene episulfide or *cis*-cyclooctene episulfide was followed in deuterated benzene at 75 °C by ^1H and ^{31}P NMR under pseudo-first order kinetic conditions: episulfide:PPh_3:$Tp'ReO_3$ = 5:3:1, $Tp'ReO_3$ 9.03 mM in 0.50 mL C_6D_6. Tetramethylsilane was used as an internal integration standard. The sample tube was periodically removed and cooled to 25°C, and the ^1H NMR and ^{31}P spectra were collected. The products were characterized by NMR, MS(FAB) and compared with independently synthesized products. 1,2- *trans*-Cyclooctane dithiodiolate and 1,2- *cis*-cyclooctane dithiodiolate and the corresponding alkenes were established as major products from desulfidation of *trans*-cyclooctene episulfide and *cis*-cyclooctene episulfide, respectively, in an order, and also the ratio of alkene/dithiodiolate was measured as well. Both dithiodiolates are highly thermally stable to alkene loss; even heated at 75 °C for one week no alkene was be observed.

Dithiodiolate formation occurred very fast relatively to epoxide/diolate conversion. The ratio of alkene/dithiodiolate for *trans*-cyclooctene episulfide was 17.1:1 after the reaction proceeded for 5 minutes, and also a decrease in the alkene/dithiodiolate ratio was found over time as shown in Figure

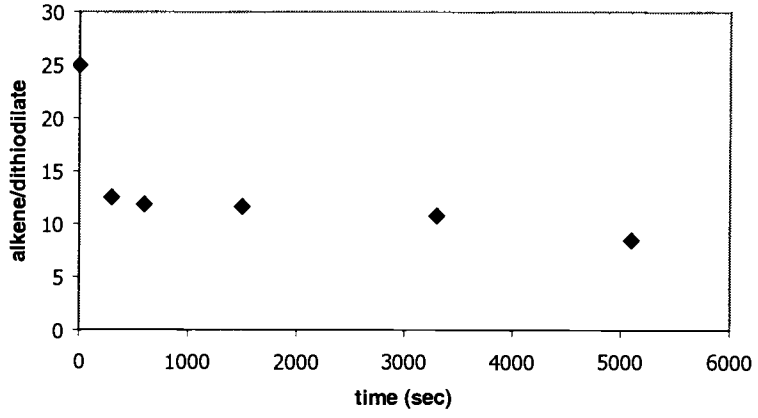
2.23. Desulfidation of *cis*-cyclooctene episulfide gave an alkene/dithiodiolate ratio at 12.5, and a slower decrease in the alkene/dithiodiolate ratio was found over time relative to the *trans*-cyclooctene episulfide case as shown in Figure 2.8. Two possible conclusions can be drawn: (1) alkene underwent cycloaddition to $Tp'ReOS_2$ to form dithiodiolate, or (2) dithiodiolate forms by ring expansion from Tp'ReOS.

Figure 2.23: Decrease in the Alkene /Dithiodiolate Ratio

a) *trans*-cyclooctene episulfide



b) *cis*-cyclooctene episulfide



From the ^{31}P NMR, the ratio of $S{=}PPh_3/O{=}PPh_3$ was obtained.(Table 2.6)

Table 2.6: Ratio of $S{=}PPh_3/O{=}PPh_3$

a) *trans*-cyclooctene episulfide

Expt	t(sec)	$[S{=}PPh_3]$mM	$[O{=}PPh_3]$mM	$[PPh_3]$mM	$S{=}PPh_3/O{=}PPh_3$
1	0	8.34	1.67	16.68	5.00
2	300	8.89	9.70	8.08	0.92
3	600	13.98	12.70	0.00	1.10
4	1500	13.34	13.34	0.00	1.00
5	3300	12.35	14.33	0.00	0.86
6	5100	12.47	14.21	0.00	0.88

b) *cis*-cyclooctene episulfide

Expt	t(sec)	[S=PPh_3]mM	[O=PPh_3]mM	[PPh_3]mM	S=PPh_3/O=PPh_3
1	0	10.24	1.91	12.91	5.37
2	300	18.04	4.23	0.00	4.26
3	600	17.56	4.17	0.00	4.21
4	1500	17.85	3.96	0.00	4.51
5	3300	17.78	3.53	0.00	5.04
6	5100	16.85	3.92	0.00	4.30

From Figure 2.23 and Table 2.6, desulfidation of cis-cyclooctene episulfide gave an alkene/dithiodiolate ratio of about 10:1 and S=PPh_3/O=PPh_3 ratio of about 4:1 while *trans*-cyclooctene episulfide gave half alkene/dithiodiolate or 1:1 S=PPh_3/O=PPh_3, and also *cis*-cyclooctene episulfide consumed all PPh_3 after the reaction proceeded for 5 minutes at 75 °C. Consequently, direct S-atom transfer was favored by *cis*-cyclooctene episulfide by at least two times over *trans*-cyclooctene episulfide since both dithiodiolates are thermodynamically favored.

2.4.5 Monothiodiolate vs. Dithiodiolate

Even though dithiodiolate formation was initially claimed via Tp'ReOS and Tp'ReO_2S intermediates (ch 1.7, p. 19), monothiodiolate had never been observed, and for cyclooctene episulfide there was no

monothiodiolate formed either. Chemical properties of Tp'ReO_2S compared to Tp'ReO_3 should be similar.

Earlier studies showed Tp'ReO_3 undergoes cycloaddition to *trans*-cyclooctene to form 1,2-*trans*-diolate[47], and also independently synthesized compounds *trans*-diolate, *trans*-monothiodiolate, cis- and *trans*-dithiodiolate as noted in 2.4.1-2.4.3 are stable for at least one week at 75 °C. One possibility was that Tp'$ReOS_2$ might be very reactive toward with PPh_3 to give Tp'ReOS followed by a final step to form dithiodiolate.

Tp'ReO(OH)(OEt), a phosphine free source of Tp'ReO_2 (9.03 mM), was used to react with cis- or *trans*-cyclooctene episulfide (45.20 mM; TMS 0.23 mM as an internal standard in 0.5 mL C_6D_6). *trans*-Monothiodiolate was observed in the reaction with *trans*- and *cis*-dithiodiolate as shown in Table 2.7. Formation of alkene and dithiodiolate supported the direct S-atom transfer.

Table 2.7 PPh_3Free System

a) *trans*-cyclooctene episulfide

Expt	t(sec)	[trans-monothiodiolate]mM	[trans-dithiodiolate]mM	[cis-dithiodiolate]mM
1	0	0	0	0
2	300	0	0	0
3	86400	0.61	1.92	0.59

b) *cis*-cyclooctene episulfide

Expt	t(sec)	[cis-monothiodiolate]mM	[cis-dithiodiolate]mM	[cis-cyclooctene]mM
1	0	2.5608*	0.8052	7.92
2	300	4.7784*	1.5312	8.1048

*** Structure not confirmed yet: ^{1}HNMR: 5.23 (m, 1H), and 3.92 (m, 1H) ppm Comparison with trans-cyclooctane dithiodiolate ^{1}H NMR: 4.88 (m, 1H), and 3.95 (m, 1H) ppm**

This result shows that the thermodynamically favored monothiodiolate will form under the right conditions, but the most possible reason why monothiodiolate had never been observed in the presence of PPh_3 is due to kinetic control factors. Both systems (with and without PPh_3) generate $Tp'ReO_2$. If monothiodiolate formed by ring expansion, then it would be expected to form under both conditions. However, if it forms by cycloaddition to $Tp'ReO_2S$, then suppressing accumulation of this intermediate would prevent monothiodiolate formation. Rapid reaction of PPh_3 would form either $Tp'ReO_2$ (S-atom transfer) and continued catalytic desulfidation, or Tp'ReOS. The latter can lead to dithiodiolate by either ring expansion (1 step) or by S-atom transfer and alkene cycloaddition (2 steps).

cis-Dithiodiolate formation in trans-cyclooctene episulfide system was attributed to isomerization of *trans*-cyclooctene. The control experiment

using $Tp'ReO_3/PPh_3$ and *trans*-cyclooctene showed 10% of trans-cyclooctene converts to cis-cyclooctene within 19 hours at 75 °C. In contrast, *trans*-cyclooctene by itself showed no change, and also when only $Tp'ReO_3$ was used with *trans*-cyclooctene, *trans*-diolate was the only product. This evidence suggested $Tp'ReO_2$ (or Tp'ReOS) can catalyzed the isomerization.

For cis-cyclooctene episulfide, there were 5 species formed during reaction; *cis*-cyclooctene was the major product forming by direct S-atom transfer since monothiolate and dithiodiolate are stable at 75 °C. cis-Dithiodiolate (*syn*, *anti*) was formed in a 1:4 ratio with alkene. *cis*-Monothiodiolate formation was assigned on the basis of comparison to *trans*-monothiodiolate's ^1H NMR spectrum. The last one gave a multiplet NMR signal at 4.10 ppm in a 1: 2.5 with ratio alkene. The last two products also dominated in the reaction of $Tp'ReO_3/PPh_3$ and cis-episulfide which may have contributed to rapid PPh_3 consumption during the reaction. Even more, these unknown species would be involved in desulfidation.

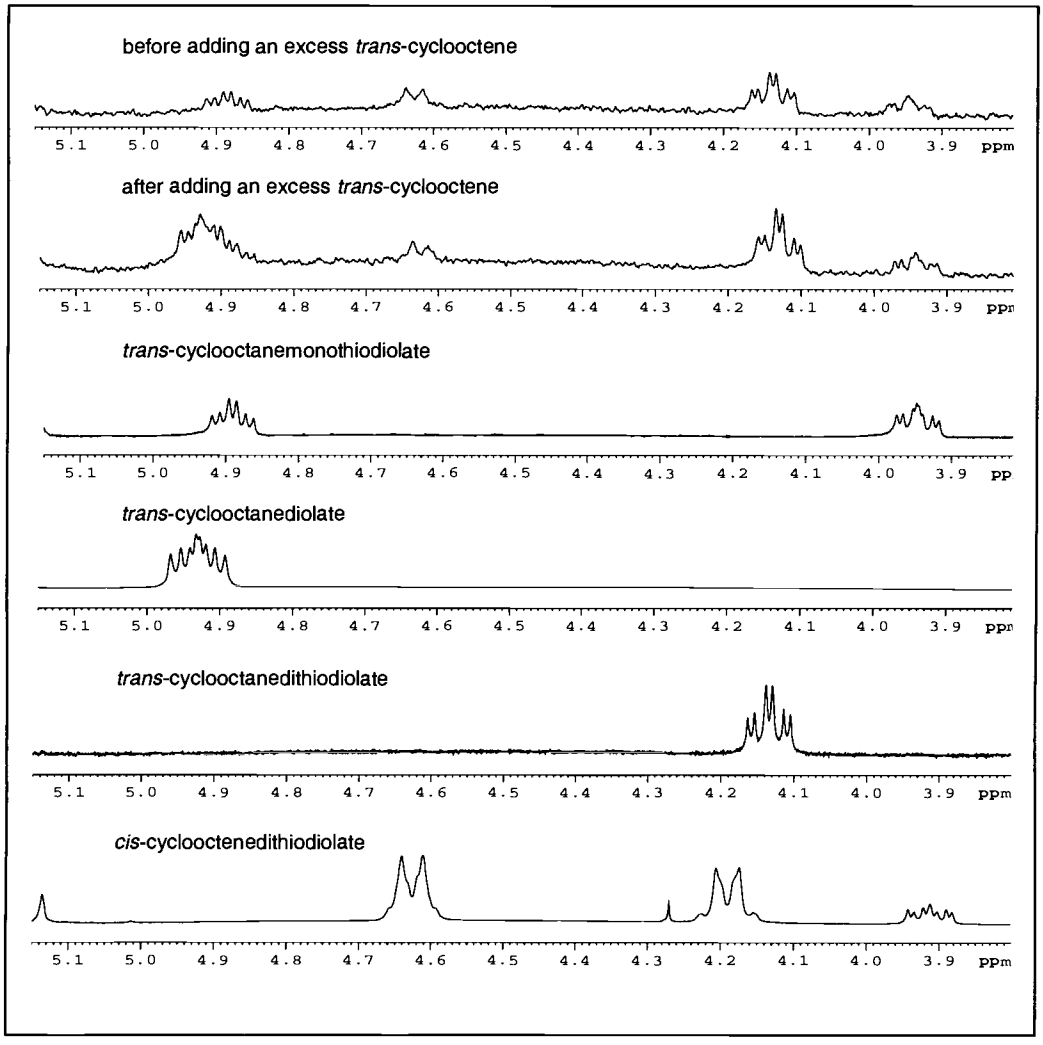
For *trans*-cyclooctene desulfidation with $Tp'ReO_3/PPh_3$, there was no *cis*-dithiodiolate or *trans*-monothiodiolate to be observed but another unknown signal appeared: ^1H NMR δ 4.38(m, 1H), 3.72(m, 1H) ppm in 1:3 ratio during the initial 30 minutes of reaction, and with *trans*-cyclooctane dithiodiolate in a 1:1.5 ratio with *trans*-dithiodiolate late in the reaction after

3 days at 75°C, and also the 10% isomerization of trans-cyclooctene to cis-cyclooctene was observed after 55 minutes of reaction .

2.4.6 Metal Oxo Donor and Acceptor

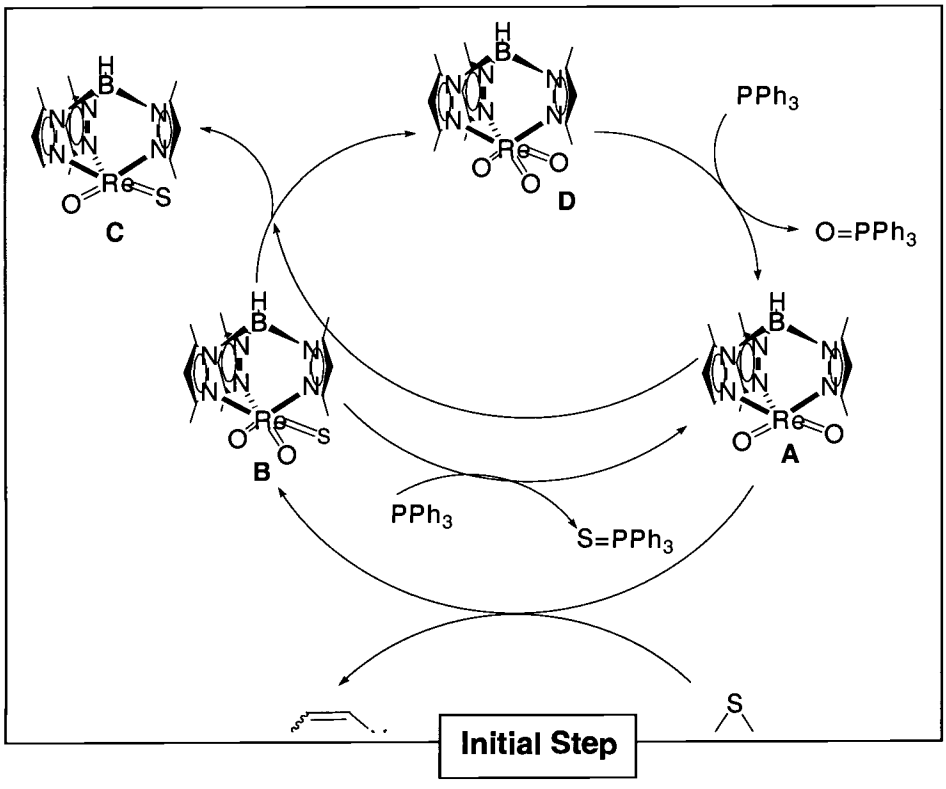
Formation of dithiodiolates under phosphine-free conditions, Table 2.7, showed the internal oxo transfer reaction[18] leading to metal-centered oxidation and reduction of reactants. In this reaction, a high-valent oxorhenium group is the atom donor, ($Tp'ReO_2S$, Re(VII)) and a rhenium center with two oxo groups or one oxo and one sulfido the acceptors, ($Tp'ReO_2$ or Tp'ReOS, Re(V)). Either O or S could be transferred, leading to a mixture of $Tp'ReO_3$, $Tp'ReO_2S$, $Tp'ReOS_2$ and $Tp'ReS_3$. $Tp'ReO_3$ formation in reaction was tested by adding an excess amount, 2.5 mg, of *trans*-cyclooctene into reaction tube after sixth day. *trans*-Cyclooctene diolate was observed at 0.40 mM after heated 24 hours at 75±0.1 ^{0}C as shown in Figure 2.24. The initial concentration of Tp'ReO(OH)(OEt) was 9.03 mM, and trans-episulfide was 45.20 mM in 0.50 mL C_6D_6.

Figure 2.24: Diolate formation in Tp'ReO(OH)(OEt) system



The new desulfidation catalytic cycle was proposed as shown in Fig 2.10 and 2.11.

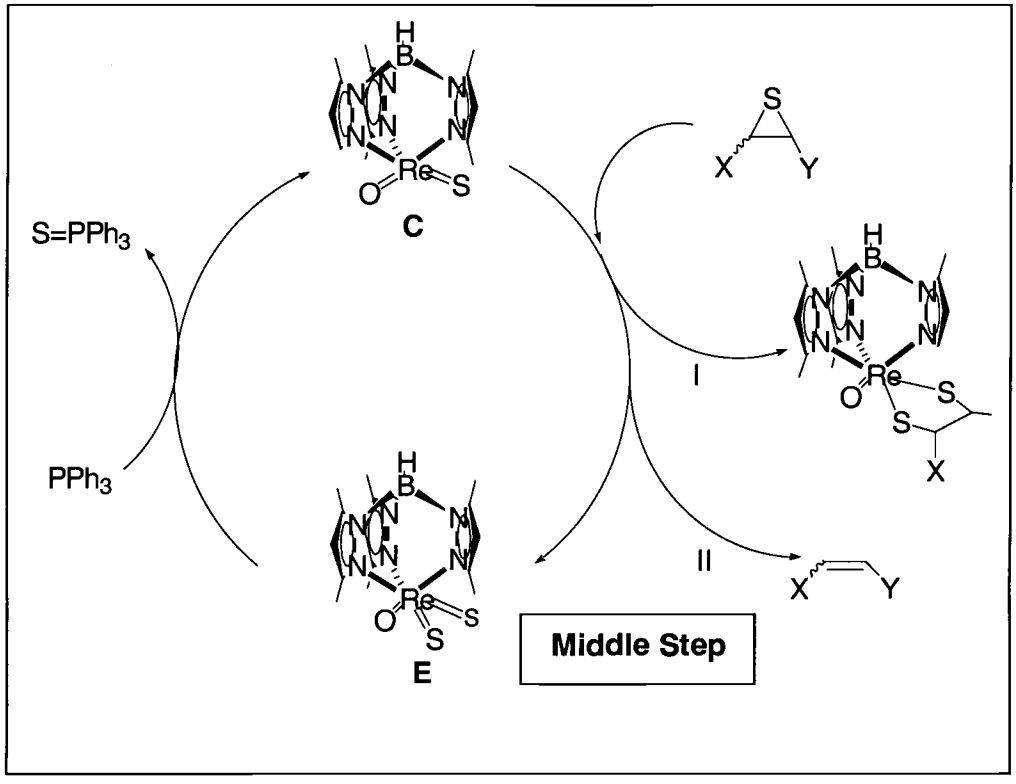
Figure 2.25: Desulfidation Catalytic Cycle, Initial Step



In the initial step, sulfur atom abstraction by the $Tp'ReO_2$, **A**, gives $Tp'ReO_2S$, **B**, which presumably is highly reactive with PPh_3. It is rapidly reduced; without PPh_3 it can react with more $Tp'ReO_2$ to either do a degenerate S-atom transfer, or an O-atom transfer. Then $Tp'ReO_3$, **D**, is reused in the catalytic cycle. Quantitatively, two moles of $Tp'ReO_3$ are

needed to give one mole of Tp'ReOS, **C**, for the next step leading to dithiodiolate.

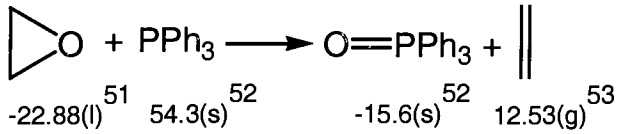
Figure 2.26: Desulfidation Catalytic Cycle, Middle Step



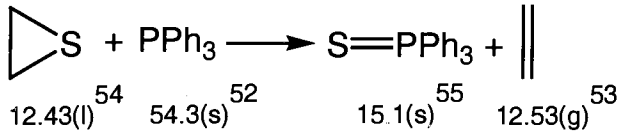
Obviously, Tp'ReOS or Tp'ReO_2 can serve as S-atom carriers to PPh_3, leading to catalytic turnover via direct S-atom transfer while ring expansion or alkene cycloaddition processes will shut down the cycle by forming inert thiodiolates.

2.4.7 Epoxide vs. Episulfide Selectivity

Obviously, our results demonstrated for direct atom transfer that it is easier to abstract a sulfur atom from an episulfide mediated by rhenium species than it is to remove an oxygen atom from an epoxide, and also the enthalpy of reactions for the non-catalyzed reaction shows it is thermodynamically more favored to abstract a sulfur atom. The non-catalyzed reactions are given in kcal/mol unit as shown.



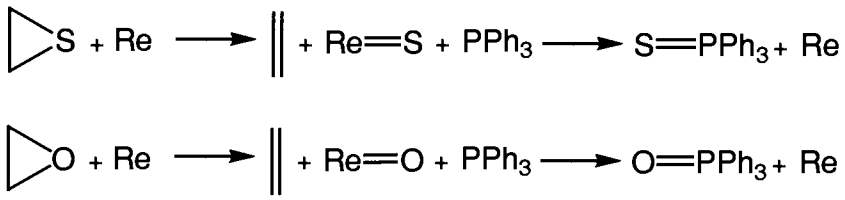
ΔH^0= -34.5 kcal/mol



ΔH^0= -39.1 kcal/mol

Since all PPh_3 was consumed rapidly in the catalyzed desulfidation for *cis*- and *trans*-episulfides, the rhenium complex effectively by lowered the transition state barrier, $\Delta G^{\neq}$, of the desulfidation, more so than the deoxygenation.

Catalyzed reaction by rhenium species:



For *cis*- and *trans*-isomers, there will be more steric hindrance in *trans*-episulfide or epoxide complexes which is consistent with our result: the *trans*-isomer reacted more slowly in both cases. Although the *trans*-isomer has bond strain energy to drive the reaction, it needs to form the coordinated epoxide or episulfide complex first before reacting to give alkene or diolate.

Combining the kinetic data and thermodynamic data, *cis*-episulfide is the most reactive and *trans*-oxide is the least reactive as follow: *cis*-cyclooctene episulfide> *trans*-cyclooctene episulfide> *cis*-cyclooctene oxide>*trans*-cyclooctene oxide.

Chapter 3. Experimental

3.1 General Methods

All reactions were performed using either standard bench top or inert atmosphere techniques[56] on a double-manifold Schlenk line or in a nitrogen-filled glove-box (Vacuum-Atmospheres Co. HE 493). All deuterated solvents were used as purchased from Cambridge Isotope Labs. Benzene, dichloromethane, and THF were dried, degassed and distilled under vacuum prior to use. Benzene was pre-dried with CaH_2 overnight then dried with Na/K alloy. Dichloromethane was distilled from CaH_2. THF was distilled from Na/benzophenone. Chemical reagents were used as purchased from Aldrich or Acros (Fisher), unless otherwise noted. Triphenylphosphine was recrystallized from hexane. Silica gel (Scientific, Catalog Number: 162544, Particle Size: 32-63, Lot Number 322303201 and 322044201) was used for flash column chromatography. Molecular Sieves (4 Å, Fisher) were activated by heating at 150 °C overnight prior to use. Hydrido-*tris*-(3,5-dimethyl-1-pyrazolyl)borato(trioxo)rhenium(VII), Tp'ReO_3, and Hydrido-*tris*-(3,5-dimethyl-1-pyrazolyl)borato(ethoxy)(hydroxyl)(oxo)-rhenium, Tp'ReO(OH)(OEt), were prepared according to the procedure described by Brown[42].

GC-MS spectra were collected on an HP 5890 II GC/5971A MSD under 99.999% helium using an RTX-20 column, 0.25 mm diameter, 30 m long with a 5 m guard column, coated with a 1 μm film of 20% diphenyl and 80% dimethyl polysiloxane.

Fast atom bombardment/mass spectroscopy (FAB/MS) were performed on a Kratos MS-50TC (Manchester, England, United Kingdom) double focusing instrument operated at unit resolution. The analyte of interest was mixed on the probe tip with a 3-nitrobenzyl alcohol (98%, Sigma-Aldrich) matrix. Xenon gas was used to generate the primary ionizing beam from an Ion-Tech gun operated at 7-8 kV. For high mass accuracy measurements with the FAB/MS, polyethylene glycol (PEG) was used a reference compound. The mixture consisted of PEG compounds in three masses: 600, 800, and 1000. The ratio of PEG's was 4:2:1, respectively.

Infrared spectra (KBR pellet) were run on a Nicolet Magna-IR560.

3.2 NMR Measurement

All NMR spectra were collected on either a Brüker DP300 (operating at 300.13 MHz for ^{1}H or 75.409 MHz for ^{13}C, 121.50 MHz for ^{31}P) or a Brüker DPX400 (operating at 400.134 MHz for ^{1}H or 100.614 MHz for ^{13}C). All chemical shifts were referenced to residual protons or carbons in

deuterated solvents and reported in ppm downfield from tetramethylsilane. T_1 measurements were done by the inversion-recovery method[57]. Baseline correction was performed on all FIDs and Fourier transformed spectra. For quantitative NMR work, relaxation delays of 70 s (>5 T_1, T_1 = 12.829 s) per pulse for the sample using tetramethylsilane as an internal standard or 30 s (>5 T_1) for the sample using anisole as an internal standard were collecting on the Brüker DPX400 at 16 scans.

3.3 Measurement of Kinetics

Reaction rates were followed by measuring ^1H or ^{31}P NMR integrations; a relaxation delay of 70 s (>5 T_1) per pulse at 15 scans was used in collecting NMR spectra to ensure accurate integration. Tetramethylsilane or anisole was used as an internal integration standard. All epoxide and episulfide solutions were prepared by mixing epoxide or episulfide with C_6D_6, PPh_3 and pre-dried tetramethylsilane in C_6D_6 solvent over CaH_2, decanting, then adding to solid Tp'ReO_3 or Tp'ReO(OH)(OEt) .

A representative example is given for deoxygenation of *trans*-cyclooctene oxide. To make a stock solution of anisole/C_6D_6, anisole (5.0 mg, 46.24 mmol) was added to a 4 mL volumemetric flask of C_6D_6 then a 0.5 mL aliquot was dissolved with C_6D_6 to make a stock solution totaling 3 mL of anisole in a 3 mL volumemetric flask with *trans*-cyclooctene oxide

(21.40 mg, 0.17mmol, 56.60 mM) which was then pre-dried with CaH_2 overnight at 10 °C. A 0.50 mL aliquot was then added to an NMR tube containing Tp'ReO_3 (2.4 mg, 0.0045 mmol) and triphenylphosphine (3.55 mg, 0.0135 mmol), then sealed under vacuum.

The tube was then submerged and heated to 75.0 ± 0.1°C in a water/ethylene glycol bath. The sample tube was periodically removed and cooled to 25°C and the ^1H NMR spectrum was collected. Other kinetic measurements used analogous procedures.

3.4 Synthetic Procedures

3.4.1 *trans*-Cyclooctene Oxide

trans-Cyclooctene was prepared according to Cope's procedure[58]. By adopting Sharpless's epoxidation procedure[59], *trans*-cyclooctene oxide was obtained in high yield. To a solution of *trans*-cyclooctene (1.15 g, 9.13 mmol) in 1.60 mL THF was added *bis*-(trimethylsilyl) peroxide, BTSP, (3.30 g, 18.5 mmol). The reaction vial was placed into an ice/water bath under an argon atmosphere. Portions of a solution of Re_2O_7 (0.567g, 0.117 mmol, 1.3 mol-% based on *trans*-cyclooctene) in 0.94 mL THF were added very slowly over 30 minutes. After stirring an addition of 40 minutes at 2 °C, the solution turned a light yellow color. The mixture was allowed to warm to room

temperature overnight and stirred. Water (3 drops) and manganese dioxide (ca. 5.5 mg) were added in order to decompose the remaining peroxide as noted by the disappearance of the yellow color. The filtered clear solution was dried over Na_2SO_4. The mixture was again filtered, and the volatiles removed under reduced pressure. The product was purified by flash column chromatography on silica gel. Dichloromethane was used to elute the colorless *trans*-cyclooctene oxide. Yield: 1.0036 g (7.97 mmol, 75.5%). ^{1}H NMR (C_6D_6): δ 0.80 (m, 2H), 0.96 (m, 2H), 1.23 (m, 2H), 1.68 (m, 2H), 1.80 (m, 2H), 2.12 (m, 2H), 2.52 (m, 2H). ^{13}C NMR (C_6D_6): δ 28.83, 28.88, 33.10, 59.02. GC-MS (EI): 126 [M^+].

3.4.2 *trans*-Cyclooctene Episulfide

This was prepared according to Adam[60]. Into a 250 mL thick walled glass bomb equipped with a Teflon valve were placed $MoO(S_2CNEt_2)_2$ (ca.0.7797 g, 2.23 mmol), sulfur (1.7375 g, 54.2 mmol), and *trans*-cyclooctene (3.4102 g, 27.1 mmol) in 50 mL of acetone. The solution was then freeze-pump-thaw degassed. The vessel was stirred at 74 °C for 24 hours. The mixture was filtered, and the volatiles removed under reduced pressure. The product was purified by flash column chromatography on silica gel. A 3:1 mixture of dichloromethane and petroleum ether was used to elute the product. Removal of solvent left *trans*-cyclooctene episulfide. Yield: 2.8796

g (20.3 mmol, 74.9%). ^{1}H NMR (C_6D_6): δ 0.87 (m, 2H), 0.94 (m, 2H), 1.35 (m, 2H), 1.67 (m, 2H), 2.31 (m, 2H), 2.45 (m, 2H). ^{13}C NMR (C_6D_6): δ 28.53, 32.08, 37.32, 43.06 GC-MS (EI): 142 [M^+].

3.4.3 *cis*-Cyclooctene Episulfide

This was prepared according to Takido[61]. Into a 500 mL round bottom flask was placed *cis*-cyclooctene oxide (25.00 g, 176 mmol) in 200 mL of dichloromethane. A solution of dimethylthioformamide (39.23 g, 440 mmol) and trifluoroacetic acid (2.53 g, 22 mmol) was added. The reaction flask was stirred at 71 °C for 6 hours under a nitrogen atmosphere. The volatiles were removed under reduced pressure. The residual mixture was extracted with 300 mL of petroleum ether and then washed with water (300 mL) to remove the remaining dimethylthioformamide and trifluoroacetic acid. The organic layer was dried over Na_2SO_4. Removal of solvent left *cis*-cyclooctene episulfide. Yield: 16.50 g (116.2 mmol, 66.0%). ^{1}H NMR (C_6D_6): δ 1.35 (m, 10H), 2.20 (m, 2H), 2.67 (m, 2H). ^{13}C NMR (C_6D_6): δ 26.65, 29.69, 30.02, 40.93. GC-MS (EI): 142 [M^+].

3.4.4 *trans*-Mercaptocyclooctanol

This was prepared according to Whitham[62]. Into a 100 mL round bottom flask were added sulfur (9.60 g, 300 mmol), and sodium borohydride (3.80 g, 100 mmol). The reaction flask was then placed in an ice/water bath and 80 mL of dry tetrahydrofuran added rapidly. The reaction flask was then placed under a nitrogen atmosphere while a large amount of hydrogen was generated. After evolution of hydrogen had ceased (10 minutes), *cis*-cyclooctene oxide (6.30g, 50 mmol) was added. Then the mixture was heated under reflux at 66 °C for 42 hours. To work up the reaction, aqueous sodium hydroxide (10% w/v 100ml) was added into the reaction flask followed by extraction with chloroform. After removal of solvent, this gave a glassy solid of crude bis-(2-hydroxycyclooctyl) disulfide (4.60g, 14.4 mmol) which was added into a 50 mL reaction flask containing 25 mL of dry ether. Excess $LiAlH_4$ (0.1 M, 30.0 mL, 30.0 mmol) was then added dropwise to reduce bis-(2-hydroxycyclo-octyl) disulfide. The mixture was heated under reflux for 3 hours and cooled to 10 °C for 16 hours. Water (7.20 g) was added dropwise into the reaction flask to decompose the remaining $LiAlH_4$, and ether was used to extract *trans*-mercaptocyclooctanol. The volatiles were removed under reduced pressure to leave *trans*-mercaptocyclooctanol. Yield: 2.80 g (17.5 mmol, 35.0%). ^1H NMR (C_6D_6): δ 1.45 (m, 2H), 1.66 (m, 2H), 1.81 (m, 2H), 2.751 (m, 1H), 3.56 (m, 1H). ^{13}C

NMR (C_6D_6): δ 24.91, 25.73, 33.53, 33.64, 48.22, 77.70 GC-MS (EI): 160 [M^+].

3.4.5 Hydrido-*tris*-(3,5-dimethyl-1-pyrazolyl)borato(*trans*-cyclooctane-1,2-diolato)(oxo)rhenium(V)

This was prepared from *trans*-cyclooctanediol according to Ness[63].

3.4.6 Hydrido-*tris*-(3,5-dimethyl-1-pyrazolyl)borato(*cis*-cyclooctane-1,2-diolato)(oxo)rhenium(V)

This was prepared from *cis*-cyclooctanediol according to Gable[35].

3.4.7 Hydrido-*tris*-(3,5-dimethyl-1-pyrazolyl)borato(*trans*-cyclooctane-1,2-monothiodiolato)(oxo)rhenium(V)

This was prepared according to Gable[64]. Into a 250 mL thick-walled glass bomb equipped with a Teflon valve were placed Tp'ReO_3 (0.1441 g, 0.27 mmol), triphenylphosphine (0.0822 g, 0.31 mmol), *p*-toluenesulfonic acid monohydrate (0.0507 mg, 0.27 mmol), ground molecular sieves (1.0 g), and *trans*-2-mercaptocyclooctanol (0.043 g, 0.27 mmol) in 5.0 mL of dry THF. The solution was then freeze-pump-thaw degassed. The vessel was stirred

at room temperature for 24 hours. The blue-green solution was filtered, and the volatiles removed under reduced pressure. The product was purified by flash column chromatography on silica gel. A 1:1 mixture of dichloromethane and hexane was used to elute the blue-green product. Removal of solvent left a light blue solid. Yield: 0.0109 g (0.0166 mmol, 6.1%). The stereochemistry of this compound was determined by the NOESY and nOe experiments discussed in Chapter 2. ^{1}H NMR (C_6D_6): δ 1.38 (m, 1H), 1.53 (m, 2H), 1.68 (m, 2H), 1.77 (m, 1H), 1.82 (m, 1H), 1.88 (s, 3H), 1.99 (m, 1H), 2.02 (m, 1H), 2.22 (s, 3H), 2.35 (s, 3H), 2.55 (m, 1H), 2.82 (m, 1H), 3.95 (ddd, J= 4.85, 9.15, 13.90, 1H), 4.89 (ddd, J= 4.76, 10.70, 13.90, 1H), 5.16 (s, 3H), 5.56 (s, 1H), 5.56 (s, 1H). ^{13}C NMR (C_6D_6): δ 12.13, 12.13, 12.13, 12.52, 15.84, 17.02, 24.95, 26.70, 27.15, 27.56, 38.90, 40.26, 62.69, 106.47, 107.17, 107.95, 108.29. IR (KBr): 2921, 2852, 2538 (ν_{BH}), 1545, 1452, 1416, 1383, 1206, 1066,1044, 950 (ν_{ReO}), 920, 816, 657 cm^{-1}. MS (FAB): (^{187}Re) 658.6 [M^{+}].

3.4.8 Hydrido-*tris*-(3,5-dimethyl-1-pyrazolyl)borato(*trans*-cyclooctane-1,2-dithiodiolato)(oxo)rhenium(V)

Into a 250 mL thick-walled glass bomb equipped with a Teflon valve were placed Tp'ReO_3 (0.5752 g, 1.08 mmol), triphenylphosphine (0.9935 g, 3.79 mmol), *trans*-cyclooctene episulfide (0.5006 g, 3.52 mmol) in 4 mL of dry

C_6D_6. The solution was then freeze-pump-thaw degassed. The vessel was stirred at 75°C for 24 hours. The dark brown solution was filtered, and the volatiles removed under reduced pressure. The product was purified by flash column chromatography on silica gel. A 1:1 mixture of dichloromethane and hexane was used to elute the dark brown product. Removal of solvent left a dark brown solid. Yield: 0.1748 g (0.259 mmol, 23.59%). The stereochemistry of this compound was determined by the NOESY and nOe experiments discussed in Chapter 2. ^{1}H NMR (C_6D_6): δ 1.54 (m, 2H), 1.63 (m, 1H), 1.73 (m, 2H), 1.74 (m, 1H), 1.86 (m, 1H), 1.89 (s, 3H), 1.92 (m, 1H), 2.01 (m, 1H), 2.17 (s, 3H), 2.17 (s, 3H), 2.43 (s, 3H), 2.52 (m, 1H), 2.86 (m, 1H), 3.06 (s, 3H), 3.20 (m, 1H), 3.58 (ddd, J= 3.38, 9.70, 13.45, 1H), 4.13 (ddd, J= 3.48, 9.61, 13.45, 1H), 5.20 (s, 1H), 5.58 (s, 1H), 5.59 (s, 1H). ^{13}C NMR (C_6D_6): δ 12.17, 12.37, 12.37, 15.95, 16.10, 17.47, 26.39, 26.96, 27.17, 27.20, 38.02, 39.57, 63.88, 71.77, 107.84, 108.58, 108.60. IR (KBr): 2923, 2549 (ν_{BH}), 1545, 1452, 1417, 1384, 1213, 1067,1041, 941 (ν_{ReO}), 669, 649 cm^{-1}. MS (FAB): (^{187}Re) 674.1 [M$^+$]. Also a 1:1 mixture of dichloromethane and acetone was used to elute the yellow-green product, an unknown. Removal of solvent left a yellow-green solid 18.1 mg. Spectroscopy data of this unknown compound is in appendix II.

3.4.9 Hydrido-*tris*-(3,5-dimethyl-1-pyrazolyl)borato(*cis*-cyclooctane-1,2-dithiodiolato)(oxo)rhenium(V)

Into a 250 mL thick-walled glass bomb equipped with a Teflon valve were placed Tp'ReO_3 (0.136 g, 0.256 mmol), triphenylphosphine (0.236 g, 0.90 mmol), *cis*-cyclooctene episulfide (0.128 g, 0.901 mmol) in 3 mL of dry C_6D_6. The solution was then freeze-pump-thaw degassed. The vessel was stirred at room temperature for 24 hours. The dark brown solution was filtered, and the volatiles removed under reduced pressure. The product was purified by flash column chromatography on silica gel. A 1:1 mixture of dichloromethane and hexane was used to elute the dark brown product. Removal of solvent left a dark brown solid. Yield: 0.0123 g (0.018 mmol, 7.03%). By NMR analysis, it was confirmed products are 10:7 ratio of *anti* and *syn* isomers. The stereochemistry of this compound was determined by the NOESY and nOe experiments discussed in Chapter 2.

IR and MS of Mixture:

IR (KBr): 2924, 2850, 2548, 2360 (ν_{BH}), 1525, 1452, 1416, 1367, 1213, 1066, 1041, 941 (ν_{ReO}), 861, 818, 778, 648 cm^{-1}. MS (FAB): (^{187}Re) 674.6 [M^+].

Spectroscopic data for *anti*-isomer:

^{1}H NMR (C_6D_6): δ 1.43 (m, 1H), 1.60 (m, 1H), 1.88 (s, 3H), 2.18 (s, 6H), 2.20 (m, 1H), 2.29 (m, 1H), 2.43 (s, 3H), 3.07 (s, 6H), 4.63 (m, 1H), 5.20 (m, 1H), 5.59 (s, 2H) ^{13}C NMR (C_6D_6): δ 12.18, 12.62, 16.48, 17.07, 26.27, 33.98, 65.32, 107.62, 108.68.

Spectroscopic data for *syn*-isomer:

^{1}H NMR (C_6D_6): δ 1.60 (m, 1H), 1.71 (m, 1H), 1.89 (s, 3H), 2.19 (s, 6H), 2.46 (m, 3H), 2.64 (m, 1H), 3.03 (m, 1H), 3.10 (s, 6H), 4.19 (m, 1H), 5.21 (m, 1H), 5.61 (s, 2H) ^{13}C NMR (C_6D_6): δ 12.19, 12.65, 16.48, 17.84, 30.39, 34.83, 67.20, 107.95, 108.80.

3.5 Procedure for Recrystallization of Hydrido-*tris*-(3,5-dimethyl-1-pyrazolyl) borato(*trans*-cyclooctane-1,2-dithiodiolato)(oxo)rhenium(V)

Crystals of hydrido-*tris*-(3,5-dimethyl-1-pyrazolyl)borato(*trans*-cyclooctane-1,2-dithiodiolato)(oxo)rhenium(V) were grown by re-crystallization from CH_3CN/H_2O. A saturated solution of the *trans*-cyclooctanedithiodiolate complex was prepared by adding dark brown solid to 5 mL acetonitrile until no more solid dissolved. The vial was sealed and left overnight. Then the

solution was filtered, and the filtrate was placed into the new 5 mL vial. This solution was then placed into a saturated atmosphere of water vapor at 10°C. The crystals of *trans*-cyclooctanedithiodiolate were obtained by filtration after 4 weeks.

Chapter 4. Conclusion and Future Work

Catalyst development for O-atom and S-atom transfer is important in academic and industrial chemistry. Our research has developed rhenium oxo complexes to use in deoxygenation or desulfidation. Both applications are very powerful approaches to saving environmental resources by converting low value materials to more valuable substances since the reactivity and selectivity have been studied. Since our rhenium complex is similar to molybdenum complexes, understanding desulfidation mediated by the rhenium species can lead to developing new catalysts to substitute for molybdenum sulfide derivatives for HDS.

We succeeded in measuring deoxygenation rate constants for *trans*-cyclooctene oxide. The ring expansion rate constant is $(1.24\pm0.03)\times10^{-5}$ s^{-1} and direct atom transfer is $(6.02\pm0.02)\times10^{-6}$ s^{-1}. *cis*-Cyclooctene showed a higher preference to give alkene (24.5:1) than *trans*-cyclooctene. The observed rate constant for direct atom transfer is 5.07×10^{-5} s^{-1} and the ring expansion rate constant is 2.07×10^{-6} s^{-1}.

The desulfidation catalytic model was extended in this work. We observed $Tp'ReO_3$ in the PPh_3 free system which used Tp'ReO(OH)(OEt) as $Tp'ReO_2$ source, and also direct atom transfer was also confirmed by forming dithiodiolate and alkene in this experiment.

Bibliography

1. *Homogeneous Catalysis*; Parshall, G. W., Wiley : New York 1980.

2. (a) Cuenoud, B.; Szostak, J. W. *Nature* **1995**, *375*(6532), 611-4. (b) Opazo, C. H. X.; Cherny, R. A.; Moir, R. D.; Masters, C.L.; Tanzi, R. E.; Inestrosa, N. C.; Bush, A.I.; *J. Biol. Chem.* **2002**, *277*(43), 4.0302-8.

3. *Cytochrome P-450: Stucture, Mechanism, and Biochemistry*; Ortez de Montellano, P. R., Ed.; Plenum: New York, 1985.

4. (a) Chianelli, R. R.; Pecordo, T.A. *J. Catal* **1981**, *67*, 430-445. (b) Bianchini, C.; Meli, A. *Acc. Chem. Res.* **1998**, *31*, 109-116.

5. (a) Evans, D. A.; Bender, S. C.; Morris, J. *J. Am. Chem. Soc.* **1998**, *110*, 2506. (b) Hanson, Rm.; Sharpless, K. B. *J. Org. Chem.* **1986**, *51*, 1992.

6. *Advance Organic Chemistry*, 4th Ed., Part B; Carey , F. A., Sunberg R. J.; Plenum: New York, 2001, 501.

7. Dittman , W.; Kirchhof, W.; Stumf, W.; *Ann. Chem. (Liebigs).* **1965**, *481*, 30.

8. Jacobsen, E. N. In *Catalytic Asymmetric Synthesis*, Ojima, I., Ed.; VCH Publishers: New York, 1993 and references cited therein.

9. Lee, D.G.; Chen, T. *J. Am. Chem. Soc.* **1989**, *111*, 1534.

10. Kolb, H.C.; Anderson, P.G.; Sharpless, K.B. *J. Am. Chem. Soc.* **1994**, *116*, 1278.

11. N. A. Milas, *J. Am. Chem. Soc.* **1937**, *58*, 1302.

12. *Fundamental Reaserch in Organometallic Chemistry*; Tsutsui, M., Ishii, Y., Yaozeng, H.; Science Press, 1980.

13. Hanson, R. M.; Sharpless, K. B. *J. Org. Chem.* **1986**, *51*, 1922.

14. Zhang, W.; Loebach, J. L.; Wilson, S. R.; Wilson, S. R.; Jacobson, E. N. *J. Am. Chem. Soc.* **1990**, *112*, 2801.

15. Adam, W.; Bargon, R. M.; Schenk, W. A.; *J. Am. Chem. Soc.* **2003**, *125*, 3871-3876.

16. *Transition Metal Sulfur Chemistry*; Stiefel, E. I., Matsumato, K., Ed.; ACS Symp. Ser. 1996 No. 653,

17. Riaz, U.; Curnow, O.; Curtis, M.D. *J. Am. Chem. Soc.* **1991**, *113*, 1416.

18. Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401-1449.

19. Sharpless, K. B.; Teranishi, A. Y.; Backvall, J. -E. *J. Am. Chem. Soc.* **1977**, *99*, 3120.

20. Brown, S. N.; Mayer, J. M. *J. Am. Chem. Soc.* **1996**, *118*, 12119.

21. (a) Cook, G. K.; Andrews, M. A. *J. Am. Chem. Soc.* **1996**, *118*, 9448. (b) Andrews, M. A.; Klaeren, S. A.; Gould, G. L. In *Carbohydrates as Organic Raw Materials II*, Descotes, G., Ed; VCH: New York, 1993.

22. (a) McCoy, M. *Chem. Eng. News* **1999**, 17-25 (b) Upson, L. L.; Schnaith, M. W. *Oil Gas J.* **1977**, 47-51

23.Chianelli, R. R.; Pecoraro, T. A.; Halbert, T. R.; Pan, W. H.; Stiefel, E.I. *J. Catal.* **1984**, *84*, 226-230

24. Sweeny, Z. K.; Polse, J. L.; Anderson, R. A.; Bergman, R.G. *J. Am. Chem. Soc.* **1998**, *120*, 7285-7834.

25. Rakowski DuBois, M.; Jagirdar, B.; Noll, B.; Dietz, S. *ACS Symp. Ser.* **1996**, No. 653, 259-281.

26. Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *Inorg. Chem.* **1986**, *25*, 4617-4618.

27. Coucouvanis, D. *Adv. Inorg. Chem.* **1998**, *45*, 1-73.

28. Goodman, J.T.; Rauchfuss, T.B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2083-2084.

29.Herrman, W. A.; Marz, D.; Herdtwick, E.; Schafer, A.; Wagner, W.; Kneupe, H. J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 462-464.

30. Cook, G. K.; Andrews, M. A. *J. Am. Chem. Soc.* **1996**, *118*, 9448.

31. Herrmann, W. A.; Serrano, R.; Küsthardt, U.; Ziegler, M. L.; Guggolz, E.; Zahn, T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 515.

32. Gable, K. P.; Juliette, J. J. J.; Gartman, M.A. *Organometallics* **1995**, *14*, 3138.

33. Gable, K. P.; Zhuravlev, F. A.; Yokochi, A. F. T. *Chem. Commun.* **1998**, 799-900.

34. Herrmann, W. A., et al, *Inorg. Chem.,* **1992**, *31*, 4431-4432.

35. (a) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3170-3177. (b) Mayer, J. M.; Northcutt, T. O.; Brugman, J.; Bennett, B. K.; Lovell, S. *Organometallics,* **2000**, *19*, 2781-2790.

36. Gable, K. P.; Abubaker, A.; Zientara, K.; Wainwright, A. M. *Organometallics* **1999**, *18*, 173-179.

37. Gable, K. P.; Chuawong, P.; Yokochi, A. F. T. *Organometallics* **2002**, *21*, 929-933.

38. Murray, H. H.; Wei, L. W.; Sherman, S. E.; Greney, M. A.; Eriksen, K. A.; Carstensen, B,; Halbert, T.R.; Stiefel, E.I. *Inorg. Chem.* **1995**, *34*, 841-853.

39. Goodman, J.T.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1999**, *121*, 5017-5022.

40. Rappe, A. K.; Goddard, W.A.; *J. Am. Chem. Soc.* **1982**, *104*, 3287-3294.

41. Gable, K. P.; Brown, E. C.; *Organometallics*, **2000,** *19*, 944-946.

42. Brown, E. C., Ph.D. Dissertation, Oregon state University, Corvallis, OR 2002 Chapter 2.

43. Gable, K. P.; Brown, E. C.; *J. Am. Chem. Soc*; 2003, *125*, Web Edition published 8/13/03.

44. Gable, K. P.; Brown, E. C.; *Organometallics*, **2003,** *22*, 3096-3101.

45. Rakowski-DuBois, M.; Pawicki, S. H.; Noll, B. C.; Kanney, J. A. *Inorg. Chem.* **2003**, *42*, 1556-1563.

46. Parkin, G. *Prog. Inorg. Chem.* **1998**, *47*, 1-166.
47. Chuawong, P., M.S. Thesis, Oregon State University, Corvallis, OR, 20001 Chapter 2.

48. Gable, K.P. Unpublished Work.

49. (a) *Oragnic Syntheses by oxidation with Metal compounds*; Mijs, W.J.; deJonghe C. R. H. I. Plenum: New York, 1986. (b) *Metal Catalyzed Oxidation of Organic Compounds*; Sheldon, R. A.; Kochi, J. K. Acdademic: New York, 1981 (c) *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; Wiley: New York, 1995; Vol. 3 pp 1649, 2078.

50. Sharpless, K. B.; Umbreit, M. A.; Nieh, M. T.; Flood, T. C. *J. Am. Chem. Soc.* **1972**, *94*, 6538.

51. *Thermochemistry of Organic and Organometallic Compounds*; Cox, J.D.; Pilcher, G.; Academic Press, New York, 1970, 1-636.

52. Bedford, A. F.; Mortimer, C. T. *J. Chem. Soc*, **1960**,1622-5.

53. *NIST-JANAF Themochemical Tables,* 4th Ed, J. Phys. Chem. Ref. Data, Monograph 9; Chase, M.W., Jr.; 1998, 1-1951.

54. Sunner, S. *Acta Chem. Scand.*, **1963**, *17*, 728-730.

55. Kirklin, Duane R.; Chickos, James S.; Liebman, Joel F. Chemical *Structural Chemistry*, **1996**, *7*(5/6), 355-361.

56. *Manipulation of Air-sensitive Compounds*; Shriver, D. F., Drezdzon, M. A.; Wiley: New York, 1986.

57. *150 and More Basic NMR Experiments*; Braun, S. Kalinnowski, H, -O; Wiley-VCH: New York, 1987.

58. Cope, A.C.; Bach, R.D. *Org. Syn.* **1969**, *49*, 39-44.

59. Sharpless, K. B.; Yudin, A. K. *J. Am. Chem. Soc.* **1997**, *119*, 11536-11537.

60. Adam, W.; Bargon, R. M. *Chem. Commun.* **2001**, 1910-1911.

61. Takido, T.; Kobayashi, Y.; Itabashi, K. *Synthesis* **1989**, *9*, 779-8.

62. Whitham, G. H.; Jones, M.; Temple, P.; Thomas, E.J.; *J. Chem. Soc., Perkin Trans. I* **1974**, 433.

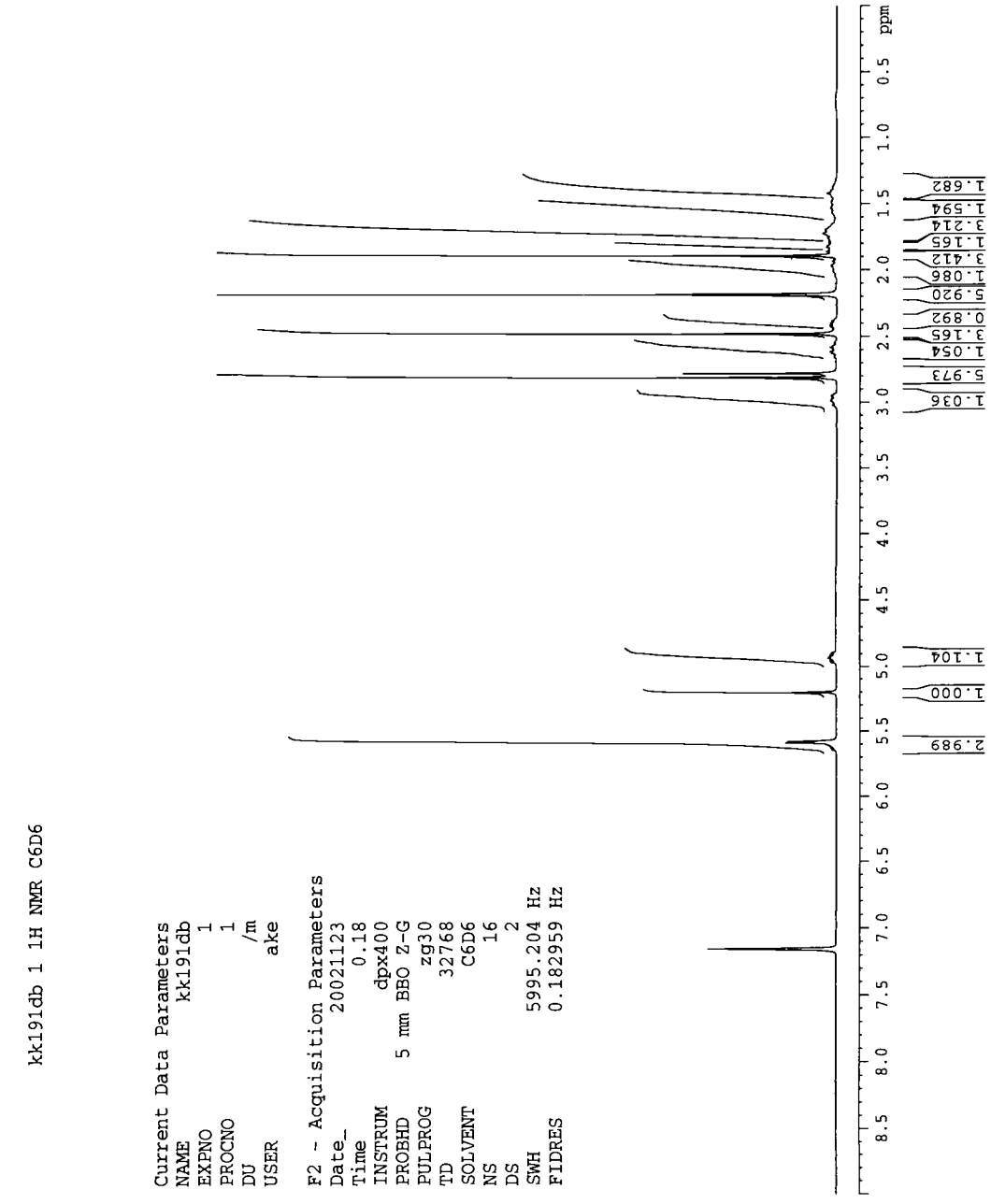
63. Ness, S. L., M.S. Thesis, Oregon State University, Corvallis, OR, 1999, Chapter 3.

64. Gable, K. P. *Organometallics* **1994,** *13*, 2486-2489

Appendix

Appendix I. NMR Spectra in C_6D_6

Figure A1.1: ^{1}H NMR and ^{13}C of 1,2-*trans*-Cyclooctanediolate



kk191db Exp 3 Stdcarb Tp;ReOOOtrans-cycloocene C6D6

```
Current Data Parameters
NAME                 kk191db
EXPNO                      3
PROCNO                     1
DU                        /m
USER                     ake

F2 - Acquisition Parameters
Date_               20021212
Time                   20.24
INSTRUM                dpx400
PROBHD     5 mm BBO Z-G
PULPROG              zgpg30
TD                     65536
SOLVENT                C6D6
NS                      1258
DS                         4
SWH                25125.629 Hz
FIDRES                 0.383387 Hz
AQ                  1.3042164 sec
RG                      4096
DW                    19.900 usec
DE                     6.00 usec
TE                    300.0 K
D1                 0.00300000 sec
D11                0.03000000 sec
D12                0.00002000 sec

============ CHANNEL f1 =============
NUC1                      13C
P1                       7.50 usec
PL1                     -3.00 dB
SFO1             100.5936186 MHz

============ CHANNEL f2 =============
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2                      0.00 dB
PL12                    17.40 dB
PL13                    18.00 dB
SFO2             400.0116000 MHz

F2 - Processing parameters
SI                         65536
SF               100.5825550 MHz
WDW                           no
SSB                            0
LB                        0.00 Hz
GB                             0
PC                         1.40

1D NMR plot parameters
CX                        20.00 cm
F1P                      200.000 ppm
F1                     20116.51 Hz
F2P                      0.000 ppm
F2                       0.00 Hz
PPMCM                 10.00000 ppm/cm
HZCM               1005.82556 Hz/cm
```

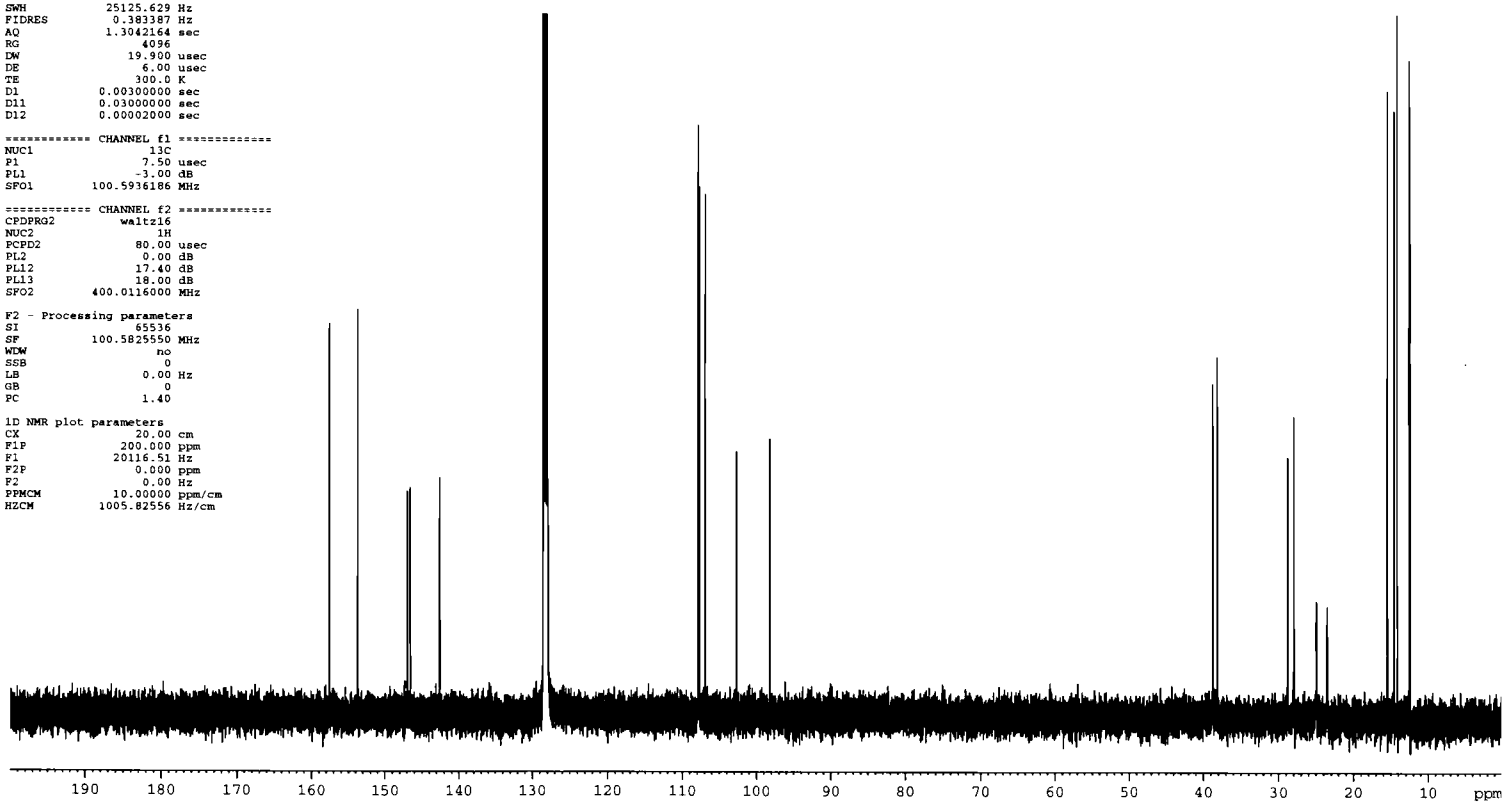
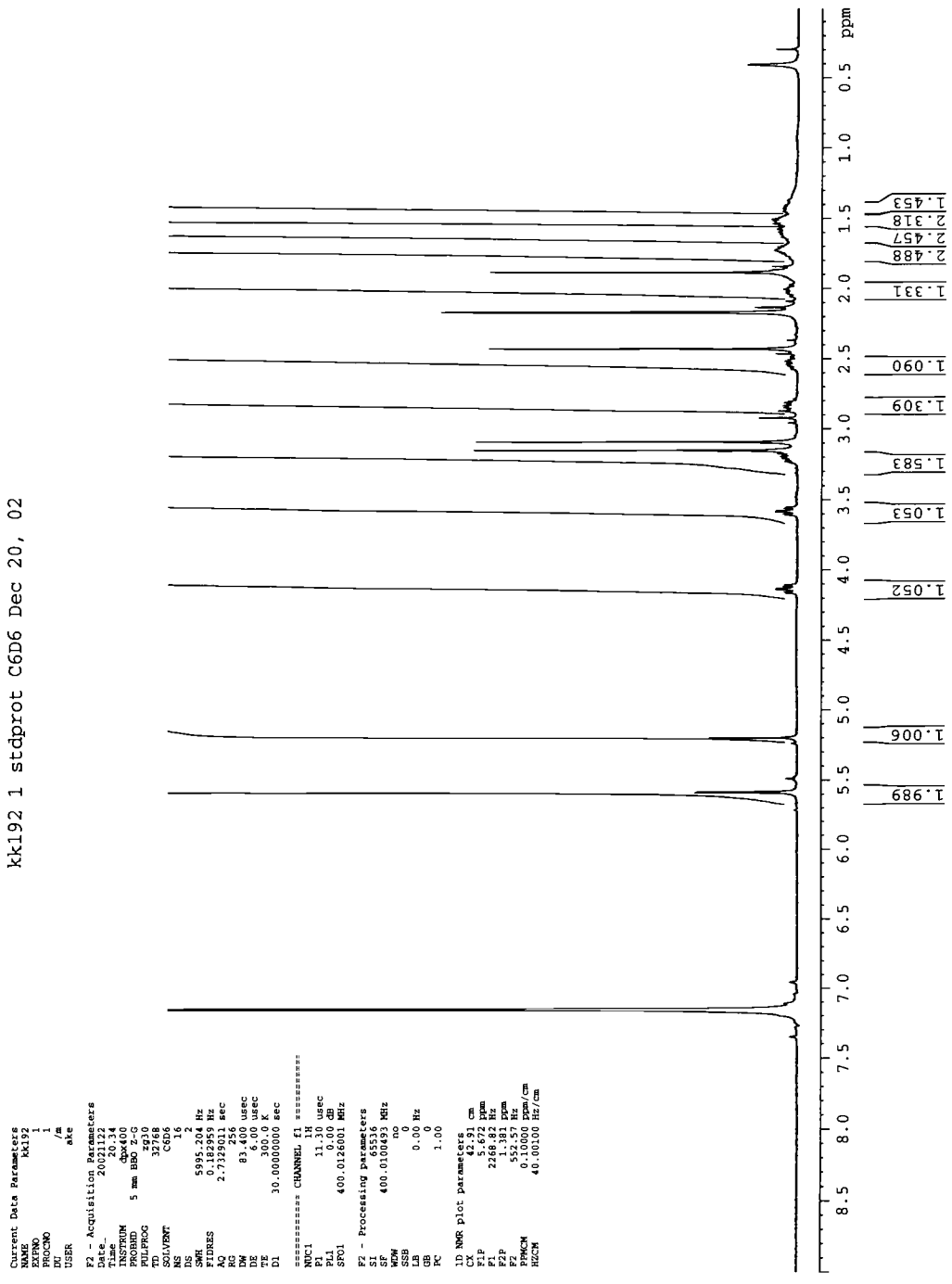


Figure A1.2: ^{1}H NMR and ^{13}C of 1,2-*trans*-Cyclooctanedithidiolate



kk192 3 stdcarb Tp'ReOSStrans-cyclooctene C6D6 Dec 12, 02

```
Current Data Parameters
NAME                  kk192
EXPNO                     3
PROCNO                    1
DU                       /m
USER                    ake

F2 - Acquisition Parameters
Date_              20021212
Time                  21.53
INSTRUM              dpx400
PROBHD     5 mm BBO Z-G
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1922
DS                        4
SWH              25125.629 Hz
FIDRES            0.383387 Hz
AQ               1.3042164 sec
RG                     1024
DW                  19.900 usec
DE                   6.00 usec
TE                  300.0 K
D1              0.00300000 sec
D11             0.03000000 sec
D12             0.00002000 sec

============ CHANNEL f1 =============
NUC1                  13C
P1                   7.50 usec
PL1                 -3.00 dB
SFO1         100.5936186 MHz

============ CHANNEL f2 =============
CPDPRG2           waltz16
NUC2                  1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                17.40 dB
PL13                18.00 dB
SFO2         400.0116000 MHz

F2 - Processing parameters
SI                    65536
SF           100.5825550 MHz
WDW                      no
SSB                       0
LB                    0.00 Hz
GB                        0
PC                    1.40

1D NMR plot parameters
CX                   20.00 cm
F1P                 200.000 ppm
F1                20116.51 Hz
F2P                   0.000 ppm
F2                    0.00 Hz
PPMCM            10.00000 ppm/cm
HZCM           1005.82556 Hz/cm
```

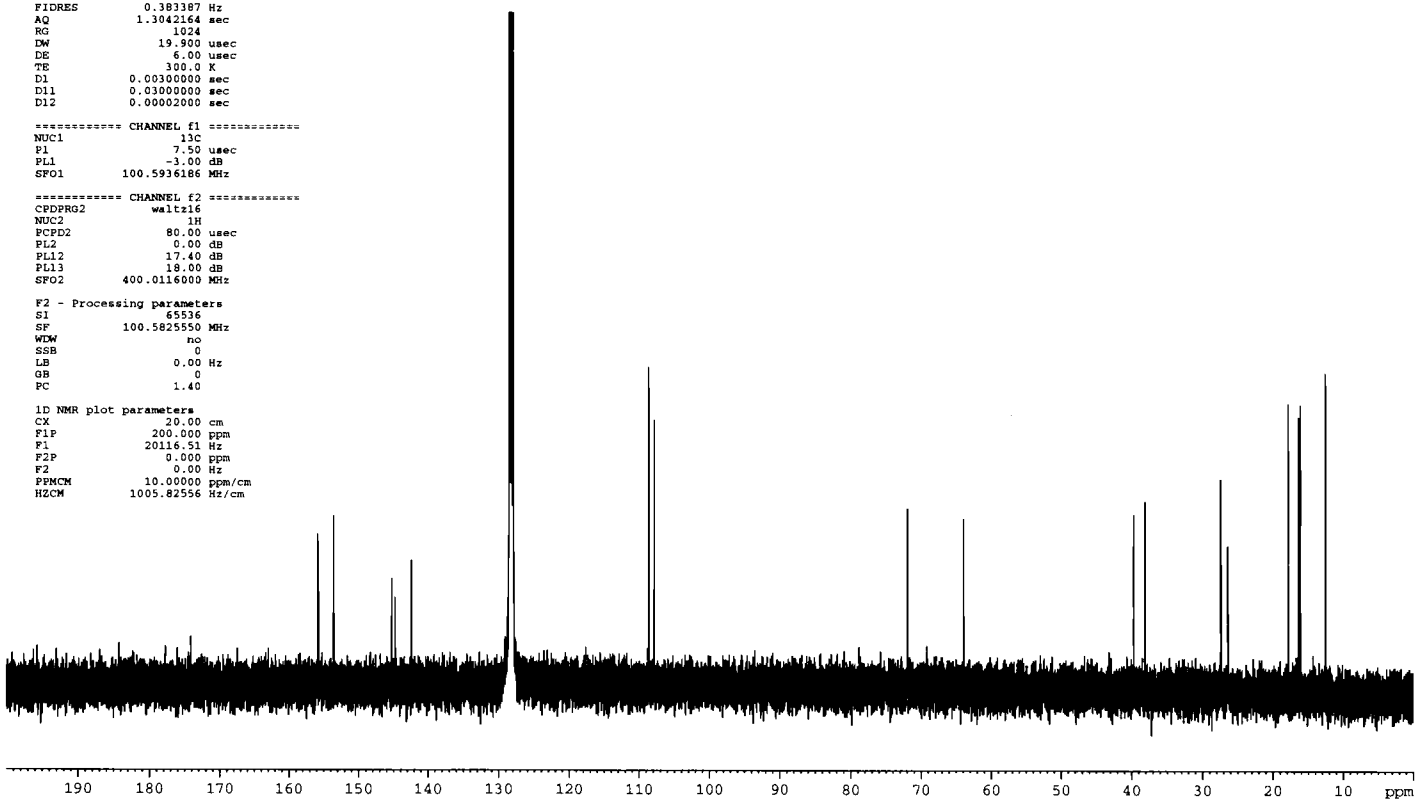


Figure A1.3: ^{1}H NMR of 1,2-*cis*-Cyclooctanediolate

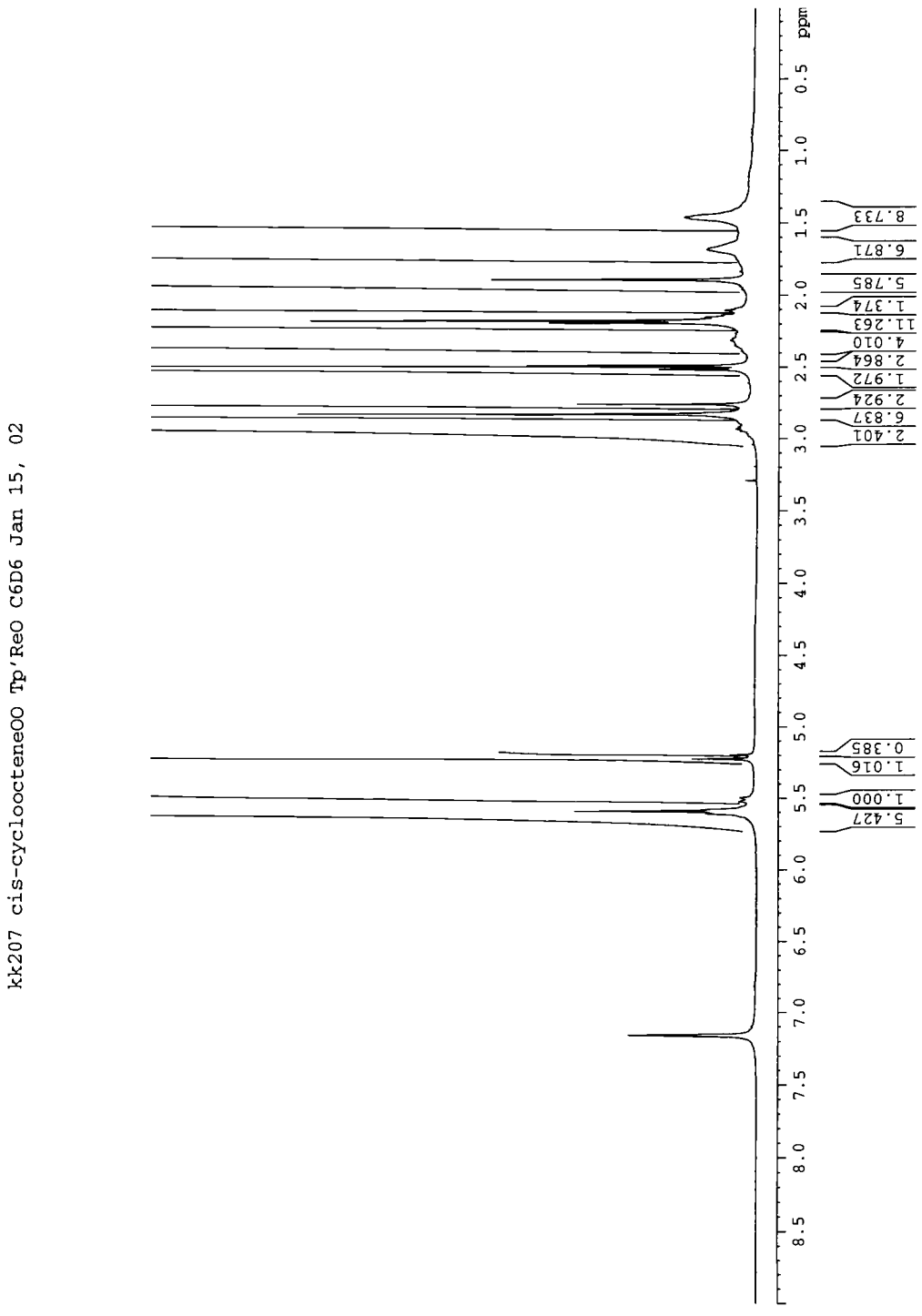
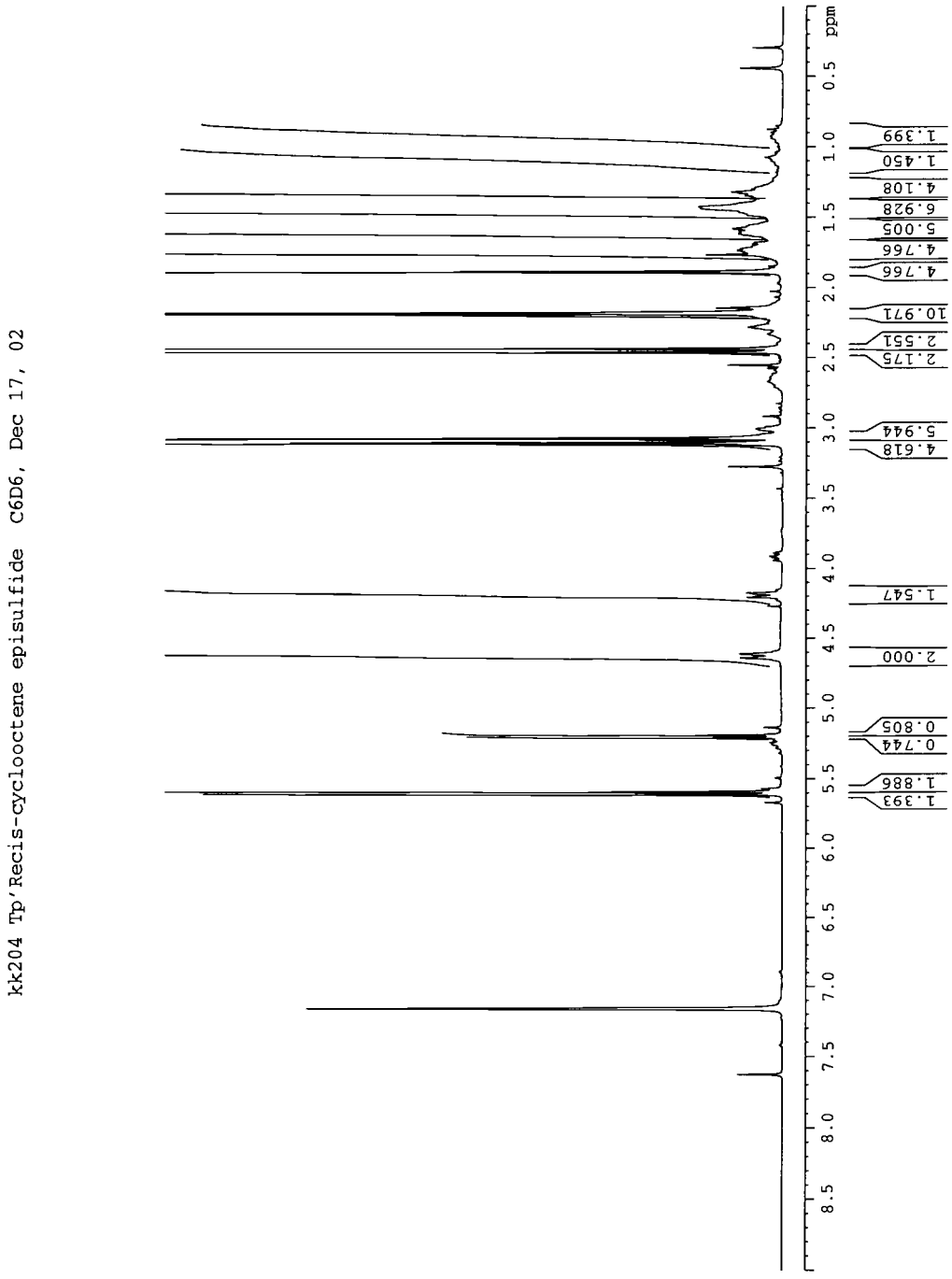


Figure A1.4: ^{1}H NMR and ^{13}C of 1,2-*cis*-Cyclooctanedithiodiolate



kk204 3 dept135 C6D6 Dec 17, 02

```
Current Data Parameters
NAME                 kk204
EXPNO                    3
PROCNO                   1
DU                      /m
USER                   ake

F2 - Acquisition Parameters
Date_               20021217
Time                   23.10
INSTRUM              dpx300
PROBHD     5 mm QNP  1H
PULPROG             dept135
TD                     65536
SOLVENT
NS                       263
DS                         2
SWH                17361.111 Hz
FIDRES              0.264910 Hz
AQ                  1.8874868 sec
RG                     9195.2
DW                     28.800 usec
DE                      6.00 usec
TE                     300.0 K
D1                 1.00000000 sec
D2                 0.00345000 sec
D12                0.00002000 sec
DELTA              0.00000968 sec

============= CHANNEL f1 =============
NUC1                     13C
P1                      7.60 usec
P2                     15.20 usec
PL1                    -3.00 dB
SFO1               75.4749190 MHz

============= CHANNEL f2 =============
CPDPRG2              waltz16
NUC2                     1H
P3                      8.85 usec
P4                     17.80 usec
PCPD2                  80.00 usec
PL2                    -3.00 dB
PL12                   17.55 dB
SFO2              300.1315007 MHz

F2 - Processing parameters
SI                      131072
SF                 75.4677190 MHz
WDW                        no
SSB                         0
LB                       0.00 Hz
GB                          0
PC                       1.40

1D NMR plot parameters
CX                      20.00 cm
F1P                    200.000 ppm
F1                   15093.54 Hz
F2P                    -10.000 ppm
F2                    -754.68 Hz
PPMCM                 10.50000 ppm/cm
```

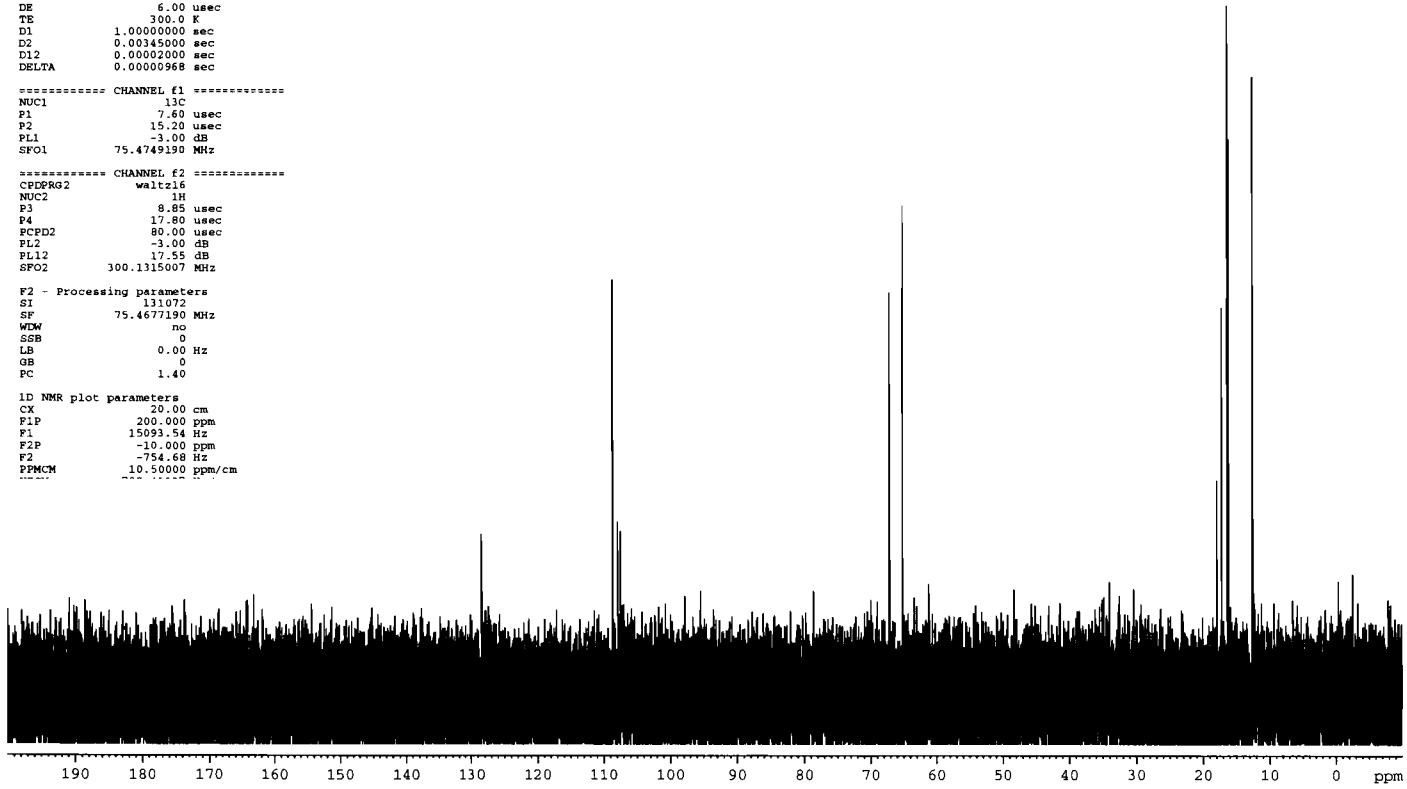
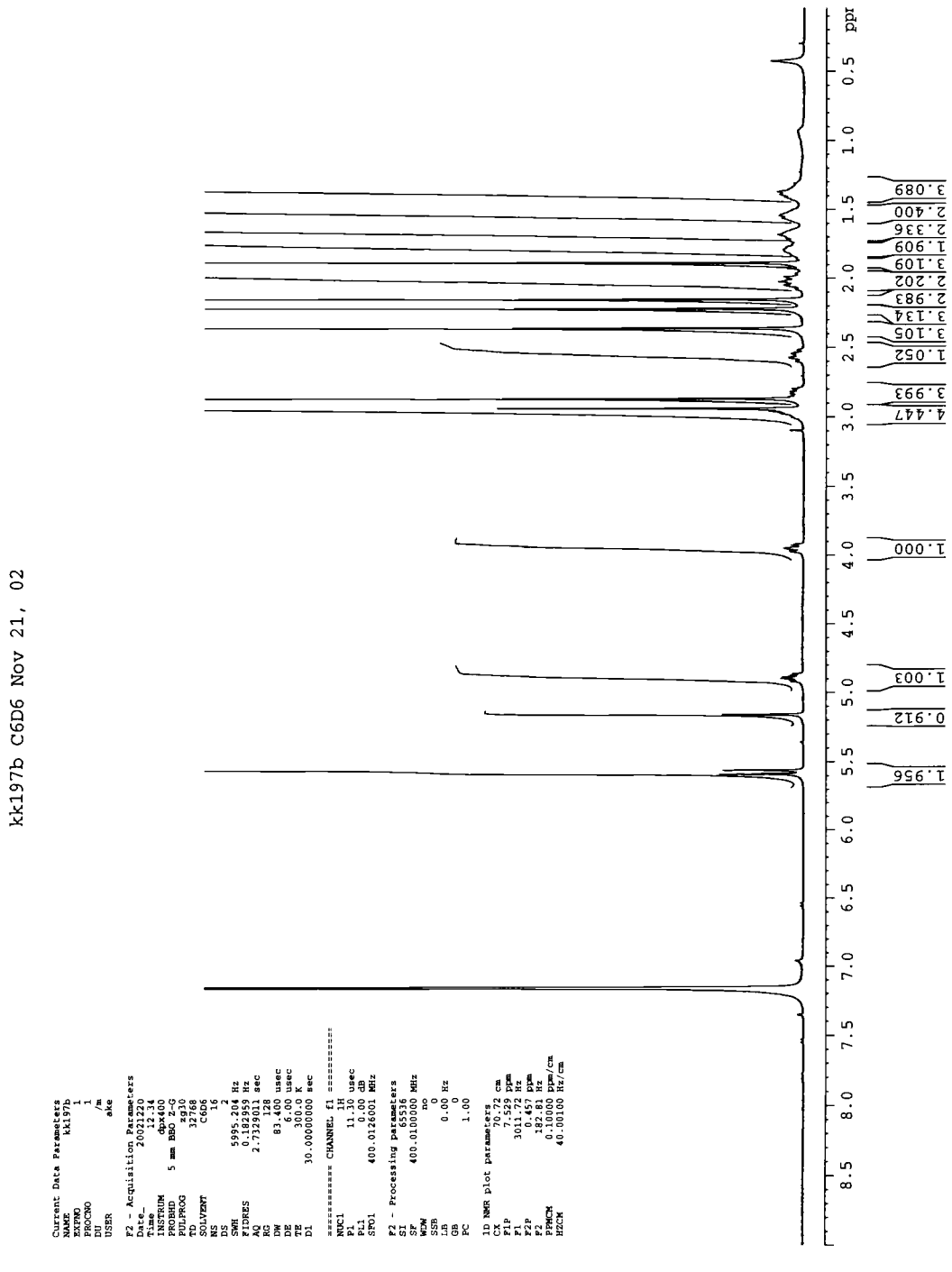


Figure A1.5: ^{1}H NMR and ^{13}C of 1,2-*trans*-Cyclooctanemonothiodiolate



kk197b 3 C-13 C6D6 Dec 20, 02

```
Current Data Parameters
NAME                  kk197b
EXPNO                      3
PROCNO                     1
DU                        /m
USER                     ake

F2 - Acquisition Parameters
Date_               20021219
Time                   20.46
INSTRUM              dpx400
PROBHD       5 mm BBO Z-G
PULPROG             zgpg30
TD                   65536
SOLVENT                C6D6
NS                     3500
DS                        4
SWH              25125.629 Hz
FIDRES           0.383387 Hz
AQ               1.3042164 sec
RG                  2580.3
DW                  19.900 usec
DE                   6.00 usec
TE                  300.0 K
D1              0.00300000 sec
D11             0.03000000 sec
D12             0.00002000 sec

============ CHANNEL f1 ==============
NUC1                  13C
P1                   7.50 usec
PL1                 -3.00 dB
SFO1         100.5936186 MHz

============ CHANNEL f2 ==============
CPDPRG2            waltz16
NUC2                  1H
PCPD2               80.00 usec
PL2                  0.00 dB
PLL2                17.40 dB
PLL3                18.00 dB
SFO2         400.0116000 MHz

F2 - Processing parameters
SI                   65536
SF           400.0100000 MHz
WDW                     no
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   21.00 cm
F1P                 10.000 ppm
F1                4000.10 Hz
F2P                -0.500 ppm
F2               -200.01 Hz
PPMCM             0.50000 ppm/cm
HZCM            200.00500 Hz/cm
```

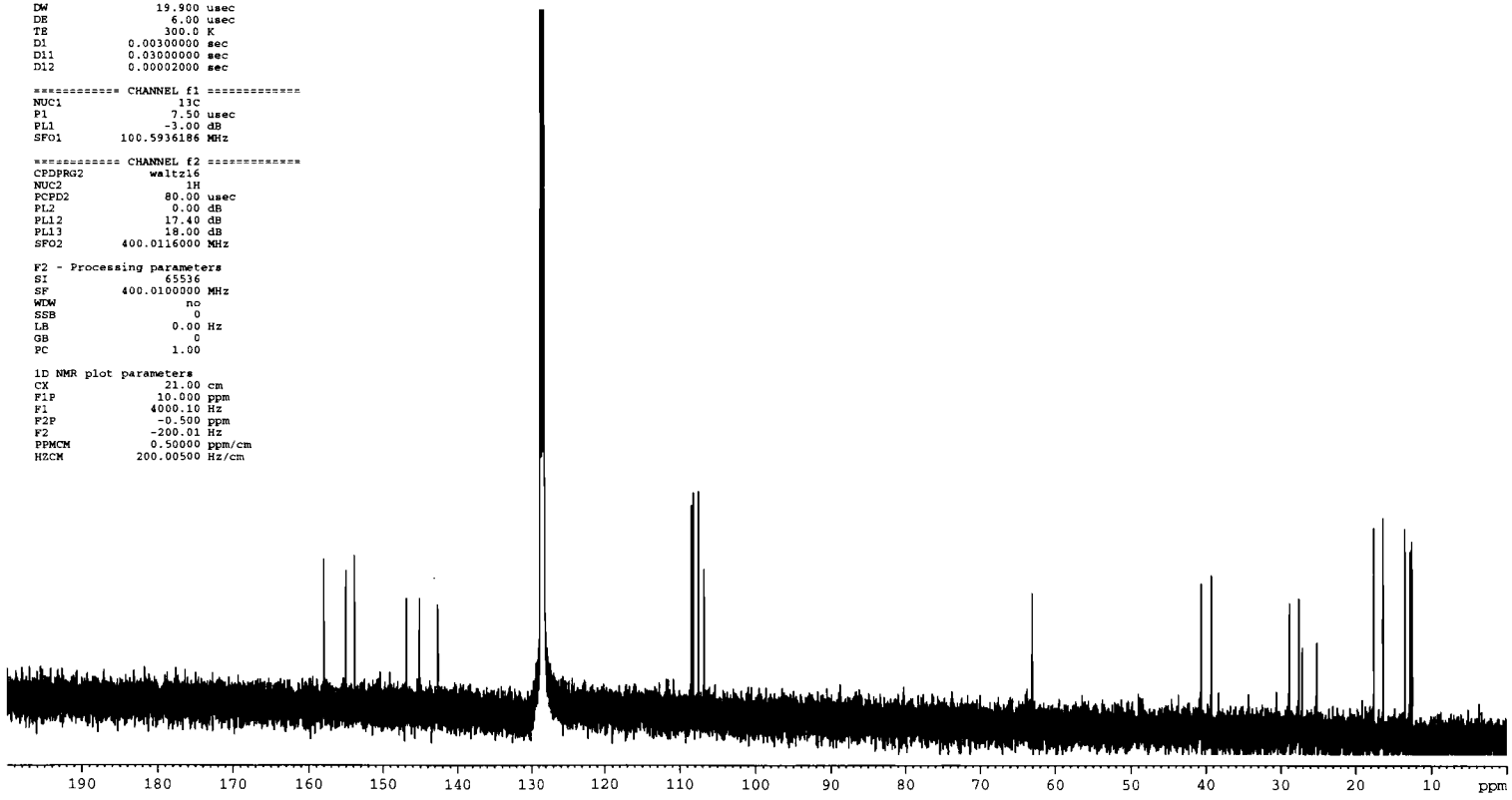


Figure A1.6: ^{1}H NMR of *trans*-Cyclooctene Oxide

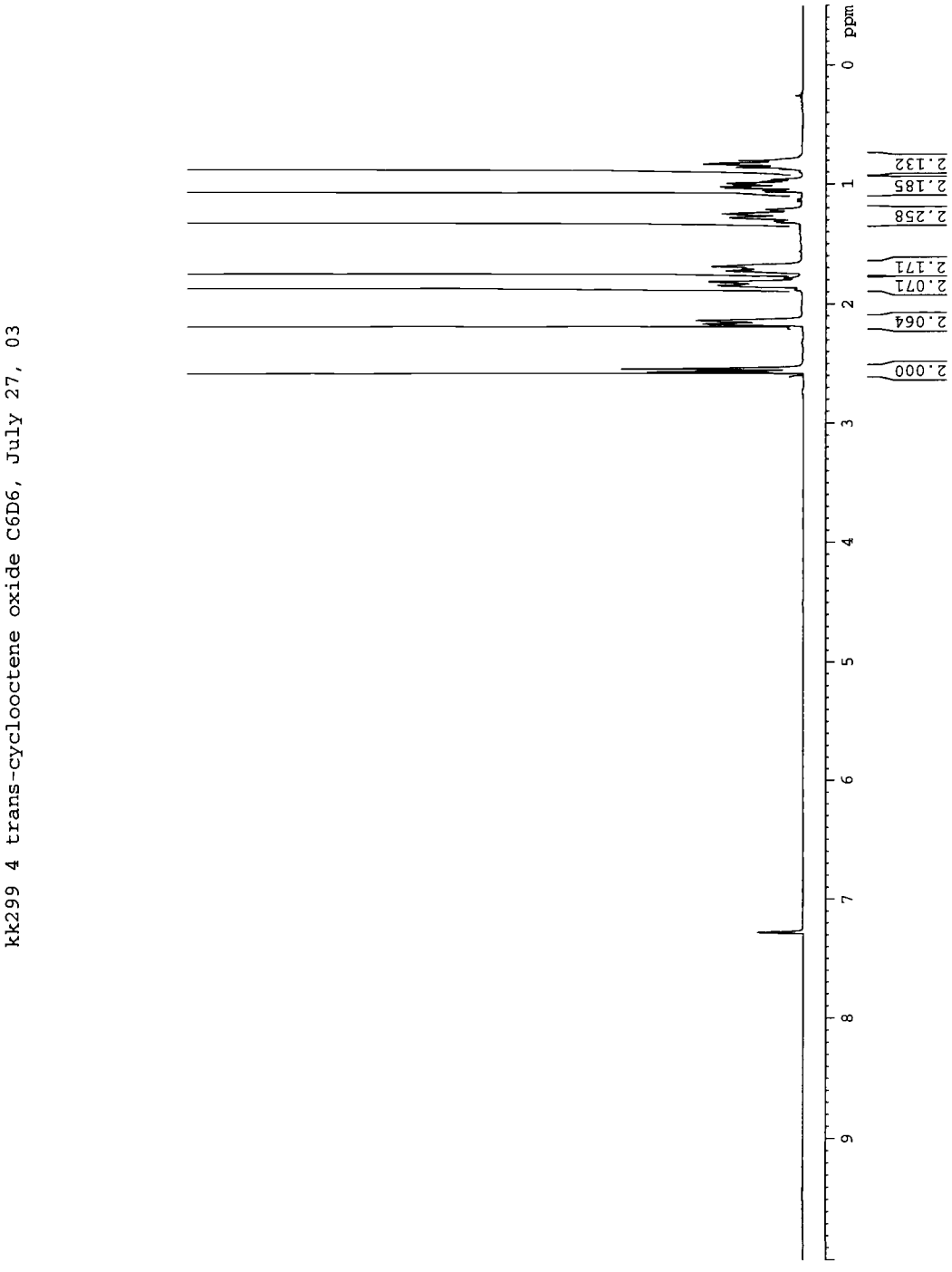


Figure A1.7: ^{1}H NMR of *trans*-Cyclooctene Episulfide

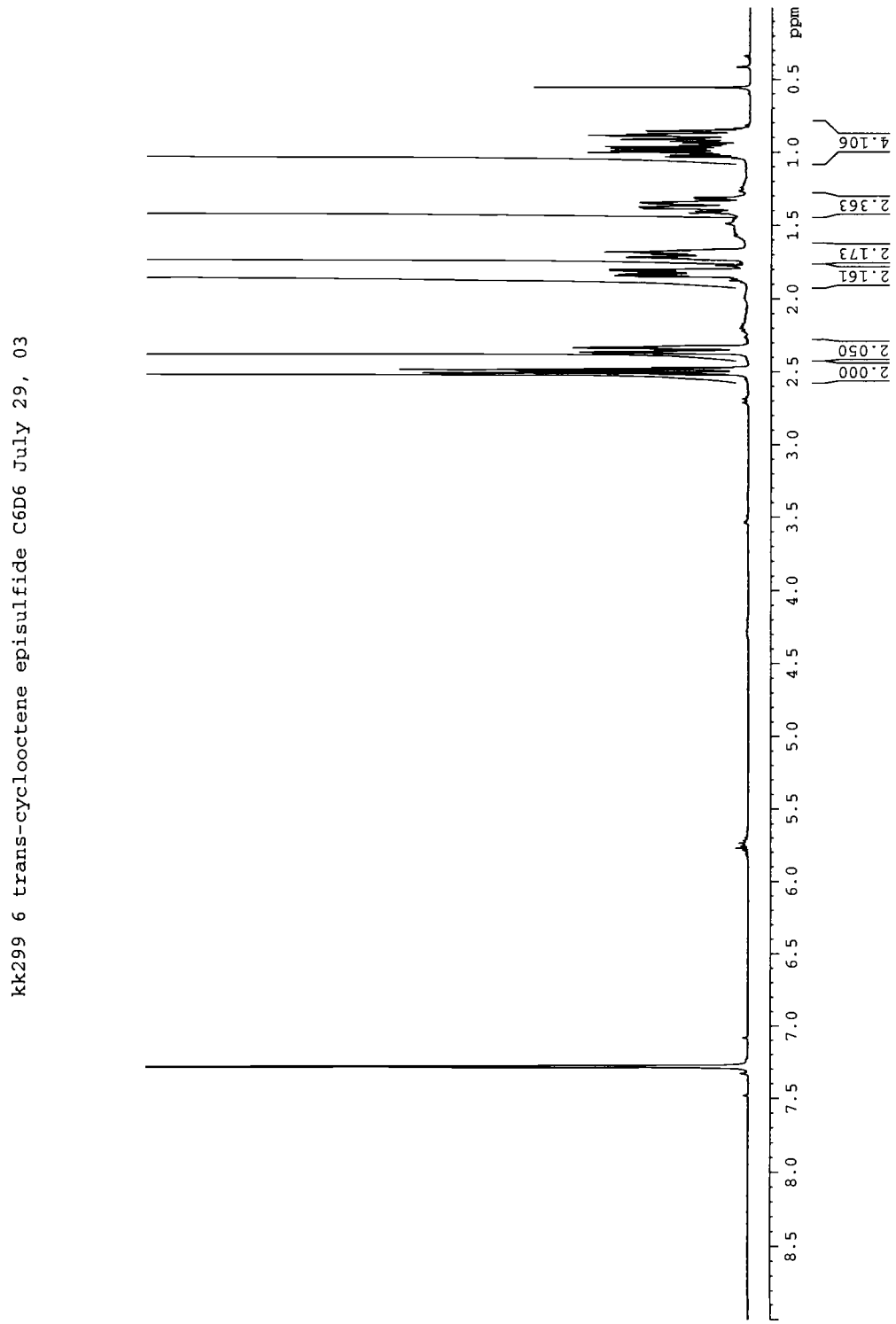


Figure A1.8: ^{1}H NMR of *cis*-Cyclooctene Oxide

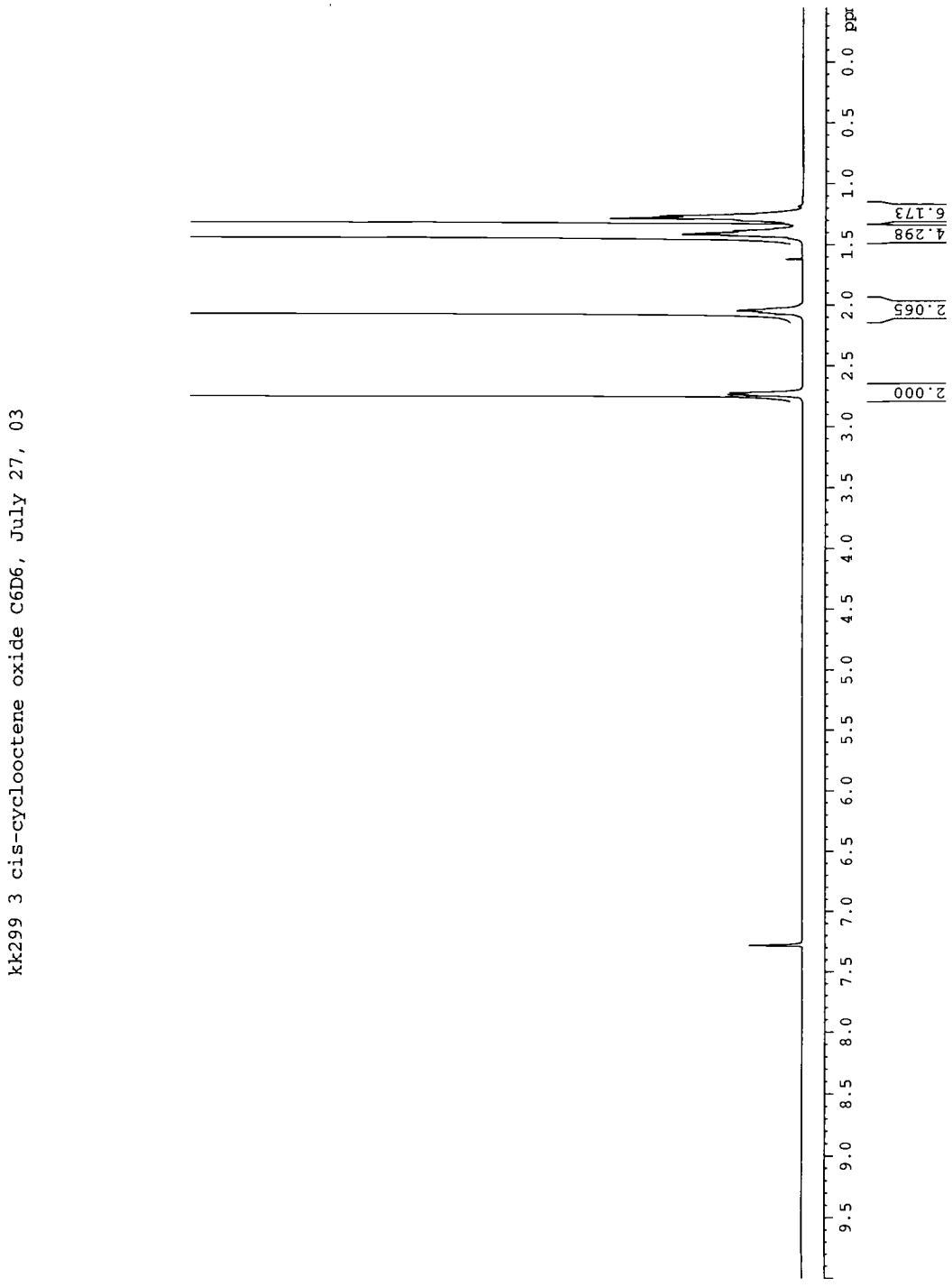
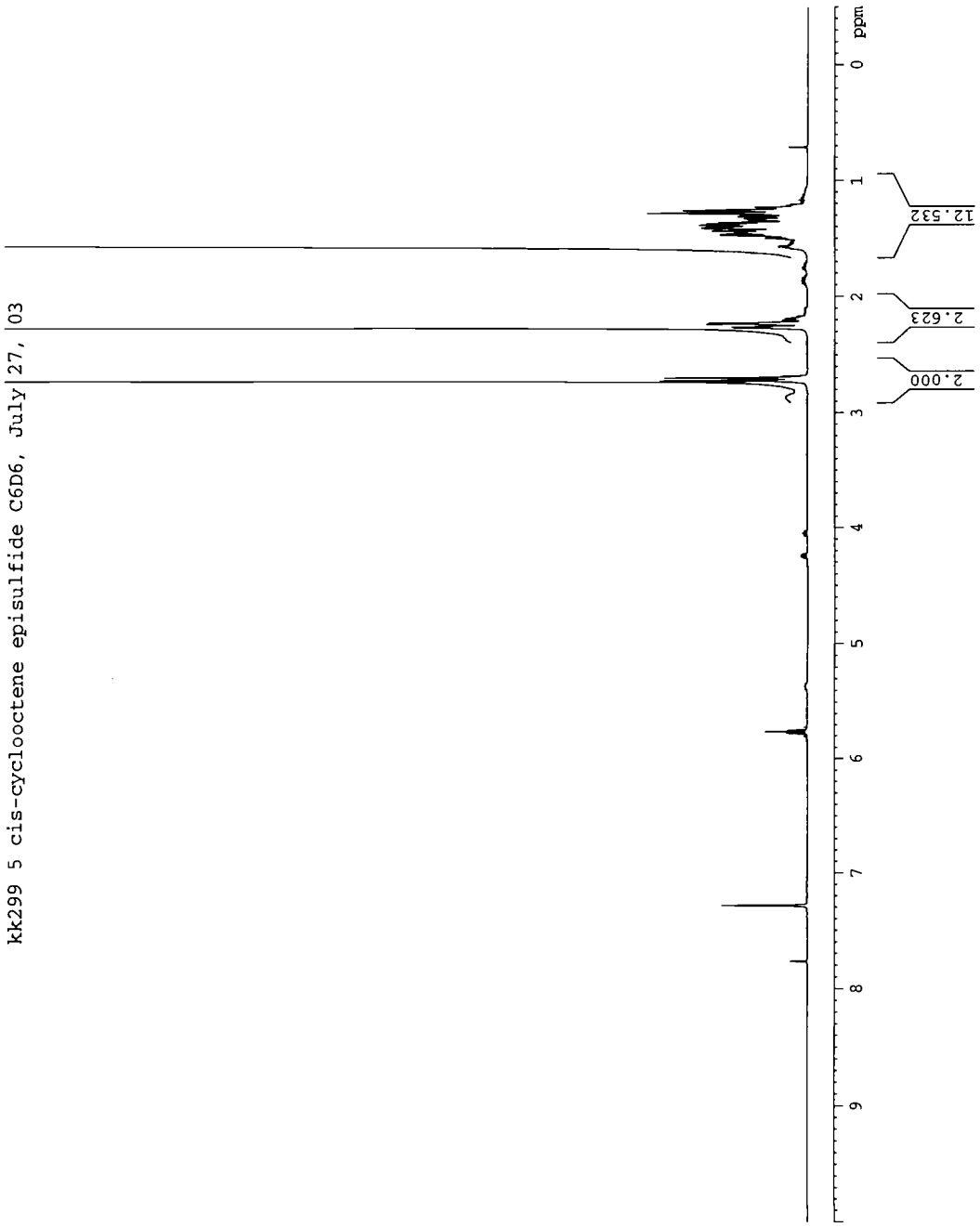
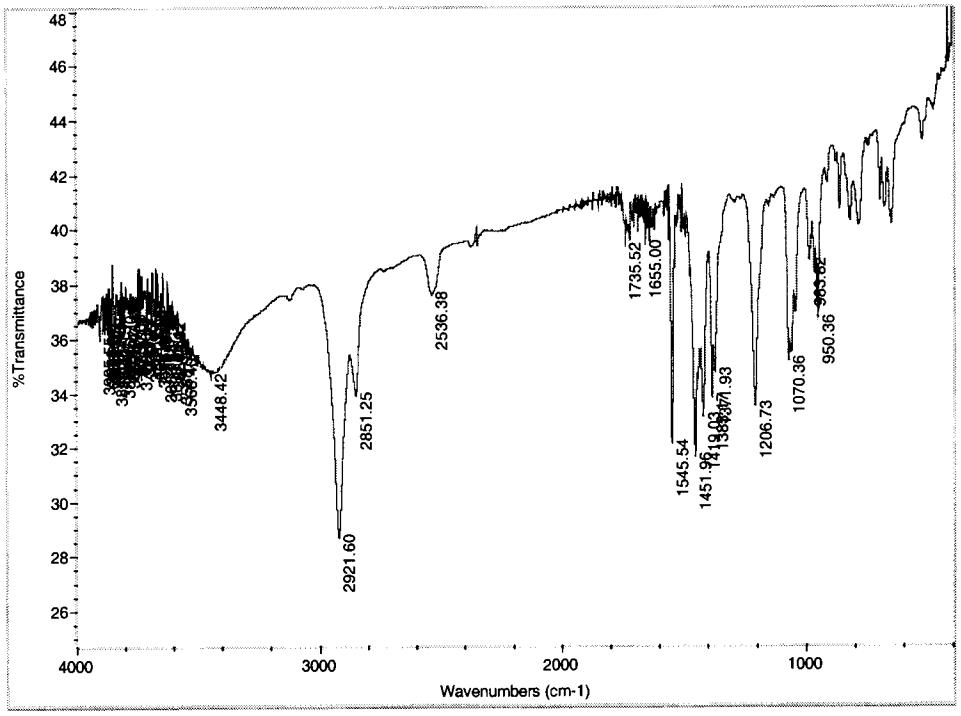


Figure A1.9: ^{1}H NMR of *trans*-Cyclooctene Episulfide



Appendix II. Spectra of Yellow-Green Compound

Figure A2.1: IR



IR (KBr): 2921, 2851, 2536.36, 1735, 1655, 1545, 1451, 1419, 1207, 1070, 950, 904 cm^{-1}.

MS (FAB): 816.1, 707.8, 673.9, 655.9, 641.9, 531.8, 499.8 391.2, 371.2, 307, 219.1, 154, 107 m/z.

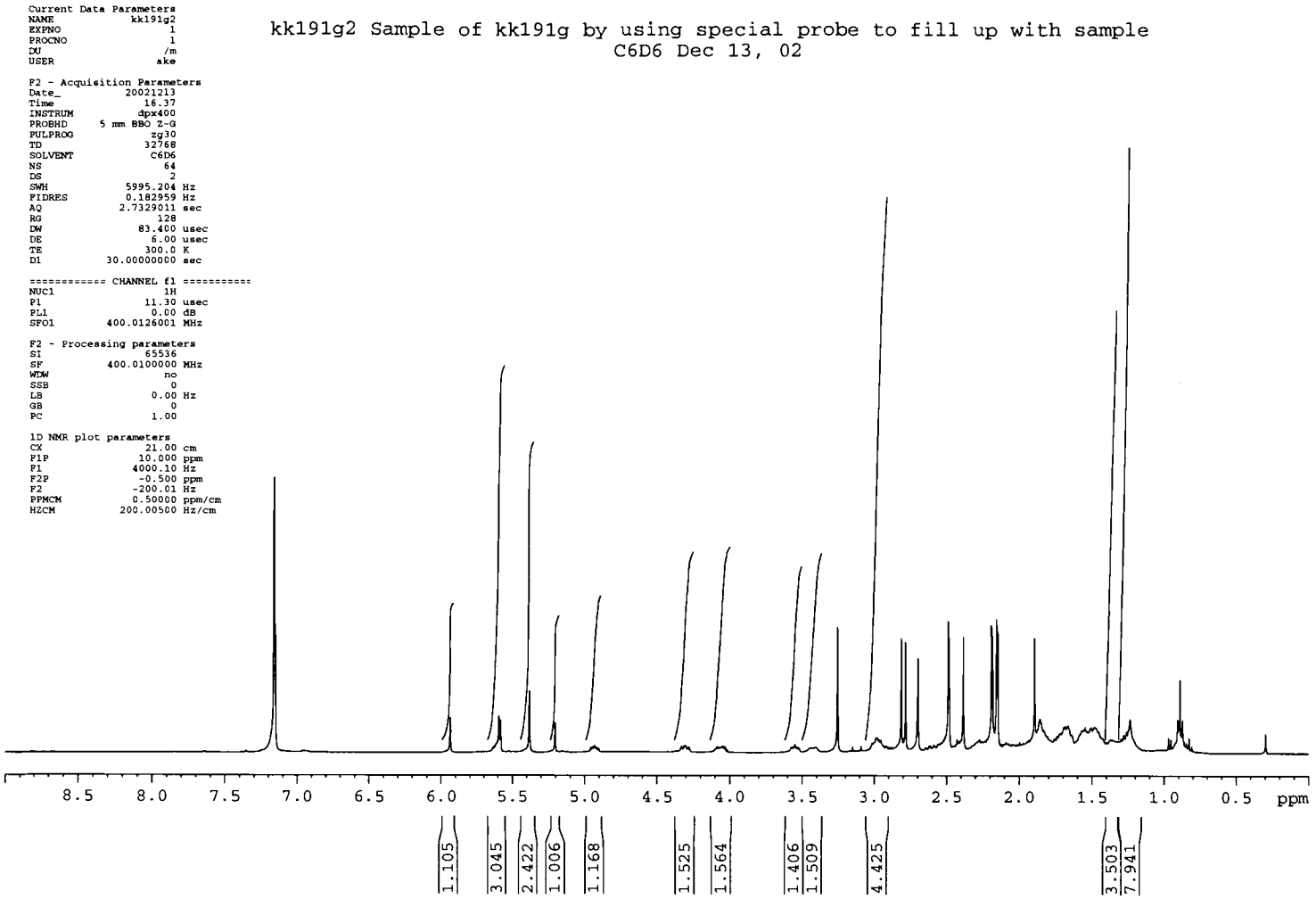


Figure A2.2: ^{1}H NMR and ^{13}C

kk191g2 2 C-13 Green compound C6D6, Dec 14, 02

```
Current Data Parameters
NAME                  kk191g2
EXPNO                       2
PROCNO                      1
DU                         /m
USER                     ake

F2 - Acquisition Parameters
Date_               20021214
Time                   14.29
INSTRUM                dpx400
PROBHD     5 mm BBO Z-G
PULPROG              zgpg30
TD                        65536
SOLVENT                  C6D6
NS                        2055
DS                           4
SWH                25125.629 Hz
FIDRES             0.383387 Hz
AQ                 1.3042164 sec
RG                      1024
DW                    19.900 usec
DE                     6.00 usec
TE                    300.0 K
D1               4.00000000 sec
D11              0.03000000 sec
D12              0.00002000 sec

============ CHANNEL f1 =============
NUC1                     13C
P1                     7.50 usec
PL1                   -3.00 dB
SFO1           100.5936186 MHz

============ CHANNEL f2 =============
CPDPRG2              waltz16
NUC2                     1H
PCPD2                 80.00 usec
PL2                    0.00 dB
PL12                  17.40 dB
PL13                  18.00 dB
SFO2           400.0116000 MHz

F2 - Processing parameters
SI                        65536
SF             100.5825550 MHz
WDW                         no
SSB                          0
LB                     0.00 Hz
GB                           0
PC                     1.40

1D NMR plot parameters
CX                    20.00 cm
F1P                  200.000 ppm
F1                 20116.51 Hz
F2P                    0.000 ppm
F2                     0.00 Hz
PPMCM                10.00000 ppm/cm
HZCM               1005.82556 Hz/cm
```

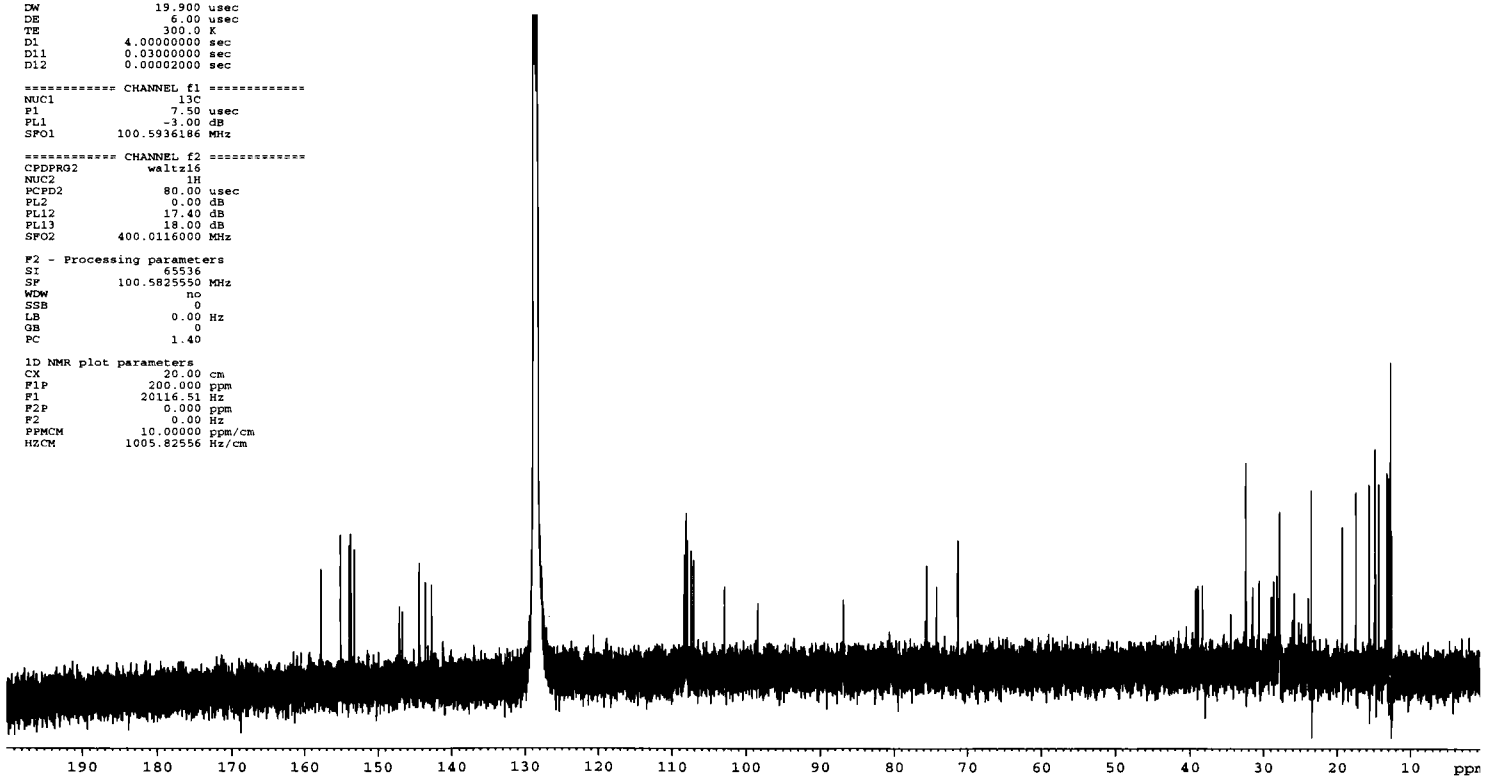


Figure A2.3: COSY

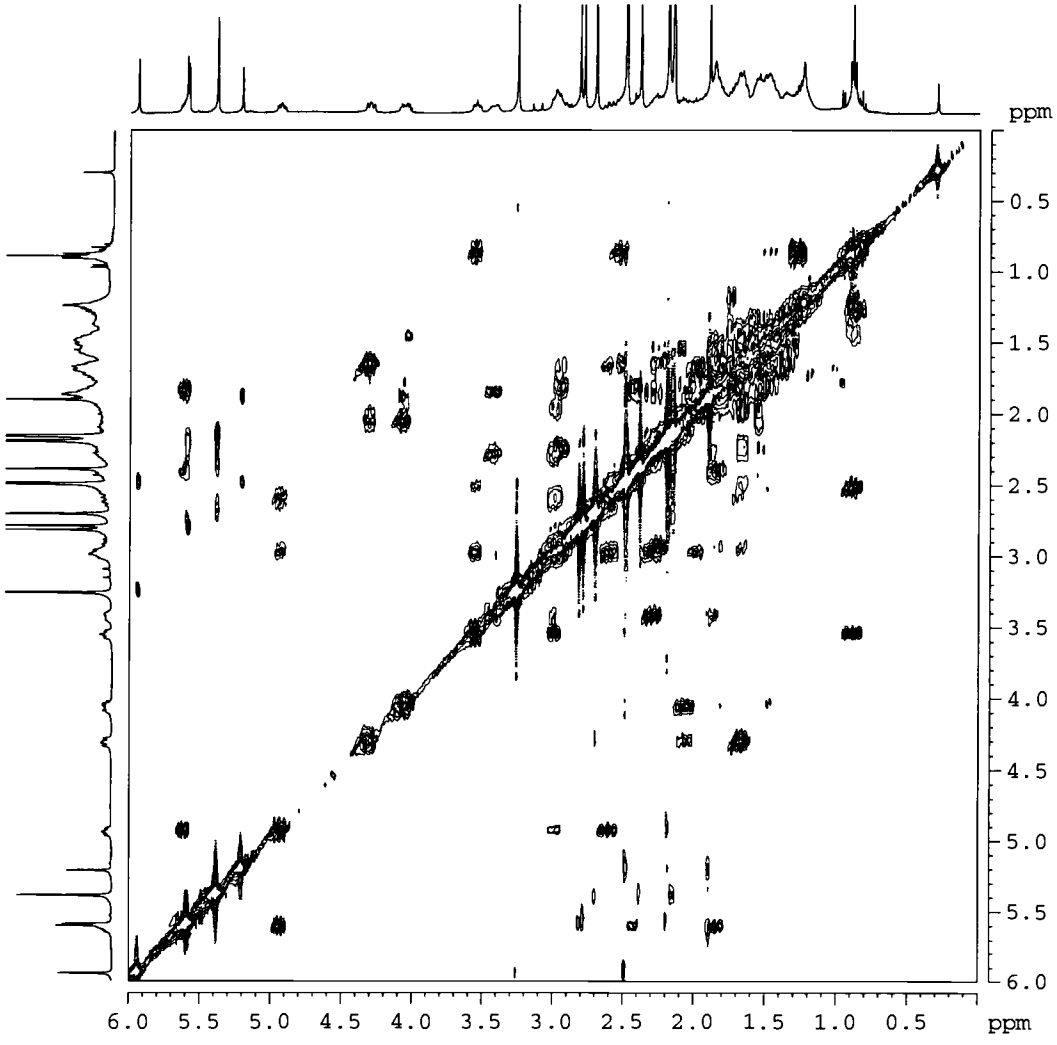


Figure A2.4: HSQC