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**ISOMERIZATION, REACTIVITY, AND STRUCTURAL STUDY OF A
THIOPEROXIDE-BRIDGED DIMOLYBDENUM(V) DIMER**

By

Chi Minh Tuong
B.S., University Paul Sabatier, 1996

A Thesis
Submitted to the Faculty of the
Graduate School of the University of Louisville
In Partial Fulfillment of the Requirements
For the Degree of

Master of Science

Department of Chemistry
University of Louisville
Louisville, Kentucky

May 2004

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A Thesis Approved on

April 8, 2004

By the following Reading Committee:

(Thesis Director)

DEDICATION

To my parents, my brother, and my entire family, for their love and support;
and, to all my friends, for all their help and encouragement.

ACKNOWLEDGMENTS

I would like to express my gratitude to my advisor, Dr. Mark E. Noble, for his advice and guidance throughout my studies. I would also like to thank my other committee members, Dr. Robert M. Buchanan, Dr. Craig A. Grapperhaus, Dr. Kyung A. Kang, and Dr. Christine L. Rich, for their constructive advice. I would like to thank Dr. Mark S. Mashuta for solving my crystal structures and Dr. Neal Stolowitch for his help with the NMR spectroscopy. I also thank my fellow group members for their friendship and helpful discussions.

ABSTRACT

Isomerization, Reactivity, and Structural study of a Thioperoxide-bridged Dimolybdenum(V) Dimer

Chi Minh Tuong

April 8, 2004

The synthesis of the methyl thioperoxide-bridged dimolybdenum(V) dimer, $[\text{Mo}_2(\text{NTo})_2(\text{S}_2\text{P}(\text{OEt})_2)_2\text{S}(\text{O}_2\text{CMe})(\text{SOMe})]$, was improved and the compound was structurally characterized by crystallography. The compound proved to be very stable to light and heat. The possibility of photolytic or thermolytic rearrangement of the methyl thioperoxide ligand ($\mu\text{-S-O-R}$) to a methyl sulfinyl ligand ($\mu\text{-S(=O)R}$) was investigated. These studies showed that the methyl thioperoxide compound did not produce the desired sulfinyl isomer. The photolyses produced mainly a derivative of the methyl thioperoxide compound, where a hydroxo bridge is thought to have replaced the acetate bridge. Minor products formed in general agreement with the photolysis chemistry of organic sulfenate esters ($\text{R}'\text{S-OR}$). The thermolyses cleaved the S-O bond, led to an intramolecular reaction and to some decomposition.

The reaction of $[\text{Mo}_2(\text{NTo})_2(\text{S}_2\text{P}(\text{OEt})_2)_2\text{S}(\text{O}_2\text{CMe})(\text{SOMe})]$ with HBF_4 resulted in the protonation of the S-O bond's oxygen and the synthesis of a new compound, $[\text{Mo}_4(\text{NTo})_4(\text{S}_2\text{P}(\text{OEt})_2)_4\text{S}_3(\text{O}_2\text{CMe})_2(\text{SOMe})](\text{BF}_4)$.

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CHAPTER I

INTRODUCTION

Metal-sulfur chemistry has been involved over several decades in a variety of areas.^{1,2} While some studies of these metal-sulfur systems have investigated the coordination of metals to sulfur ligands or substrates,³⁻⁷ others, including our research group, have focused on the chemistry at the sulfur site.⁸⁻²¹ Molybdenum-sulfur complexes are one of the most important metal-sulfur systems. Their chemistry covers a wide range of biological and industrial processes.^{9,10} For example, they are present in some enzymes such as nitrogenase, nitrate reductase, xanthine oxidase, or sulfite oxidase; and, they are used in some catalytic processes such as Hydrodesulfurization (HDS) or Hydrodenitrogenation (HDN).

Only a few metal-sulfur systems have well characterized reactions at a sulfide, disulfide, or polysulfide site.¹¹⁻²⁴ In the course of our studies, we recently focused our interest on the chemistry of a particularly stable molybdenum-sulfur complex, the methyl thioperoxide-bridged molybdenum(V) dimer.³⁰ This compound is characterized as having a thio-peroxide ligand, μ -S-O-R, distinctive of metallo-sulfenate esters (M_x -S-O-R). This ligand is isomeric to the sulfenate anion ($R'-S-O^-$), which is the conjugate base of sulfenic acids ($R'SOH$). Despite their isomeric relation to metallo-sulfinyl complexes, $M_x-S(=O)R$, whose chemistry is well developed,³¹⁻³⁶ these metallo-sulfenate esters are rare or have not yet been isolated. They are hypothesized as intermediates in some

reactions.³⁵ Their chemistry is of importance in view of the possible applications of their organic sulfenate ester counterparts ($R'SOR$) or of the closely related organic sulfoxides ($R'S(=O)R$) and sulfenic acids ($R'S-OH$).³⁷⁻⁴⁹ The controlled rearrangement between organic sulfenate esters ($R'SOR$) and sulfoxides ($R'S(=O)R$), by photolytic or thermolytic means,^{37,38,49} offers a very useful tool in many syntheses. The pathway of thermolytic rearrangement, as well as its spontaneity, can be controlled by the choice of substituent on sulfur.⁴⁹ For example, some allyl sulfenate esters can rearrange thermally to allyl sulfoxides via a [2,3]-sigmatropic shift.⁴⁹ Allyl, crotyl and α,α -dimethylallyl sulfenate esters spontaneously rearrange to the corresponding sulfoxides at low temperature (eq 1, a) while cinnamyl and γ,γ -dimethylallyl esters require higher temperatures (eq 1, b). These rearrangements are thought to follow a concerted intramolecular mechanism (route a), or an ionization mechanism (route b).⁵⁶

On the other hand, benzyl *p*-toluenesulfenate rearranges to the corresponding sulfoxide but is slow to do so, possibly because of a concerted intramolecular mechanism.

These possible rearrangements have already found many uses, such as: the racemization of diaryl, alkyl aryl, and dialkyl sulfoxides;⁵¹⁻⁵³ new syntheses of allyl alcohols;^{40,45} the synthesis of α,β -unsaturated ketones;⁵⁴ and the synthesis of functionalized dienes.⁴² They have also been successfully used to stereoselectively control the synthesis of prostaglandins and to achieve highly selective total syntheses.⁴⁷

Another important aspect of the sulfenate esters is that they can be generated from

sulfoxides by a photolysis reaction.⁵⁵⁻⁵⁸ UV light cleaves homolytically the S-C bond of the sulfoxide and forms a radical pair that can recombine and produce the sulfenate ester. In the process some secondary reactions can occur and increase the variety of products of the reaction, as described by Y. Guo and W. S. Jenks for the photolysis of several aryl benzyl sulfoxides.^{42,55,56} Other applications of the photolysis of sulfenate esters are the syntheses of alkoxy and alkyl radicals.⁴¹ Despite the reported transformations, however, a reversible sulfenate-sulfoxide isomerization has never been cleanly observed.

Metal ions have demonstrated the ability to stabilize highly reactive sulfur ligands. In their discovery of the first transition metal thiosulfinate, $[\text{Ir}(\eta^2\text{-S}_2\text{OMe})(\text{dppe})_2]^{2+}$, and sulfenate ester, $[\text{Ir}(\eta^1\text{-SOMe})(\text{MeNC})(\text{dppe})_2]^{2+}$, Rauchfuss and coworkers⁸ suggested the use of metal ions in future developments of alkyl O-sulfenic acid derivatives.

Since then, metals have been used to stabilize species like alkylsulfenates. Krueger and coworkers have shown,^{11,12} in the case of the highly reactive cysteine sulfenate anion, that these thiolates can facilitate the study of nucleophilic or electrophilic reactivities by chelating to the metal and by forming the nonlabile sulfinyl and sulfinato cobalt(III) complexes: $[\text{Co}(\text{en})_2\{\text{NH}_2\text{CH}(\text{COO})\text{CH}_2\text{SO}\}]\text{ClO}_4$ and $[\text{Co}(\text{en})_2\{\text{NH}_2\text{CH}(\text{COO})\text{CH}_2\text{SO}_2\}]\text{ClO}_4$. Metal-sulfur coordination has been helpful^{5,6,8,11,12} in the stabilization, characterization, and investigation of the chemistry of highly reactive species like noncoordinated sulfenic acids which have an important role as transient intermediates in many organic reactions.³⁸ Several physical and chemical aspects have been studied⁵ and have shown that sulfinyl cobalt(III) complexes and noncoordinated species behave similarly, although the nucleophilic reactivity of the cobalt complexes is

reduced compared to their noncoordinated species. Metal-sulfur chemistry has also been used to introduce chirality into an organic sulfoxide molecule.^{33-35,37-39}

This thesis deals with the chemistry and characteristics of a recently synthesized and stable thioperoxide-bridged molybdenum(V) dimer.³⁰ This compound is composed of an Mo₂S₂ core (Figure 1) wherein one sulfur bridge has been functionalized to a methyl thioperoxide bridge (Me-O-S⁻). A sulfide and acetate bridge the two molybdenums, while a dithiophosphate and a *p*-tolylimido group also chelate each molybdenum.

Figure 1. The molybdenum(V) dimer core representation using stick-diagrams.

This metallo-sulfenate ester complex will be further abbreviated as Mo₂SOMe or compound **1**. Other compounds based on the Mo₂S₂ core will be abbreviated as Mo₂SZ (mono-substituted) or as ZSMo₂SZ' (di-substituted), where Z and Z' are bridge sulfur functionalities.

Mo₂SOMe

Mo₂SZ

ZSMo₂SZ'

In solution, these compounds can give two sulfur inversion isomers, a distal invertomer and a proximal invertomer, for every tricoordinate sulfur that they possess. The distal and proximal designations are assigned relative to the *p*-tolylimido ligands. Mo₂SOMe will thus have two inversion isomers (Figure 2).

Figure 2. Invertomers of Mo₂SOMe.

As part of a series of similar complexes based on this Mo₂S₂ core, the study of this molecule and its unusual thioperoxide linkage, μ -S-O-R (R=alkyl), aims at bringing us more information on the effect of a metal on sulfur-based ligands. The structure of Mo₂SOMe is compared to similar Mo₂SZ compounds. Since the chemistry of metal-sulfinyl complexes M_x-S(=O)R is well developed, the possibility of isomerization (Figure 3) of Mo₂SOMe to the sulfinyl complex Mo₂S(=O)Me is examined here. This is done through the study of thermal or photochemical cleavage of the S-O and O-C bonds and also by trying to establish a parallel with the chemistry of noncoordinated, simple

Figure 3. Isomerization between Mo₂SOMe and Mo₂S(=O)Me.

organic sulfenate esters. The nucleophilicity of the sulfur and oxygen centers is also discussed herein to further understand the chemistry of the metallo-sulfenate ester complex.

CHAPTER II

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF METHYL THIOPEROXIDE-BRIDGED MOLYBDENUM(V) DIMER [Mo₂(NT_o)₂(S₂P(OEt)₂)₂S(O₂CMe)(SOMe)]

Introduction

While there have been many organic sulfenate esters, RS-OR' (R, R'=alkyl or aryl), studied over the past three decades,^{37,38} the occurrence of stable metal-sulfur complexes possessing a sulfur bound thioperoxide anion ligand, M_xS-OR (x=1 or 2; R=alkyl or aryl), has been rare.^{8,36} Recently, the successful synthesis of alkyl thioperoxide-bridged molybdenum(V) dimers³⁰ has allowed the completion of a series of isostructural bridge-substituted dimolybdenum(V) compounds including the sulfenamides, the persulfide-bridged complexes, and the sulfenyl halide complexes, all of which display classical "sulfen" behavior (Figure 4).^{13-17,60,61}

Figure 4. Isostructural series of bridge-substituted dimolybdenum(V) dimers.

The synthesis of the most simple of these Mo₂SOR complexes, Mo₂SOMe, was improved in order to increase its availability, and its crystal structure was then obtained. The structure of these thioperoxide-bridged compounds raises several questions with respect to their chemistry when compared to organic sulfenate esters or to similar metal-sulfur complexes. Mo₂SSEt and Mo₂SNH₂ compounds (pictured above) were chosen for the closest structural comparison possible to Mo₂SOMe. All three Mo₂SZ compounds possess the same Mo₂S₂ core. They differ mainly from one another by their μ -S-Z ligand. The persulfide and sulfenamide complexes have been structurally characterized in previous studies.^{15,60}

Experimental Section

[Mo₂(NTo)₂(S₂P(OEt)₂)₂S(O₂CMe)(SOMe)], Mo₂SOMe. To a solution of BzSMo₂SO (0.2003 g, 0.200 mmol) in dry CH₂Cl₂ (4 mL), CF₃SO₃Me (25 μ L, 0.22 mmol) was added under red light and N₂(g) in a glove bag. The solution was stirred for 15 min. Volatiles were then removed by rotary evaporation. Standard room lighting was then used. The residue was redissolved in acetone (10 mL), and PPN⁺I⁻ (0.1994 g, 0.300 mmol) was added. The solution was allowed to stir for 8 min. Volatiles were then removed by rotary evaporation. The residue was washed with petroleum ether (2.5 mL) and filtered, and then vacuum dried. It then was dissolved in THF (2.5 mL) and filtered by positive pressure. The collected filtrate was reduced to a volume of about 1 mL and treated with 6 mL of EtOH/ H₂O (2/1). The resulting solid was collected, washed with EtOH/ H₂O (4/1), and vacuum dried. A red solid was obtained (0.1270 g, 70%).

Crystallography

The crystals of Mo₂SOMe were prepared in an NMR tube by layering a nearly saturated solution of Mo₂SOMe in benzene with 1-propanol. The data collection and structure solution were conducted by Dr. M. S. Mashuta, Department of Chemistry, University of Louisville.

Results and Discussion

The synthesis was derived from that of Brian Allred.³⁰ The main improvement obtained in this work was changing the solvent. The starting compound BzSMo₂SO was methylated with CF₃SO₃Me under moisture-free conditions (eq 1). The resulting product

was debenzylated by nucleophilic attack using PPN⁺I⁻ (eq 2). This was achieved by using acetone, a solvent more polar than the previously used methylene chloride. To further

improve the synthesis, the solid was washed with petroleum ether after evaporation of the solvent in order to eliminate possible traces of benzyl iodide that could affect the recrystallization step. By this method, yields of 70% are typical; the yield by the prior

method was 46%.

Crystal Structure. The crystal data, experimental details, and selected positional parameters, bond lengths, and angles of Mo₂SOMe, can be found in Tables 1-4 at the end of this chapter. The structure and crystallographic data for Mo₂SSEt and Mo₂SNH₂ are reported from previous work from our group members^{15,60} and can also be found at the end of this chapter in Tables 2-4. The ORTEP of Mo₂SOMe is shown as Figure 5. ORTEPs for Mo₂SSEt and Mo₂SNH₂ follow as Figures 6 and 7. For an easier comparison between structures, some atoms in the original ORTEP diagrams of Mo₂SSEt and Mo₂SNH₂ have been renumbered to correspond to the numbering system used here for Mo₂SOMe. Two essentially identical molecules of Mo₂SOMe were contained within the same unit cell. For simplification purposes, only one structure is presented and described here.

General features for the three compounds are as follows. When examining the Mo₂S₂ core of these compounds, one can notice that the Mo₂S₂ core of Mo₂SOMe is close to planarity, as it was for Mo₂SSEt and Mo₂SNH₂. Indeed, the calculated dihedral angles between the S(1)-Mo(1)-Mo(2) and S(2)-Mo(1)-Mo(2) planes are 179.31 (3)°, 178.79 (6)°, and 178.69 (4)° for Mo₂SOMe, Mo₂SSEt, and Mo₂SNH₂ respectively. The geometry of all three Mo₂S₂ cores is characterized by Mo-S bridging bonds that are longer to the tricoordinate sulfur S(1) than to dicoordinate S(2). This could be due to a transfer of π bond character from Mo $\cdots$ S(1) bonds to Mo $\cdots$ S(2) bonds following the formation of the bond with methoxy. The acetate symmetrically bridges the molybdenum atoms and is almost identical to the acetate bridge of Mo₂SSEt and Mo₂SNH₂.

Most importantly, the structural difference of the three compounds lies between their μ -sulfur ligands: ethane perthiolate, sulfenamide, and methyl thioperoxide. The S(1)-N(3) bond of Mo₂SNH₂ is almost symmetrical relative to the Mo₂S₂ core but the S(1)-O(7) bond vector of Mo₂SOMe is skewed away from a symmetric position relative to the Mo₂S₂ core. This is also the case for the S(1)-S(7) bond vector of Mo₂SSEt. The S(1)-O(7) and O(7)-C(25) bonds of Mo₂SOMe are much smaller than the S(2)-S(7) and S(7)-C(25) bonds of Mo₂SSEt respectively. S(1)-O(7) of Mo₂SOMe is also smaller than the S(1)-N(3) bond of Mo₂SNH₂. The S-Z bond distance seems to follow the same trend as the size of Z: $d_{S-S} > d_{S-N} > d_{S-O}$. The distal orientation of the methoxy group of Mo₂SOMe parallels that of the other compounds. It corresponds to the major invertomer in solution with a distal/proximal invertomer ratio of 4.0 determined by NMR. The Mo $\cdots$ O(7) distance is 3.459 (1) Å for Mo(1) and 3.305 (1) Å for Mo(2),⁶² which indicates that they are too long for a possible direct interaction. This confirms the assignment of the thioperoxide ligand as bridging only by its sulfur. The measured O(7) $\cdots$ C(15) distance (2.88 Å) for Mo₂SOMe is less than the sum of the van der Waals radii⁶³ of the two atoms (3.10 Å), whereas the O(7) $\cdots$ (1) and O(7) $\cdots$ O(2) distances (2.94 and 2.85 Å) are longer (by 0.14 and 0.05 Å). This result is almost identical to what was found for Mo₂SNH₂ and Mo₂SSEt. For Mo₂SNH₂, the N(3) $\cdots$ C(15) distance (3.03 Å) is shorter than the van der Waals sum of N and C atoms (by 0.19 Å), while the N(3) $\cdots$ O(1) and N(3) $\cdots$ O(2) distances (2.97 and 3.06 Å) are longer (by 0.07 and 0.16 Å). As for Mo₂SSEt, the S(7) $\cdots$ C(15) distance (3.16 Å) is shorter than the van der Waals sum of S and C atoms (by 0.39 Å), and the S(7) $\cdots$ O(1) and S(7) $\cdots$ O(2) distances (3.12 and 3.27 Å) are also shorter (by 0.02 and 0.13 Å). These observations tend to suggest that there could be a possibility for

interaction within Mo_2SOMe , Mo_2SNH_2 , and Mo_2SSEt between the bridge sulfur functionality and the carboxylate carbon, due to their proximity. Alternatively, this close contact could be a packing feature. This possible interaction will be mentioned later in Chapter III.

Table 1. Crystallographic data for Mo₂SOMe

Formula	Mo ₂ C ₂₅ H ₃₉ N ₂ O ₇ P ₂ S ₆
FW	1851.52
Space Group	P2 ₁ /c
<i>a</i> , Å	29.861 (4)
<i>b</i> , Å	12.7316 (15)
<i>c</i> , Å	20.720 (3)
α , deg	90
β , deg	89.972 (2)
γ , deg	90
<i>T</i> , °C	23
<i>V</i> , Å ³	7877.4 (16)
<i>Z</i>	4
λ , Å	0.71073 (Mo K α)
ρ_{calcd} , g cm ⁻³	1.561
μ , cm ⁻¹	10.76
no. of measd reflcns	66486
indept. reflections	18374

Table 2. Selected Positional Parameters ($\times 10^4$ Å) for Mo₂SOMe and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$).

Atom	x	y	z	U(eq)
Mo(1)	1191(1)	-445(1)	2729(1)	51(1)
Mo(2)	1207(1)	607(1)	3936(1)	50(1)
S(1)	1252(1)	1452(1)	2884(1)	54(1)
S(2)	1142(1)	-1207(1)	3754(1)	63(1)
S(3)	967(1)	-2254(1)	2370(1)	80(1)
S(4)	1043(1)	-172(1)	1521(1)	73(1)
S(5)	987(1)	122(1)	5066(1)	80(1)
S(6)	1041(1)	2404(1)	4425(1)	73(1)
P(1)	889(1)	-1682(1)	1477(1)	75(1)
P(2)	943(1)	1650(1)	5256(1)	78(1)
O(1)	479(1)	-109(2)	2804(1)	52(1)
O(2)	485(1)	669(2)	3763(1)	52(1)
O(7)	775(1)	2089(1)	2784(1)	64(1)
N(1)	1766(1)	-471(2)	2616(1)	60(1)
N(2)	1781(1)	693(2)	4036(1)	57(1)
C(1)	2223(1)	-417(2)	2550(2)	56(1)
C(8)	2241(1)	721(2)	4109(1)	55(1)
C(15)	287(1)	311(2)	3278(1)	49(1)
C(16)	-215(1)	391(3)	3261(2)	70(1)
C(25)	641(1)	2248(3)	2127(2)	84(1)

Table 3. Selected Bonding and Non-Bonding Distances (Å) for Mo₂SOMe, Mo₂SSEt, and Mo₂SNH₂.

	Mo ₂ SOMe	Mo ₂ SSEt	Mo ₂ SNH ₂
Mo(1)-Mo(2)	2.8375 (4)	2.8336 (4)	2.8283 (6)
Mo(2)-S(2)	2.3474 (9)	2.338 (1)	2.347 (1)
Mo(2)-S(1)	2.4354 (8)	2.451 (1)	2.439 (1)
Mo(2)-S(5)	2.5085 (9)	2.520 (1)	2.510 (1)
Mo(2)-S(6)	2.5509 (9)	2.553 (1)	2.557 (1)
Mo(2)-O(2)	2.1867(18)	2.171 (4)	2.198 (2)
Mo(2)-N(2)	1.731 (2)	1.734 (5)	1.731 (3)
Mo(1)-S(2)	2.3392 (9)	2.350 (1)	2.351 (1)
Mo(1)-S(1)	2.4424 (8)	2.446 (1)	2.431 (1)
Mo(1)-S(3)	2.5111 (9)	2.511 (1)	2.517 (1)
Mo(1)-S(4)	2.5648 (10)	2.552 (2)	2.550 (1)
Mo(1)-O(1)	2.1729 (18)	2.185 (4)	2.202 (2)
Mo(1)-N(1)	1.732 (2)	1.721 (4)	1.723 (2)
S(1)-Z ^a	1.651(2)	2.068 (2)	1.709 (3)
S(5)-P(2)	1.9883 (16)	1.987 (2)	1.988 (2)
S(3)-P(1)	2.0030 (15)	1.996 (2)	1.995 (2)
S(4)-P(1)	1.9785 (13)	1.992 (2)	1.982 (2)
S(6)-P(2)	1.9925 (14)	1.988 (2)	1.988 (2)
Z ^a -C(25)	1.435 (4)	1.789 (7)	-
O(1)-C(15)	1.258 (3)	1.266 (5)	1.253 (6)
O(2)-C(15)	1.252 (3)	1.269 (6)	1.255 (4)

Table 3, continued

	Mo₂SOMe	Mo₂SSEt	Mo₂SNH₂
N(2)-C(8)	1.381 (3)	1.380 (7)	1.388 (3)
N(1)-C(1)	1.375 (4)	1.375 (7)	1.382 (3)
C(15)-C(16)	1.502 (4)	1.510 (9)	1.504 (4)
Mo(1)···Z ^a	3.459 (1)	3.841 (2)	3.425 (4)
Mo(2)···Z ^a	3.305 (1)	3.690 (2)	3.507 (4)
C(15)···Z ^a	2.880 (2)	3.160 (6)	3.030 (5)
O(1)···Z ^a	2.935 (2)	3.119 (6)	2.967 (5)
O(2)···Z ^a	2.852 (1)	3.267 (6)	3.055 (4)

^aZ = O(7) or S(7) or N(3)

Table 4. Selected Bond Angles (deg) for Mo₂SOMe, Mo₂SSEt, and Mo₂SNH₂.

	Mo ₂ SOMe	Mo ₂ SSEt	Mo ₂ SNH ₂
S(2)-Mo(2)-S(1)	107.15 (3)	107.53 (4)	107.41 (4)
S(2)-Mo(2)-S(5)	83.49 (3)	83.41 (4)	84.03 (4)
S(1)-Mo(2)-S(6)	88.28 (3)	89.24 (4)	88.20 (4)
S(5)-Mo(2)-S(6)	78.41 (4)	78.00 (4)	78.05 (5)
O(2)-Mo(2)-N(2)	173.73 (10)	169.7 (2)	172.0 (1)
Mo(1)-Mo(2)-O(2)	81.68 (5)	82.26 (6)	82.60 (8)
Mo(1)-Mo(2)-N(2)	98.74 (8)	97.3 (1)	97.0 (1)
S(2)-Mo(1)-S(1)	107.18 (3)	107.35 (4)	107.54 (4)
S(2)-Mo(1)-S(3)	82.63 (3)	83.43 (5)	85.19 (4)
S(1)-Mo(1)-S(4)	90.42 (3)	88.67 (4)	86.83 (4)
S(3)-Mo(1)-S(4)	77.82 (3)	78.21 (5)	78.10 (5)
O(1)-Mo(1)-N(1)	169.18 (10)	172.6 (2)	173.8 (1)
Mo(2)-Mo(1)-O(1)	82.03 (5)	81.81 (8)	81.42 (7)
Mo(2)-Mo(1)-N(1)	96.42 (8)	100.3 (2)	98.9 (1)
Mo(2)-S(2)-Mo(1)	74.52 (2)	74.37 (5)	74.02 (3)
Mo(2)-S(1)-Mo(1)	71.14 (2)	70.73 (4)	71.02 (3)
Mo(2)-S(1)-Z ^a	106.39 (8)	116.19 (7)	114.3 (2)
Mo(1)-S(1)-Z ^a	113.90 (8)	109.42 (7)	110.4 (1)
Mo(2)-S(5)-P(2)	87.77 (4)	88.04 (7)	87.86 (6)
Mo(1)-S(3)-P(1)	88.36 (4)	88.21 (7)	87.71 (7)
Mo(1)-S(4)-P(1)	87.39 (5)	87.19 (7)	87.06 (7)

Table 4, continued

	Mo₂SOMe	Mo₂SSEt	Mo₂SNH₂
Mo(2)-S(6)-P(2)	86.51 (5)	87.12 (6)	86.58 (6)
S(1)-Z-C(25) ^a	115.4 (2)	101.5 (3)	-
S(3)-P(1)-S(4)	106.42 (6)	106.40 (9)	106.84 (8)
S(5)-P(2)-S(6)	106.92 (5)	106.82 (7)	106.75 (9)
Mo(1)-O(1)-C(15)	125.85 (17)	126.3 (3)	126.4 (2)
Mo(2)-O(2)-C(15)	125.80 (17)	126.3 (3)	125.0 (2)
Mo(2)-N(2)-C(8)	177.8 (2)	170.4 (4)	177.7 (4)
Mo(1)-N(1)-C(1)	175.5 (2)	174.9 (4)	178.8 (4)
O(1)-C(15)-O(2)	124.4 (2)	123.3 (5)	124.2 (2)
O(1)-C(15)-C(16)	117.8 (3)	118.1 (4)	135.4 ()
O(2)-C(15)-C(16)	117.8 (3)	118.6 (4)	117.9 ()

^aZ = O(7) or S(7) or N(3)

Figure 5. ORTEP view of Mo_2SOMe .

Figure 6. ORTEP view of Mo₂SSEt.

Figure 7. ORTEP view of Mo_2SNH_2 .

CHAPTER III

PHOTOLYSIS AND THERMOLYSIS STUDY OF METHYL THIOPEROXIDE-BRIDGED MOLYBDENUM(V) DIMER [Mo₂(NT_o)₂(S₂P(OEt)₂)₂S(O₂CMe)(SOMe)]

Introduction

The photochemistry and thermochemistry of organic sulfoxides and sulfenate esters have been extensively studied because of their mechanistic and stereochemical interest and because of their synthetic utility.^{37,38,49} These molecules have demonstrated useful synthetic properties related to their S-O, S-C, and O-C bonds. For example, sulfenate esters can be photolyzed to give precursors of alkyl and alkoxy radicals.^{41,44} They can also be thermolyzed to produce the corresponding sulfoxides, which in turn can be photolyzed back to sulfenate esters.^{55-58,64} Therefore some investigations into the photolysis and thermolysis of Mo₂SOMe were undertaken to determine if it could isomerize to the sulfoxide Mo₂S(O)Me (eq 1), maybe via a C-O bond homolysis or an intramolecular concerted mechanism.

The sulfoxides Ar-SO-R (Ar= aryl group, R= benzyl, etc) have been shown to produce photolytically the corresponding sulfenate esters Ar-S-O-R.⁵⁵ Then these sulfenate esters, by thermolysis, reversibly rearrange themselves to give the originating sulfoxide. In the instance of benzyl *p*-tolyl sulfoxide To-SO-CH₂Ph and benzyl phenyl

sulfoxide Ph-SO-CH₂Ph, the photolysis reaction produced benzyl *p*-tolyl sulfenate To-S-O-CH₂Ph and benzyl phenyl sulfenate Ph-S-O-CH₂Ph respectively.⁵³ The first step of the reaction consisted of the cleavage of the S-CH₂ bond to form a sulfinyl/benzyl radical pair. It was followed by a rearrangement/recombination of the radical pair into a sulfenate ester (eq 2).

Further photolysis of these benzyl arenesulfenate esters cleaved the S-O bond homolytically and yielded arenethiols, benzaldehyde, disulfides, and benzyl alcohol (eq 3).

Viscosity of the solvent, as well as its reactivity, and the radiation wavelength used, affected the outcome of the reaction. Essentially, conditions that limited the escape of the radical species from the solvent cage allowed the formation of mostly arenethiols and benzaldehyde. The reaction is also subject to competing mechanisms when performed in a very polar solvent, with traces of acid.

Among the many sulfenate ester-sulfoxide thermal rearrangements, one of the best known [2,3]-sigmatropic rearrangements (Evans-Mislow rearrangement)^{49,53,65} is the reversible interconversion of allylic sulfenate esters to sulfoxides. It has shown to be a key reaction to control the stereochemistry in the total syntheses of natural products.^{46,47} This reaction occurs via an intramolecular rearrangement pathway but other types of rearrangements are possible like the thermolysis of cinnamyl-4-nitrobenzenesulfenate, which follows a radical pair mechanism (eq 4).⁶⁴ The homolytic cleavage of the carbon-

oxygen bond of the sulfenate ester is followed by the radical recombination and formation of a sulfur-carbon bond of the sulfoxide.

The potential to reversibly go from a sulfoxide to a sulfenate ester by choosing to cleave homolytically either an S-O bond or a C-O bond opens the door to greater control and variety of the chemistry of these molecules. Both computational and experimental studies have brought a better understanding of the chemistry of these reactions, although in some instances the exact mechanisms are not definitive.

On the other hand, stable metal-sulfur complexes with a sulfenate ester group are rare and not well studied. Rauchfuss and coworkers⁸ have described the finding of an iridium sulfenate ester, $[\text{Ir}(\eta^1\text{-SOMe})(\text{MeNC})(\text{dppe})_2]^{2+}$, and our group recently synthesized Mo_2SOMe ,³⁰ characterized by its stability. Mo_2SOMe is structurally similar to Mo_2SSEt (see Chapter II). Mo_2SSR compounds can undergo a photolysis reaction through the formation of $\text{Mo}_2\text{S}\cdot$ and $\cdot\text{SR}$ radicals with, in some cases ($\text{R}=\text{Ph}$ or To), a photoequilibrium (eq 5).⁶¹

The photolability of Mo_2SSR compounds is sensitive to the type of R substituent. S-alkyl bridge groups, compared to S-aryl bridge groups, require a source of higher energy in the form of UV radiation in order to achieve S-S bond dissociation. If Mo_2SOMe followed a photolysis mechanism close to that of Mo_2SSR compounds or organic sulfenate esters,

one would expect Mo₂SH, H₂CO, Mo₂SSMo₂, and CH₃OH to form. The reaction would involve a radical pathway with Mo₂S• and •OCH₃ radical intermediates. Indeed the photolysis of Mo₂SOMe forms products that are the recombination of initial Mo₂S• and •OCH₃ radicals possibly through a photoequilibrium (eq 6).

Radicals are known to be produced two ways: by thermolytic or by photolytic means. Their pathway is not necessarily identical and, as organic sulfenate esters have shown, the bond cleaved might not be the same.⁶⁴ In light of the chemistry of organic sulfenate esters, the behavior of Mo₂SOMe with respect to photolysis and thermolysis will thus be the focus of this chapter.

Experimental section

Reactions were conducted open to air and under normal lighting conditions except as noted. Mo₂SOMe was prepared according to Chapter II. Mo₂SNH₂ was prepared as previously reported.¹⁴ All commercial reagents were used as received.

UV-Vis absorbance spectra of the samples were obtained with a Perkin-Elmer 330 spectrophotometer using HPLC grade CHCl₃ and 1.0 cm quartz cuvettes.

³¹P {¹H} and ¹H NMR spectra were obtained in CDCl₃ in the case of the photolysis and thermolysis reactions, and also in C₆D₅Cl for the thermolysis reactions, on a Varian spectrometer at 202 MHz and 500 MHz, with a Unity Inova console. ³¹P {¹H} and ¹H spectra are reported as downfield shifts from external 85% H₃PO₄ and internal Me₄Si respectively.

Photolyses were conducted in either of two apparatuses of in-house construction.

Both used 5 cm × 5 cm, square Corning cutoff filters and a Hanovia 679A36-825629 lamp as the source of UV light. One apparatus consisted of a dark chamber with a square window (of dimensions 5 cm × 5 cm), a mountable filter and a manual shutter. It was used for NMR tube experiments. The solution was set in a quartz NMR tube and centered in the window opening. The lamp was mounted horizontally to the NMR tube containing the solution to photolyze. The distance between the tube and the lamp was 50 cm. The other apparatus was a closed box with only a round opening fitted for a 19/22 round-bottom flask. It was used for large-scale experiments that required stirring. The opening was covered with the filter enclosed in a window. The solution was set in the round bottom flask and continuously stirred using a magnetic stir bar. The lamp was mounted horizontally to the filter. The light source was placed flat and centered above the opening of the flask at a distance of 15-25 cm. A cooling fan was used to decrease the temperature of the apparatus.

NMR-tube photolysis reactions. Photolysis in solution was performed in CDCl_3 in a quartz NMR tube. The solutions were photolyzed over several periods of time and monitored by NMR spectroscopy at each stage.

$[\text{Mo}_2(\text{NT}_\text{o})_2(\text{S}_2\text{P}(\text{OEt})_2)_2\text{S}(\text{O}_2\text{CMe})(\text{SOMe})]$, Mo_2SOMe , (4.7 mg, 0.0051 mmol) in CDCl_3 (0.5 mL) was photolyzed using a Corning 9-54 filter. ^{31}P and ^1H spectra were obtained at 2 h, 5 h, 10 h, and 14 h (total times).

The photolysis of a solution of Mo_2SOMe was separately performed under air-free conditions using dry CDCl_3 and following the same process as above. The solution was prepared in a glove bag under nitrogen atmosphere to avoid traces of moisture and oxygen.

The photolysis of Mo₂SOMe, in powder form, was performed for 24 h under air-free conditions. It was dissolved in CDCl₃ and ³¹P and ¹H NMR spectra were obtained.

Large-scale photolysis reactions. Mo₂SOMe (65 mg, 0.071 mmol) was dissolved in CDCl₃ (3.2 mL) in a 10 mL round-bottom flask. The solution was photolyzed using a 9-54 Corning filter. An aliquot of the solution was taken at 2 h, 5 h, 20 h, and 32 h (total times) and analyzed by NMR spectroscopy. Volatiles were then removed by rotary evaporation. The residues were redissolved in CDCl₃ and a second NMR analysis was performed. Each time, the aliquots were returned to the solution for further photolysis and ³¹P, ¹³C, ¹H NMR spectra were obtained.

Thermolysis of Mo₂SOMe. Mo₂SOMe (4.8 mg, 0.0052 mmol) was dissolved in C₆D₅Cl (0.5 mL) in an NMR tube and heated at an average of 148 (±8)°C in a silicone oil bath. The reaction was monitored by NMR spectroscopy at 2 h, 5 h, and 24 h. At these defined times, the tube was removed from the bath and allowed to cool down to room temperature. ³¹P and ¹H NMR spectra were taken.

Results

The photolysis of Mo₂SOMe in solution, using UV radiation without any filter, leads to the rapid decomposition of the compound within about 15 minutes. Filters were used to determine the range of absorbance that would give less decomposition and a fairly clean reaction. The best outcome was obtained using a Corning 9-54 filter. The UV-Vis spectrum (see Figure 9) of Mo₂SOMe showed two maxima and a shoulder at 313 nm ($\epsilon = 25400 \text{ M}^{-1} \text{ cm}^{-1}$), 410 nm ($\epsilon = 7320 \text{ M}^{-1} \text{ cm}^{-1}$), and 510 nm ($\epsilon = 1400 \text{ M}^{-1} \text{ cm}^{-1}$). As can be seen in Table 5, the UV-Vis data are similar to Mo₂SNH₂ and various Mo₂SR

and Mo₂SSR compounds.¹⁶ All compounds exhibit absorption at similar wavelengths although with different extinction coefficients. The extinction coefficient of Mo₂SOMe was especially lower in the UV region of ~300 nm.

The reactivity of Mo₂SOMe could only be achieved significantly by using UV radiation as a source of higher energy. At this energy level, the compound and its direct products tend to undergo many decomposition reactions. Cleaner reactions were achieved using Corning cutoff filters. A Corning 9-54 filter (10% and 80% transmittance at 240 nm and 276 nm respectively) gave the best results by giving fewer and more identifiable products. The photolyses did not reach completion in the allotted time of the studies. Solutions of Mo₂SOMe and Mo₂SOEt left in the dark at room temperature for several days were used as controls. They showed no reaction.

Photochemistry of Mo₂SOMe. Mo₂SOMe did not photolyze with visible light when in solid state or solution. The photolysis of Mo₂SOMe powder under air-free conditions, over 24 h, has shown also that it is not sensitive to UV light in the solid state. Its large-scale solution photolysis in CDCl₃ using UV light and a 9-54 filter showed, after 32 hours, three major products in the ³¹P NMR spectrum (Figure 11): 39% of a product at 107.8 ppm and 16% of a product at 114.2 ppm and 87.2 ppm, while 32% Mo₂SOMe was unreacted at 114.9 ppm. The photolysis did not reach completion in the allotted time of the study and several unidentified compounds were among the products; there was also a slow formation of solid upon sitting in the dark afterwards. In all of the experiments, ¹H NMR spectra showed (Figure 10) the formation, between 2.10 ppm and 2.17 ppm, of CH₃COOH/CH₃COO⁻ species. The presence of a methanol peak at 3.45 ppm was observed in the ¹H NMR spectra of the solution before solvent and volatiles were stripped

off. Each of these was definitively confirmed by addition of acetic acid and methanol vapors to the solution. The ^{31}P peaks at 114.2 ppm and 87.2 ppm (Figure 11) are respectively attributable to the bidentate dithiophosphate ligands and to the bridge dithiophosphate of a dithiophosphate disulfide-bridged dimer $\text{Mo}_2\text{SSPS}(\text{OEt})_2$, compound **2**, which has been previously characterized.¹⁴

This finding is substantiated by the ^1H NMR data (Figure 10) showing two doublets of tolyl ring protons at 6.59 ppm and 6.50 ppm, multiplets of bidentate POCH_2 around 4.55 ppm and between 3.95 and 4.25 ppm, a tolyl $-\text{CH}_3$ singlet at 2.10 ppm, a triplet of the bridge POCCH_3 at 1.63 ppm, two triplets of the bidentate POCCH_3 at 1.34 ppm and 1.21 ppm. The acetate bridge singlet is buried among the other peaks at 1.33 ppm. The presence of $\text{Mo}_2\text{SSPS}(\text{OEt})_2$ suggests that a dimolybdenum radical, $\text{Mo}_2\text{S}^\cdot$, is produced during the photolysis process, because $\text{Mo}_2\text{SSPS}(\text{OEt})_2$ is a typical decomposition product of radical reactions. The free disulfide, $(\text{EtO})_2\text{P}(\text{S})\text{S}-\text{SP}(\text{S})(\text{OEt})_2$, is also a product of the subsequent photolysis of $\text{Mo}_2\text{SSPS}(\text{OEt})_2$.⁶⁷ It should appear in the ^{31}P NMR spectra around 85.4 ppm, although its small quantities make it difficult to observe in the current spectra (Figure 11).

The major product is located at 107.8 ppm in the ^{31}P NMR spectrum. Correlation between the ^{31}P , ^{13}C , and ^1H spectra allowed the identification of most of its functional groups. It is characterized in the ^1H NMR spectra (Figure 10) by two well-separated

multiplets centered at 4.37 ppm and 3.87 ppm that can be attributed to $\text{P}(\text{OCH}_2)_2$ ligand groups. The singlet at 3.77 ppm is indicative of a methoxy group. However, there is no conclusive evidence of an $\text{S}(=\text{O})\text{Me}$ group in the region of 2-3 ppm. Thus, the expected isomerization of $\text{S}-\text{OMe}$ to an $\text{S}(=\text{O})\text{Me}$ group did not occur. A $\text{To}-\text{CH}_3$ singlet is present at 2.18 ppm and two doublets of tolyl aromatic protons are discernible at 6.71 ppm and 6.64 ppm. It is important to note the absence of an acetate bridge singlet. The spectrum of this product suggests that this product has retained planar symmetry as in the initial Mo_2SOMe . The largest differences are the absence of an acetate bridge and the chemical shift separation between the two $\text{P}(\text{OCH}_2)_2$ multiplets. These differences could be explained by the replacement of the acetate bridge of Mo_2SOMe by a hydroxo bridge (Figure 8).

Figure 8. Proposed main product of the photolysis reaction.

The experiments conducted in dry and air-free CDCl_3 solvent showed that more bis-dimer disulfide Mo_2SSMo_2 formed relative to the 107.8 ppm compound and dithiophosphate disulfide-bridged dimer $\text{Mo}_2\text{SSPS}(\text{OEt})_2$ than under open-air conditions.

Thermolysis of Mo_2SOMe . Several attempts, unsuccessful, were made at various temperatures, in CDCl_3 , C_6D_6 , and $\text{C}_6\text{D}_5\text{Cl}$, to determine if any reaction would take place. Ultimately, the high boiling point, deuterated solvent $\text{C}_6\text{D}_5\text{Cl}$ was chosen to perform the thermolysis due to the significant heat required (at least 130°C). The time study of the

thermolysis has allowed the partial identification of the products of this reaction. In the ^{31}P NMR spectra (Figure 13), the main products were an unknown compound at 107.8 ppm and tetramer, $[\text{Mo}(\text{NTo})(\text{S}_2\text{P}(\text{OEt})_2\text{S})_4]$, at 111.5 ppm. Tetramer is a normal product of the decomposition of Mo_2S^+ or Mo_2S^- dimer fragments. After 5 h of thermolysis in $\text{C}_6\text{D}_5\text{Cl}$, Mo_2SOMe produces 15 % tetramer and several unknown products, including one at 107.8 ppm (17 %). ^1H NMR in $\text{C}_6\text{D}_5\text{Cl}$ (Figure 12) showed a methanol peak at about 3.20 ppm, and two singlets at 3.41 ppm and 1.76 ppm belonging, respectively, to the methoxy and methyl groups of methyl acetate. No sulfur methoxy peak was seen at 3.77 ppm, however, that could link it to the unknown found during the photolyses described above. Methanol, methyl acetate, and tetramer were definitively identified by comparison with a solution containing these three compounds in $\text{C}_6\text{D}_5\text{Cl}$. An interesting singlet at 5.34 ppm appeared, but it could not be identified. After 24 h the 107.8 ppm product disappeared, although this might have started to occur much earlier than 24 hours. The formation of methanol could be the result of the cleavage of the S-O bond of Mo_2SOMe . The presence of methyl acetate might be due to the reaction of the acetate bridge and the methoxide functionality of Mo_2SOMe that produces methyl acetate (eq 7).

This reaction might be helped by the close distance between the oxygen O(7) of the methoxy ligand and the C(15) carbon of acetate ligand as described in Chapter II.

Many sulfur invertomers of the products described above are possibly present in solution. Their identification or presence was not established and only the predominant ones are described herein.

Discussion

Prior photolysis studies of Mo₂SSR followed the photochemistry of diorganyl disulfides,^{16,61} as shown in the overall reaction (eq 8).

The initiation step of the reaction is the homolysis of the S-S bond. Then, a recombination step produces the bis-dimer disulfide.

The photolability of Mo₂SSR compounds is dependent on the R substituent. Aryl precursors are more reactive than alkyl precursors, and increase the rate of the photolysis. The greater reactivity of aryl versus alkyl radicals is due to the stabilizing resonance that aryl thiyl radicals can take.

In the case of the photolysis of Mo₂SOMe, the formation of Mo₂SSMo₂ suggests a homolytic cleavage of the S-O bond. The involvement of a methoxy radical ·OMe would then be consistent with the presence of methanol among the products. Mo₂SSPS(OEt)₂, one of the main products of the photolysis, has been identified in a prior study as a photo-

decomposition product of Mo_2SSMo_2 in CDCl_3 .⁶¹ Some $\text{Mo}_2\text{SSPS}(\text{OEt})_2$ can then decompose to the free ligand disulfide as described in the following reaction steps:

These results, as well as the formation of Mo_2SSMo_2 strongly favor a radical pathway.

The following partial mechanism can be envisioned:

The radical $\cdot\text{S}_2\text{PS}(\text{OEt})_2$ might originate from the decomposition of $\text{Mo}_2\text{S}\cdot$. Some side reactions are expected to drive irreversibly the equilibrium towards the formation of $\text{Mo}_2\text{S}\cdot$ and $\cdot\text{OMe}$ radicals. Methoxy radicals might react with any product of decomposition or with the reaction solvent to produce methanol.

Several external factors can affect in many ways the photolyses: the viscosity of the solvent, traces of acid, or the presence of oxygen or water in solution;^{55,58,64,66} these are among the factors that can affect the recombination of the radical pair formed during the photolysis. Cage products like Mo_2SH and formaldehyde are more likely to form in high viscosity solvents, while out of cage products like Mo_2SSMo_2 and MeOH are favored in low viscosity solvents (CDCl_3 in our case).

Organic sulfenate esters have been suggested as precursors to the formation of alkyl and alkoxy radicals via a photolytic process that cleaves the S-O bond and yields

thiols, aldehydes, disulfides, and alcohol moieties through a radical pathway.^{41,43,44,55} This process is described by the following reactions:

The $\cdot\text{OCH}_2\text{R}'$ radical can form $\text{R}'\text{CH}_2\text{OH}$ by abstracting a hydrogen atom from a multitude of sources. These sources could be: another $\cdot\text{OCH}_2\text{R}'$ radical, which would then give the aldehyde $\text{R}'\text{CHO}$; any hydrogen containing species present in solution. The thiols produced may recombine with other radicals in solution to produce the disulfides. If Mo_2SOMe were to follow a similar mechanism, one would expect that Mo_2SH , H_2CO , Mo_2SSMo_2 , and CH_3OH are formed and that they involve a radical pathway with the formation of $\text{Mo}_2\text{S}\cdot$ and $\cdot\text{OCH}_3$. The actual production of methanol and Mo_2SSMo_2 during the photolysis strongly suggests the cleavage of the S-O bond. The slight change in the proportions of the products between open-air and air-free solutions can lead us to think that oxygen or water are somewhat involved in the side reactions.

The formation of acetic acid and the absence of an acetate group related to the unknown 107.8 ppm photolysis product indicate that Mo_2SOMe lost its acetate bridge during the photolysis. Nevertheless, the ^1H NMR chemical shift assignments show that the unknown at 107.8 ppm has a structure similar to that of Mo_2SOMe . It possesses the same groups except for the acetate bridge. Another noticeable difference in the ^1H NMR spectra (Figure 10) is the chemical shift separation (0.5 ppm) between the two multiplets representing the methylene protons of the dithiophosphate ligands. In order to maintain a

certain symmetry of its structure, the replacement of the acetate bridge by a hydroxo bridge is proposed (Figure 8).

Thermolysis of organic sulfenate esters can produce the isomeric sulfoxides, which can then be photolyzed back to the esters. Unfortunately, with the information gathered, there was no sufficient evidence of the formation of a rearranged sulfoxide $\text{Mo}_2\text{S}(=\text{O})\text{Me}$. The production of tetramer proceeds via a mechanism not yet understood. It might result from the loss of both the methoxy substituent and the acetate group of Mo_2SOMe . The origin of the hydrogen atoms captured by the methoxy or acetate groups is unclear in the present conditions.

The reasons for the absence of isomerization reside in either the thermodynamic or kinetic nature of the reaction. If Mo_2SOMe is thermodynamically more stable than $\text{Mo}_2\text{S}(=\text{O})\text{Me}$, any thermal equilibrium between these isomers will favor Mo_2SOMe . Additionally, if the kinetic energy barrier

to produce $\text{Mo}_2\text{S}(=\text{O})\text{Me}$ is too high, no isomerization will occur and other reactions with lower energy requirements might take place.

Table 5. Selected UV-Vis Data^a

Mo ₂ SSR			
R = Et	311 (28900)	~408 (6620)	502 (1480)
Bz	310 (28800)	~407 (6990)	502 (1520)
PS(OEt) ₂	306 (31900)	~409 (6950)	502 (1530)
Mo ₂ SR			
R = Et	319 (27900)	~406 (6720)	492 (1450)
Bz	317 (27000)	~410 (6510)	496 (1590)
NH ₂	314 (27300)	~402 (7040)	500 (1600)
R = OMe	313 (25400)	~410 (7320)	510 (1400)

^aValues are wavelength (nm) (ϵ (M⁻¹ cm⁻¹)). The ~ indicates a shoulder.

Figure 9. UV spectrum of Mo₂SOMe, 1.

Figure 10. ^1H NMR spectra of the time-study photolysis of Mo_2SOMe .

Figure 11. ^{31}P NMR spectra of the time-study photolysis of Mo_2SOMe .

Figure 12. ^1H NMR spectra of the time-study thermolysis of Mo_2SOMe .

Figure 13. ^{31}P NMR spectra of the time-study thermolysis of Mo_2SOMe .

CHAPTER IV

PROTONATION OF METHYL THIOPEROXIDE-BRIDGED MOLYBDENUM(V) DIMER $[\text{Mo}_2(\text{NT}_0)_2(\text{S}_2\text{P}(\text{OEt})_2)_2\text{S}(\text{O}_2\text{CMe})(\text{SOMe})]$ WITH AN INORGANIC ACID

Introduction

As described in Chapter II, the structure of Mo_2SOMe , with its unusual linkage $\text{Mo}_2(\mu\text{-S-OR})$, is similar to that of the sulfenamide Mo_2SNH_2 , compound **3**.^{14,15} Both molecules are stable in solution and under normal lighting conditions. Their similarities extend to the electronic properties of their μ -sulfur substituent. Indeed, the electronegativity of oxygen is 3.5 on the Pauling scale and 3.0 for nitrogen, and both atoms are more electronegative than sulfur ($\text{EN}=2.5$), creating a partial negative charge on the O of Mo_2SOMe or on the N of Mo_2SNH_2 and a partial positive charge on sulfur. Also, the alkoxy oxygen on Mo_2SOMe and the amide nitrogen on Mo_2SNH_2 , possess free lone pairs of electrons that can react with a Brønsted acid.

These similarities will be in part surveyed in this chapter by comparing the protonation chemistry of both molecules.

Previous studies conducted by June Lee⁶⁷ had shed light on the reactivity of the amide nitrogen of Mo₂SNH₂. Those studies showed that the reaction of Mo₂SNH₂ with the inorganic acid HBF₄ (eq 1) leads to a new kind of compound characterized by a bis-dimer core and a sulfenamide function. This new compound was isolated, characterized

and identified as the [Mo₂SSMo₂SNH₂](BF₄) salt, compound 4. Many organic sulfenate esters thermally rearrange to sulfoxides and some of these reactions appear sensitive to the presence of acid in the solvent.^{38,51} Traces of acid seem to be responsible for competing mechanisms. Although this aspect was not studied in the previous chapter, it is of importance to understand the chemical reactivity of oxygen and sulfur for Mo₂SOR compounds. Another interesting side of the present acid-base reaction is the possible production of the electrophilic intermediate Mo₂S⁺, which could have potential use as a precursor in reactions with nucleophilic species like dienes. Therefore, a comparison is made with the reactivity of the analogous sulfenamide Mo₂SNH₂. Some aspects of the reaction of Mo₂SOMe with the inorganic acid HBF₄, are thus investigated in this chapter. The study is based on the comparison between the NMR data gathered through a time-study reaction (Figure 15) and the characterization of the products of the reaction (Figure 16).

Experimental Section

Reactions were conducted open to air except as noted. Mo₂SOMe was prepared according Chapter II. All commercial reagents were used as received.

³¹P {¹H} and ¹H NMR spectra were obtained in CDCl₃, on a Varian spectrometer at 202 MHz and 500 MHz, with a Unity Inova console. ³¹P {¹H} and ¹H spectra are reported as downfield shifts from external 85% H₃PO₄ and internal Me₄Si respectively. Minor invertomers are indicated in parentheses whenever discernible.

[Mo₄(NTO)₄(S₂P(OEt)₂)₄S₃(O₂CMe)₂(SOMe)](BF₄), compound **5**. A solution of Mo₂SOMe (93.5 mg, 0.103 mmol) in C₆H₆ (2.2 mL) was mixed with a solution of HBF₄•OEt₂ (14.7 μL, 0.103 mmol) in C₆H₆ (0.3 mL). C₆H₆ (0.6 mL) was then used to complete the transfer. The solution was stirred for one minute and left undisturbed for a few days until all the volatiles had evaporated. The residue was redissolved in CH₂Cl₂ (1.6 mL) and treated with hexanes (2.6 mL). After decantation, the supernatant was pipetted off and the oily fraction was left to dry by slow evaporation of the volatiles. A dark red solid was collected but it still contained impurities. It was redissolved in CDCl₃ and characterized by NMR spectroscopy (Figure 15 and 16).

Reaction of Mo₂SOMe with excess HBF₄(aq) in CDCl₃. A solution of Mo₂SOMe in CDCl₃ (~ 0.5 mL) was prepared in an NMR tube. 4 equivalents of HBF₄(aq) were directly added with a syringe. NMR spectra were taken after 1.5 h, 6 h, and 29 h (Figures 15). The main product, compound **5**, was identified by comparison of this study with the NMR data of [Mo₂SSMo₂SNH₂](BF₄). ³¹P NMR (ppm): 113.8 s, 109.0 s. ¹H NMR (ppm): 7.05 d, 6.90 d, 6.48 d, 6.47 d, To H; 4.0-4.3 m POCH₂; 4.32 s, OCH₃; 2.14 s, 2.13 s, To CH₃; 1.42 s, 1.18 s, O₂CCH₃; 1.34 t, 1.24 t POCCH₃.

Results

As shown in the phosphorus spectrum of the reactions studied (Figure 15), two dominant and equivalent peaks form simultaneously at 113.8 ppm and 109.0 ppm, concurrently with the disappearance of Mo_2SOME (114.8 ppm). Although full purification of the product after recrystallization was not achieved, its ^1H NMR spectrum (Figure 16) offered enough information to allow its characterization. It indicates two sets of doublets in the tolylimido region of the spectrum. Two singlets at 2.14 ppm and 2.13 ppm show the presence of two equivalent To-CH_3 groups. The well separated singlets at 1.42 ppm and 1.18 ppm belong to the methyl of the acetate-bridges of the Mo_2S_2 dimer units of different configuration: one unit is in a proximal configuration, the other in a distal configuration. The NMR also indicates a methoxy group at 4.32 ppm, downfield from 3.95 ppm for Mo_2SOME . By comparison to the NMR data of the reaction of Mo_2SNH_2 with $\text{HBF}_4\cdot\text{OEt}_2$,⁶⁷ done in identical conditions, we conclude that the main product of the reaction is $[\text{Mo}_4(\text{NTo})_4(\text{S}_2\text{P}(\text{OEt})_2)_4\text{S}_3(\text{O}_2\text{CMe})_2(\text{SOME})](\text{BF}_4)$ (eq 2). For simplification purposes this product will be abbreviated $[\text{Mo}_2\text{SSMo}_2\text{SOME}](\text{BF}_4)$.

The methanol product was clearly observable with its characteristic methyl group showing up at 3.45 ppm in the ^1H spectrum. The main product $[\text{Mo}_2\text{SSMo}_2\text{SOME}](\text{BF}_4)$ being ionic, it oils out quite readily from the solution mixture in benzene, but it dissolves

well in a polar solvent like chloroform. In non-polar solvents like benzene and with the use of etherated HBF_4 , the formation of $[\text{Mo}_2\text{SSMo}_2\text{SOMe}](\text{BF}_4)$ occurs within minutes. Due to the functionalized sulfur bridges, there are up to eight possible invertomers for the final product (Figure 14). Among the many peaks present in the spectra, some are minor invertomers of the products formed, but only the major invertomer will be studied.

Discussion

Stable metallosulfur complexes with a $\mu\text{-S-OR}$ linkage are scarce. The observations and conclusions herein are thus based upon the similarities found with the closest metallosulfur compound available: the sulfenamide Mo_2SNH_2 .^{14,15}

The sulfenamide had previously shown that protonation happened on the nitrogen atom rather than on the bridge sulfurs.⁶⁷ Likewise the site of protonation on Mo_2SOMe can either be at S or O due to the basicity of both atoms. Oxygen is more electronegative than sulfur. It has two electron lone pairs available and the inductive effect of the methyl group reinforces the basicity of the alkoxy oxygen. In the case of the reaction of Mo_2SNH_2 with $\text{HBF}_4 \cdot \text{OEt}_2$,⁶⁷ it had been shown that the amide nitrogen is protonated to produce the unstable intermediate $\text{Mo}_2\text{SNH}_3^+$, which readily lost NH_3 . An attack of the HBF_4 proton on the alkoxy oxygen of Mo_2SOMe was thus expected, as well as the formation of the $\text{Mo}_2\text{SOHMe}^+$ intermediate. Although no attempt was made to isolate this intermediate, the presence of methanol as a product of the reaction seems to indicate that the protonation occurs on the oxygen of the $\mu\text{-S-OMe}$ substituent. At this point, several mechanisms can be considered. In one case, the intermediate $\text{Mo}_2\text{SOHMe}^+$ reacts

Figure 14. Possible isomers of the cation, $[\text{Mo}_2\text{SSMo}_2\text{SOMe}]^+$.

in a concerted mechanism with either Mo_2SOMe (Scheme 1), through what June Lee described as a “back-bridge” attack or, in other words, an attack on the non-substituted sulfur. As the cation forms, its “back-bridge” sulfur reacts with the “back-bridge” of Mo_2SOMe (Scheme 1) and MeOH is simultaneously produced. In the other case, the intermediate $\text{Mo}_2\text{SOHMe}^+$ dissociates to generate the cation Mo_2S^+ and MeOH (eq 3). The production of a Mo_2S^+ intermediate would then constitute an extra step to the whole process (Schemes 2 and 3). Further attack by another proton on $\text{Mo}_2\text{SSMo}_2\text{SOMe}^+$,

followed by decomposition to Mo_2SSMo_2 and methanol, was not noticeable under the current conditions.

Despite the absence of crystal structure, a plausible hypothesis can be made regarding the configuration of the final product, $[\text{Mo}_2\text{SSMo}_2\text{SOMe}](\text{BF}_4)$. The comparison of the NMR data of the reactions for Mo_2SOMe and Mo_2SNH_2 , suggests that the two dimers in $\text{Mo}_2\text{SSMo}_2\text{S-OMe}^+$ are of opposite invertomer configuration. The dominant isomer is the one in the box in Figure 14. Although no attempt was made to isolate any intermediate, the Mo_2S^+ cation is expected to be very reactive, especially in the absence of a stabilizing polar solvent. This could lean reaction pathway towards a concerted mechanism rather than a dissociative one.

Scheme 1. Proposed concerted mechanism of $[\text{Mo}_2\text{SSMo}_2\text{SOMe}]^+$ formation

Scheme 2. Alternative mechanism of $[\text{Mo}_2\text{SSMo}_2\text{SOMe}]^+$ formation

Scheme 3. Alternative mechanism of $[\text{Mo}_2\text{SSMo}_2\text{SOMe}]^+$ formation

Figure 15. ³¹P NMR Time-study spectra of the reaction of Mo₂SOMe with HBF₄(aq) in CDCl₃.

Figure 16. ^1H Spectrum of $\text{Mo}_2\text{SSMo}_2\text{SOMe}^+$ in CDCl_3 after recrystallization.

CONCLUSION

Interestingly, Mo₂SOMe showed limited parallel to the chemistry of organic sulfenate esters counterparts. The isomerization of Mo₂SOMe to Mo₂S(=O)Me could not be achieved by the current thermolysis reactions. Instead of an O-C bond cleavage, the reactions led to what appears to be an S-O bond dissociation and to some decomposition products. Methanol and methyl acetate were produced, as well as tetramer. On the other hand, the photolysis and basicity of Mo₂SOMe demonstrated a behavior similar, in limited areas, to organic sulfenate esters. The photolysis of Mo₂SOMe produced the expected homolytic S-O cleavage, although the major pathway was the loss of the acetate bridge and the proposed formation of a hydroxo derivative of Mo₂SOMe. Other products included methanol, Mo₂SSPS(OEt)₂, and the disulfide (EtO)₂P(S)SSP(S)(OEt)₂. Mo₂SOMe displayed similar structure and basicity compared to Mo₂SNH₂. Its protonation by a strong inorganic acid like HBF₄ occurred at the S-O bond's oxygen. It successfully produced the cation Mo₂SSMo₂SOMe⁺ which synthesis and structure seem to parallel that of Mo₂SSMo₂SNH₂⁺.

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APPENDIX

LIST OF ABBREVIATIONS

Me	methyl
Et	ethyl
Bz	benzyl
To	<i>p</i> -tolyl
Ph	phenyl
en	ethylenediamine
dppe	1,2-bis(diphenylphosphino)ethane
PPN ⁺	Ph ₃ PNPPh ₃ ⁺
“tetramer”	[Mo(NTTo)(S ₂ P(OEt) ₂)S] ₄
Mo ₂ SOMe	[Mo ₂ (NTTo) ₂ (S ₂ P(OEt) ₂) ₂ S(O ₂ CMe)(SOMe)]
Mo ₂ SSEt	[Mo ₂ (NTTo) ₂ (S ₂ P(OEt) ₂) ₂ S(O ₂ CMe)(SSEt)]
Mo ₂ SMe	Mo ₂ (NTTo) ₂ (S ₂ P(OEt) ₂) ₂ S(O ₂ CMe)(SMe)]
Mo ₂ SNH ₂ or “sulfenamide”	[Mo ₂ (NTTo) ₂ (S ₂ P(OEt) ₂) ₂ S(O ₂ CMe)(SNH ₂)]
[Mo ₂ SSMo ₂ SNH ₂](BF ₄)	[Mo ₄ (NTTo) ₄ (S ₂ P(OEt) ₂) ₄ S ₃ (O ₂ CMe) ₂ (SNH ₂)](BF ₄)
Mo ₂ SSMo ₂	[Mo ₂ (NTTo) ₂ (S ₂ P(OEt) ₂) ₂ (O ₂ CMe)S ₂] ₂
Mo ₂ S or SMo ₂ S	[Mo ₂ (NTTo) ₂ (S ₂ P(OEt) ₂) ₂ (μ-S) ₂ (O ₂ CR)]
(See schematic illustrations shown below)

Representative development of “stick diagram”, using the dimer anion as an example.

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