

RHENIUM(VII) CIS-DIOXO COMPLEXES

by

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To Mom and Dad  
for all their love and support

"The time has come," the Walrus said,  
"To talk of many things:  
Of shoes - and ships - and sealing wax -  
Of cabbages - and kings -  
And why the sea is boiling hot -  
And whether pigs have wings."

-Lewis Carroll

*Through the Looking Glass*

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JARED VERRILL GOLDSTONE

Submitted to the Department of Chemistry  
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requirements for the Degree of Master of Science

## Abstract

**CHAPTER 1.** The synthesis and characterization of several rhenium (VII) *cis*-dioxo catecholate complexes is described. The trioxide  $\text{MeReO}_3$  reacts with  $1,2\text{-(OH)}_2\text{C}_6\text{Cl}_4$  and pyridine to form  $\text{MeReO}_2(1,2\text{-O}_2\text{C}_6\text{Cl}_4)(\text{pyridine})$ .  $\text{MeReO}_3$  reacts with  $1,2\text{-(OH)}_2\text{C}_6\text{H}_4$  and pyridine-N-oxide to form  $\text{MeReO}_2(1,2\text{-O}_2\text{C}_6\text{H}_4)(\text{pyridine-N-oxide})$ .  $\text{MeReO}_3$  reacts with  $1,2\text{-(OH)}_2\text{C}_6\text{H}_4$  and dimethylsulfoxide to form  $\text{MeReO}_2(1,2\text{-O}_2\text{C}_6\text{H}_4)(\text{DMSO})$ .  $\text{MeReO}_2(1,2\text{-O}_2\text{C}_6\text{H}_4)(\text{DMSO})$  catalyzes oxygen atom transfer from DMSO to  $\text{PPh}_3$  at room temperature. The catalyst is active through at least 200 turnovers. The X-ray crystallographic structure of  $\text{MeReO}_2(1,2\text{-O}_2\text{C}_6\text{H}_4)(\text{DMSO})$  shows an octahedral geometry with the *cis*-dioxo unit separated by an angle of  $108.7^\circ$ . Crystal data for  $\text{C}_9\text{H}_{13}\text{O}_5\text{ReS}$ : monoclinic,  $\text{P}2_1/\text{n}$ ,  $a = 7.92595(5) \text{ \AA}$ ,  $b = 11.9276(8) \text{ \AA}$ ,  $c = 12.8964(8) \text{ \AA}$ ,  $\beta = 95.7890(10)^\circ$ ,  $V = 1213.52(13) \text{ \AA}^3$ , to give  $Z=4$  and  $R=0.0275$ .

**CHAPTER 2.** Several rhenium (VII) *cis*-dioxo complexes of the ligand bis(*ortho*-hydroxyphenyl)phenylphosphine oxide ( $\text{H}_2\text{bipo}$ ) have been synthesized and characterized by NMR, IR, and mass spectrometry. A new synthesis of  $\text{H}_2\text{bipo}$  starting from methoxymethyl phenyl ether is described.  $\text{MeReO}_3$  reacts with  $\text{H}_2\text{bipo}$  in toluene to form  $\text{MeReO}_2(\text{bipo})$ . The electron impact mass spectrum (EI(+))MS) of  $\text{MeReO}_2(\text{bipo})$  is reported.  $\text{XReO}_3$  ( $\text{X} = \text{Cl}, \text{Br}$ ) complexes react with  $\text{H}_2\text{bipo}$  in toluene to form  $\text{XReO}_2(\text{bipo})$ .  $\text{Ph}_3\text{SiOREO}_3$  reacts with  $\text{H}_2\text{bipo}$  to form  $\text{Ph}_3\text{SiOREO}_2(\text{bipo})$ . These complexes do not transfer oxygen atoms to strained olefins.

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## **INTRODUCTION**

The chemistry of rhenium (VII) *cis*-dioxo complexes is slowly being explored. This work presents some examples of *cis*-dioxo complexes, including the use of a potentially tridentate ligand. In addition, the ability of these complexes to transfer an oxygen atom to an olefin is explored.

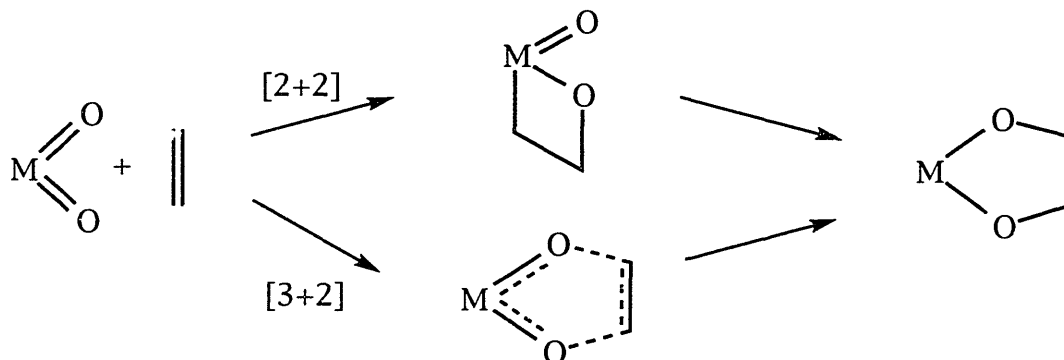
In octahedral geometry, two multiply bonded ligands adopt a geometry that maximizes  $\pi$  bonding capability. Thus, in  $d^0$  complexes such as those of Re(VII), multiply bonded ligands are mutually *cis* in order to be able to use all three  $d\pi$  orbitals in bonding.<sup>1</sup> The net bond order of such ligands is then 2.5. Multiply bonded ligands in octahedral  $d^2$  complexes are mutually *trans*, again in order to maximize  $\pi$  bonding and minimize  $\pi$  antibonding.

There are a number of *cis*-dioxo Re(VII) complexes. Hoffman and coworkers have synthesized  $\text{ReO}_2(\text{CH}_2\text{CMe}_3)_2\text{Br}$ ,  $\text{ReO}_2(\text{CH}_2\text{CMe}_3)_2\text{X}(\text{py})$  ( $\text{X} = \text{Br}, \text{Cl}, \text{F}; \text{py} = \text{pyridine}$ ), and  $\text{ReO}_2(\text{CH}_2\text{CMe}_3)_3$ ,<sup>2</sup> as well as  $\text{ReO}_2(\text{CH}_2\text{CMe}_3)_2(\text{SR})$  ( $\text{R} = \text{Me}, \text{Ph}$ ).<sup>3</sup> In addition, Wilkinson *et al.* have synthesized trimethyldioxorhenium.<sup>4</sup>  $\text{ReO}_2\text{F}_3$  has been synthesized and studied by Crocombe *et al.*,<sup>5</sup> among others.<sup>6</sup> Herrmann and coworkers have utilized  $\text{MeReO}_3$  to synthesize a number of *cis*-dioxo complexes, including  $\text{MeReO}_2(1,2\text{-O}_2\text{C}_6\text{H}_4)(\text{py})$ ,  $[\text{MeReO}_2(1,2\text{-O}_2\text{C}_6\text{H}_4)\text{X}]^-[ \text{Hpy} ]^+$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ), and  $\text{MeReO}_2(1,2\text{-S}(\text{HN})\text{C}_6\text{H}_4)(\text{py})$ .<sup>7,8</sup>

An important aspect of rhenium oxo chemistry is their use in oxygen atom transfer reactions. Methyltrioxorhenium (MTO), for example, has proved to be a selective and versatile oxidant. The mechanism by which metal oxo complexes transfer one or two oxygen atoms to an olefin has been intensively studied, although no conclusions have as yet been reached.<sup>9-11</sup> The mechanism originally proposed by Sharpless for two atom transfer involves the initial coordination of the olefin to the metal center.<sup>12</sup>

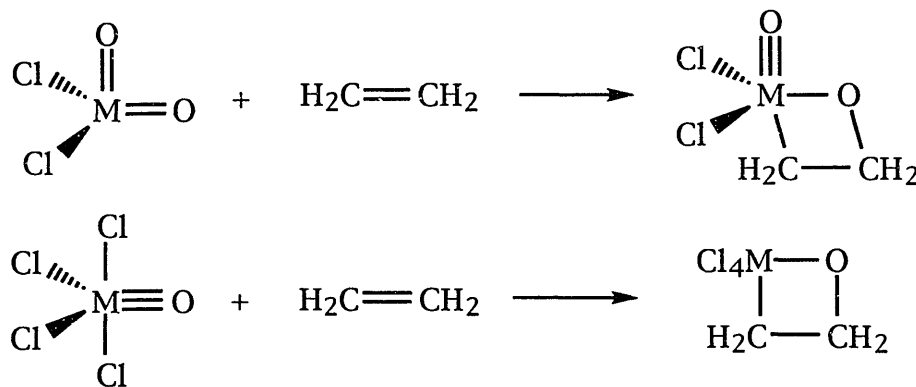


This is then followed by the formation of a metallaoxetane, and finally a [2+2] addition to form a diolate (Equation 1).<sup>1,11</sup> The alternate mechanism is a [3+2] cycloaddition proposed by Jørgensen in 1986 (Equation 1).<sup>13</sup>



Equation 1

The presence of metal-oxo bonds has been theorized to substantially stabilize intermediates in oxo-transfer reactions.<sup>14</sup> *Ab initio* studies have shown that metal-oxo bonds with triple bond character impart greater stability to metal intermediates than those metal-oxo groups that are doubly bonded.<sup>15,16</sup> It has been argued that the formation of a metal-oxygen triple bond serves as the thermodynamic driving force for oxygen atom transfer.<sup>1</sup> The reaction of  $\text{MO}_2\text{Cl}_2$  with an olefin has been calculated to be  $360 \text{ kJ mole}^{-1}$  more favorable than the analogous reaction of  $\text{MOCl}_4$  (Equation 2).<sup>17</sup>



Equation 2

In the case of the transfer of two oxygen atoms from metals including Cr, Mo, Mn, Tc, Re, and Os there is always an extra "spectator oxo" which does not overtly participate in the reaction. Those complexes with only two oxo ligands, such as [*bis*-(diethyldithiocarbamate)]*cis*-dioxomolybdenum(VI), selectively transfer only one oxygen.<sup>1</sup> The necessity of an 'extra' oxo for oxygen transfer might be determined by studying transfer reactions involving *cis*-dioxides.

By following the synthetic methodology of Herrmann *et al.*,<sup>7</sup> a number of new rhenium(VII) *cis*-dioxo complexes have been synthesized. In addition, the tridentate ligand *bis*-(*o*-hydroxyphenyl)phenylphosphine oxide has been utilized to achieve the desired coordination geometry. Since oxygen atom transfer reactions are of interest, the reactivities of these complexes towards strained olefins has also been investigated.

Several of the catecholate complexes synthesized here may be catalysts for the transfer of an oxygen atom from dimethylsulfoxide (DMSO) to PPh<sub>3</sub>. A number of other compounds can catalyze similar reactions.<sup>9,18-22</sup> These complexes include the MO<sub>2</sub>(L) systems of Holm *et al.*<sup>23</sup> and others,<sup>18,20</sup> and the Tc(III)/Tc(V) system described by de Vries *et al.*<sup>22</sup> Oxygen atom transfer catalysis continues to be an area of important and fruitful research.

## References

- (1) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley & Sons: New York, 1988.
- (2) Cai, S.; Hoffman, D. M.; Wierda, D. A. *Organometallics* **1988**, *7*, 2069.
- (3) Cai, S.; Hoffman, D. M.; Wierda, D. A. *Inorg. Chem.* **1989**, *28*, 3784.
- (4) Mertis, K.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 1488.
- (5) Beattie, I. R.; Crocombe, R. A.; Ogden, J. S. *J. Chem. Soc., Dalton Trans.* **1977**, 1481.
- (6) Sunder, W. A.; Stevie, F. A. *J. Fluorine Chem.* **1975**, *6*, 449.
- (7) Takacs, J.; Kiprof, P.; Riede, J.; Herrmann, W. A. *Organometallics* **1990**, *9*, 782.
- (8) Takacs, J.; Cook, M. R.; Kiprof, P.; Kuchler, J. G.; Herrmann, W. A. *Organometallics* **1991**, *10*, 316.
- (9) Holm, R. H. *Chem. Rev.* **1988**, *88*, 1401.
- (10) Jørgensen, K. A. *Chem. Rev.* **1989**, *89*, 431.
- (11) Jørgensen, K. A.; Schiøtt, B. *Chem. Rev.* **1990**, *90*, 1483.
- (12) Sharpless, K. B.; Teranishi, A. Y.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1977**, *99*, 3120.
- (13) Jørgensen, K. A.; Hoffman, R. *J. Am. Chem. Soc.* **1986**, *108*, 1867.
- (14) Lee, D. G.; Helliwell, S. *Can. J. Chem.* **1984**, *62*, 1085.
- (15) Rappé, A. K.; Goddard, W. A. *J. Am. Chem. Soc.* **1982**, *104*, 448.
- (16) Rappé, A. K.; Goddard, W. A. *J. Am. Chem. Soc.* **1982**, *104*, 3287.
- (17) Rappé, A. K.; Goddard, W. A. *Nature* **1980**, 285, 311.
- (18) Bhattacharjee, S.; Bhattacharyya, R. *J. Chem. Soc., Dalton Trans.* **1993**, 1151.

- (19) Cervilla, A.; Llopis, E.; Ribera, A.; Doménech, A.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1994**, 3511.
- (20) Arzoumanian, H.; Lopez, R.; Agrifoglio, G. *Inorg. Chem.* **1994**, *33*, 3177.
- (21) Gheller, S. F.; Schultz, B. E.; Scott, M. J.; Holm, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 6934.
- (22) de Vries, N.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1989**, *28*, 3728.
- (23) Holm, R. H. *Coord. Chem. Rev.* **1990**, *100*, 183.

## **CHAPTER 1**

### **Synthesis and Characterization of Several Rhenium Catecholate Complexes**

## Introduction

Rhenium (VII) catecholate complexes form readily from catechols in condensation reactions.<sup>1</sup> In addition, the catecholate ligand appears to be relatively robust. For these reasons, Re(VII) catecholates are attractive targets for the synthesis of *cis*-rhenium(VII) dioxo complexes.

Rhenium catecholate compounds occupy a number of different rhenium oxidation states. These include the Re(VI) complexes Re(DBcat)<sub>3</sub> and Re(Cl<sub>4</sub>cat)<sub>3</sub> (cat = catechol, DBcat = dibutylcatechol, Cl<sub>4</sub>cat = tetrachlorocatechol);<sup>2</sup> the Re(V) complexes ReOCl(cat)(PPh<sub>3</sub>)<sub>2</sub>, [ReO(X<sub>4</sub>cat)<sub>2</sub>(NC<sub>5</sub>H<sub>5</sub>)]<sup>-</sup>[N(CH<sub>3</sub>)<sub>4</sub>]<sup>+</sup> and [ReO(X<sub>4</sub>cat)<sub>2</sub>(MeOH)]<sup>-</sup>[N(CH<sub>3</sub>)<sub>4</sub>]<sup>+</sup> reported by Griffith *et al.*<sup>3</sup>; and more recently, the complex [ReO(cat)<sub>2</sub>(PPh<sub>3</sub>)]<sup>-</sup>[N(CH<sub>3</sub>)<sub>4</sub>]<sup>+</sup> reported by Zubieta and coworkers.<sup>4</sup> In addition, Dilworth *et al.* have reported [ReO(cat)<sub>2</sub>]<sup>-</sup>[N(CH<sub>3</sub>)<sub>4</sub>]<sup>+</sup><sup>5</sup> and Mayer and Brown have synthesized the trispyrazylborate complex (HBpz<sub>3</sub>)ReO(9,10-phenanthroline-diolate).<sup>6</sup>

The Re(VII) catechol complexes of Herrmann *et al.* are of particular interest because they contain the *cis*-ReO<sub>2</sub> moiety. These complexes are synthesized by the condensation of MeReO<sub>3</sub> with catechols to form an intermediate which can then be trapped with a coordinating base, such as pyridine.<sup>1,7</sup> These condensation products include MeReO<sub>2</sub>(cat)(NC<sub>5</sub>H<sub>5</sub>), [ReMeO<sub>2</sub>(cat)(X)]<sup>-</sup>[HNC<sub>5</sub>H<sub>5</sub>]<sup>+</sup> (X = Cl, Br, I), and MeReO<sub>2</sub>(1,2-S(NH)C<sub>6</sub>H<sub>4</sub>)(NC<sub>5</sub>H<sub>5</sub>).

Infrared spectroscopy is an essential technique in the characterization of *cis*-dioxides. The O-Re-O unit exhibits characteristic symmetric (A<sub>1</sub>) and asymmetric (B<sub>2</sub>) stretches in the IR region that appear as two strong bands generally between 900 cm<sup>-1</sup> and 1000 cm<sup>-1</sup> (Figure

1.1). These are diagnostic of the *cis*-MO<sub>2</sub> unit, as *trans*-MO<sub>2</sub> produces only one IR band (A<sub>2u</sub> antisymmetric), between 750 cm<sup>-1</sup> and 890 cm<sup>-1</sup>.<sup>8</sup>

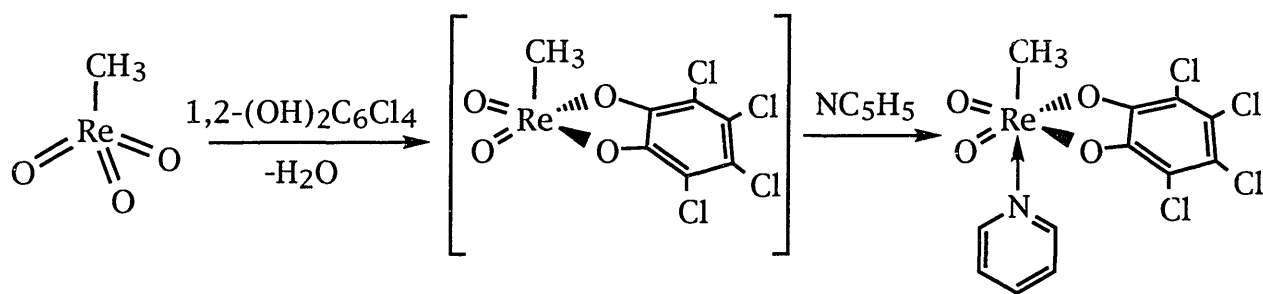
The syntheses and characterization of several Re(VII) catecholate complexes are presented here. These compounds are synthesized by condensation of catecholates with trioxo Re(VII) starting materials. The existence of *cis*-dioxo units has been confirmed by IR spectroscopy and by the X-ray crystallographic structure of MeReO<sub>2</sub>(cat)(DMSO).

The Re(VII) *cis*-dioxo unit is ideally positioned for the examination of oxygen atom transfer from Re(VII) to a substrate molecule. The results of reactions between bicyclo[2.2.1]heptadiene (norbornadiene) are presented here. In addition, these complexes may be catalysts for the transfer of an oxygen atom from dimethylsulfoxide (DMSO) to PPh<sub>3</sub>. The results of several reactions exploring this chemistry are also presented here.

## Results and Discussion

The condensation of one equivalent of catechol with  $\text{MeReO}_3$  produces the purple-violet uncharacterizable intermediate proposed by Herrmann *et al.* to be  $[\text{cis-MeReO}_2(\text{O}_2\text{C}_6\text{H}_4)]$ .<sup>1,7</sup> The chemical data presented in this work agrees with that assignment.

It is possible to use tetrachlorocatechol ( $1,2\text{-(OH)}_2\text{C}_6\text{Cl}_4$ ) in the place of catechol in this reaction. The reaction between tetrachlorocatechol monohydrate and  $\text{MeReO}_3$  produces a purple intermediate similar to that observed in the reaction with catechol. After several minutes of stirring in toluene, the addition of pyridine causes an immediate color change to a deep blue solution, from which blue crystals of  $\text{MeReO}_2(\text{O}_2\text{C}_6\text{Cl}_4)(\text{NC}_5\text{H}_5)$  can be isolated upon the addition of pentane (Equation 1).

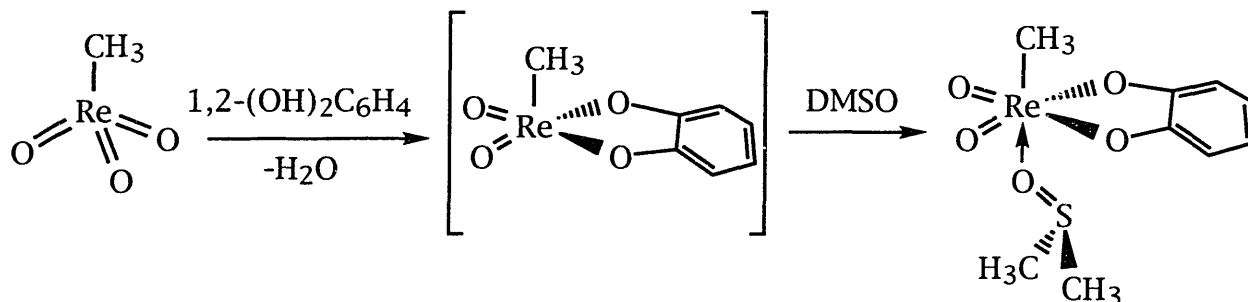


Equation 1

Proton nuclear magnetic resonance (NMR) spectroscopy shows the disappearance of the chlorocatechol phenolate resonances. The coordination of a pyridine to the metal is apparent from the downfield shift to 8.8-8.0 ppm. Infrared (IR) spectroscopy shows the existence of a *cis*-dioxo unit, with strong bands at  $958\text{ cm}^{-1}$  and at  $919\text{ cm}^{-1}$ . Correct elemental analysis supports this assignment.



By reacting the  $[\text{MeReO}_2(\text{O}_2\text{C}_6\text{H}_4)]$  intermediate with one equivalent of dimethylsulfoxide (DMSO) it is possible to produce the blue-purple DMSO adduct  $\text{MeReO}_2(\text{O}_2\text{C}_6\text{H}_4)(\text{DMSO})$  (Equation 2). The analytically pure crystalline solid can be precipitated directly from the reaction mixture by the addition of pentane to the toluene solution.



Equation 2

This complex exhibits a band in the IR assigned to the S-O stretch ( $\nu\text{S-O}$ ) at  $988\text{ cm}^{-1}$ . Drago and Meek have assigned  $\nu\text{S-O}$  to the  $1025\text{-}985\text{ cm}^{-1}$  region for DMSO coordinated to a metal through the oxygen atom.<sup>9</sup> This is similar to the S-O stretch at  $872\text{ cm}^{-1}$  observed in  $[(\text{HBpz}_3)\text{ReO}(\text{OEt})(\text{DMSO})][\text{OC}(\text{O})\text{CF}_3]$  by Mayer *et al.*<sup>10</sup> The S-O stretching frequency decreases from  $1055\text{ cm}^{-1}$  upon coordination in O-bound sulfoxide complexes and increases in S-bound complexes.<sup>9,11</sup> The strong bands at  $948\text{ cm}^{-1}$  and  $916\text{ cm}^{-1}$  belong to the asymmetric and symmetric *cis*- $\text{ReO}_2$  stretches.

An X-ray structure determination of the DMSO adduct crystallized from pentane/toluene confirms the assigned geometry. An ORTEP diagram of  $\text{MeReO}_2(\text{O}_2\text{C}_6\text{H}_4)(\text{DMSO})$  is shown in Figure 1.3. Table 1.I gives a summary of the X-ray data; the bond lengths and bond angles are given in Table 1.II. Table 1.III provides a listing of the atomic coordinates.

MeReO<sub>2</sub>(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(DMSO) exhibits an octahedral core geometry around the Re(VII) center. The chelating catecholate is symmetrically bonded, similar to Herrmann's MeReO<sub>2</sub>(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(NC<sub>5</sub>H<sub>5</sub>),<sup>1</sup> but different from the unsymmetrical catechol ligands in the ReO<sub>2</sub>(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub><sup>-</sup> anion of Dilworth *et al.*<sup>5</sup> The asymmetry in ReO<sub>2</sub>(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub><sup>-</sup> is due to the fact that each of the bidentate catechol ligands is *trans* to both an oxo and another catechol. In MeReO<sub>2</sub>(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(DMSO), as in MeReO<sub>2</sub>(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(NC<sub>5</sub>H<sub>5</sub>), the bidentate catechol is *trans* to the symmetric *cis*-dioxo unit.

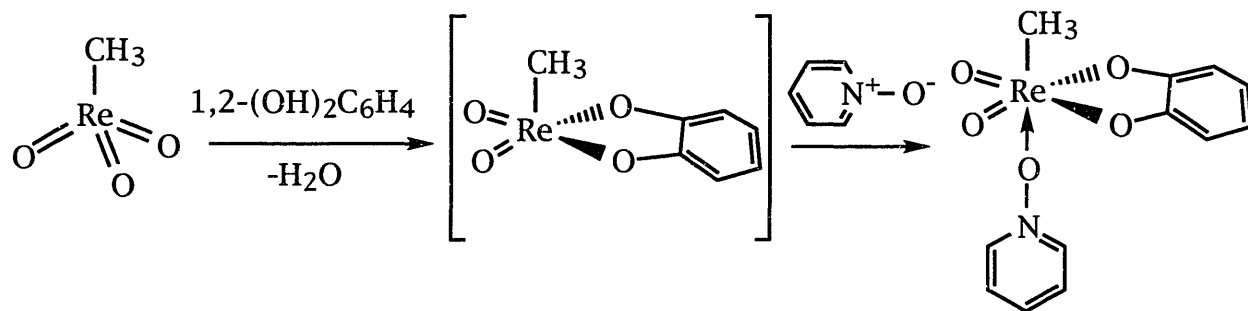
The O3-Re-O4 angle of the *cis*-dioxo moiety is 108.7°. This corresponds well with the 108.2° *cis*-dioxo angle observed in Herrmann's MeReO<sub>2</sub>(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(NC<sub>5</sub>H<sub>5</sub>) complex.<sup>1</sup>

The complex displays three different Re-O bond lengths, corresponding to the three different type of Re-O bonds: double, single, and sigma-donor. These bond lengths are 1.70Å, 2.00Å, and 2.28Å respectively. The Re-O double bond lengths are slightly elongated compared to other oxo-rhenium (VII) compounds, but almost equivalent in length to the oxo bonds in MeReO<sub>2</sub>(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(NC<sub>5</sub>H<sub>5</sub>). The S-C bond lengths are 1.767(8)Å and 1.784(9)Å, slightly shorter than that reported for free DMSO (1.80Å).<sup>11</sup> The C-S-C bond angle is marginally wider than in free DMSO (98.7° versus 97.9°), while the two O-S-C angles average to approximately the same as free DMSO (105.4° and 109.3° versus 107.2° in free DMSO). The S-O bond length is 1.46Å, approximately the same as in free DMSO (1.47Å), indicating that the S-O bond still contains the approximately 33% covalent double bond character calculated for free DMSO rather than becoming a single bond.<sup>11</sup> This result is surprising, given the decrease of 67 cm<sup>-1</sup> observed for νS-O in the IR spectrum. The distance between the oxygen atom of the bound DMSO and the metal center is 2.28Å, slightly shorter

than that observed in a previously published Re-DMSO structure.<sup>12</sup> The published structure is not similar to the above complex, however, as it is of a di- $\mu$ -acetato rhenium(III) dimer. There are few examples of characterized rhenium-DMSO adducts in the literature, although presumably rhenium- and technetium-solvent complexes involving DMSO are not rare given the extensive use of DMSO as a solvent.

The catechol ligand can be envisioned as either a dinegative ligand on a rhenium(VII) metal center or a quinone donor ligand to a rhenium(V) center (Figure 1.2). In the latter case, the bonds between C12-C13 and C14-C15 would have greater double-bond character and therefore be shorter than the other ring carbon-carbon bonds. This is not the case, demonstrating that the rhenium is indeed rhenium(VII) rather than rhenium(V). Herrmann *et al.* arrived at a similar conclusion.<sup>1</sup> The  $\pi$  orbitals of the catecholate oxygens interact with both the aromatic system of the benzene ring and the  $d\pi$  metal orbitals (Figure 1.2). This allows for the MLCT charge transfer that produces the dark purple  $d^0$  complexes.<sup>1</sup>

The  $[\text{MeReO}_2(\text{O}_2\text{C}_6\text{H}_4)]$  intermediate also reacts with pyridine-N-oxide. The violet-purple intermediate immediately turns blue-purple upon the addition of one equivalent of pyridine-N-oxide in toluene (Equation 3).



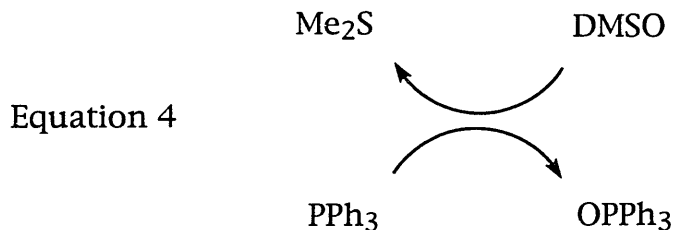
Equation 3

The IR spectrum of  $\text{MeReO}_2(\text{O}_2\text{C}_6\text{H}_4)(\text{O-NC}_5\text{H}_5)$  exhibits a band at  $1198\text{ cm}^{-1}$ , which is assigned as the N-O stretch ( $\nu\text{N-O}$ ). Free pyridine-N-oxide exhibits a band at  $1243\text{ cm}^{-1}$ .<sup>13,14</sup> The N-O stretching frequency is lowered upon coordination, attributable to the weakening of the bond by reduction of the electron density in the N-O bond when the oxygen coordinates to the  $d^0$  metal.<sup>13-15</sup> The band at  $830\text{ cm}^{-1}$  is assigned as the N-O bend ( $\delta\text{N-O}$ ). Very little difference between the free N-oxide  $\delta\text{N-O}$  bend at  $842\text{ cm}^{-1}$  and the bound N-oxide bend is observed. The small magnitude of the shift upon coordination is attributed to two competing effects: an increase in the frequency due to the coordination of the oxygen to the metal atom and an offsetting decrease attributed to the loss of double bond character in the N-O bond.<sup>14,15</sup> The strong IR bands at  $954\text{ cm}^{-1}$  and  $921\text{ cm}^{-1}$  are assigned to the characteristic asymmetric and symmetric rhenium *cis*-dioxo stretches as previously noted.

The trioxorhenium complex  $\text{Me}_3\text{SiOReO}_3$  was reacted with catechols in order to attempt to introduce different substituents *trans* to the donor ligand. This trioxorhenium complex was first synthesized by Schmidt and Schmidbauer.<sup>16</sup>  $\text{Me}_3\text{SiOReO}_3$  is produced by refluxing  $\text{Re}_2\text{O}_7$  in neat  $(\text{Me}_3\text{Si})_2\text{O}$  and crystallizing the product directly from the solution.<sup>17</sup> It is very hydrolytically unstable, and appears to hydrolyze to  $\text{ReO}_4^-$  and other products. Reactions of  $\text{Me}_3\text{SiOReO}_3$  with catechols produced a mixture of unidentified products. This may be due to the hydrolysis of the trimethylsiloxide to  $\text{Me}_3\text{SiOH}$ ,  $\text{H}^+$ , and  $\text{ReO}_4^-$ , followed by further reactions. A similar hydrolysis is proposed by Wilkinson, Hursthouse, *et al.* to be the cause of the loss of the trimethylsiloxide ligand during the reaction of  $\text{Me}_3\text{SiOReO}_3$  with  $1,2\text{-(NH}_2)_2\text{C}_6\text{H}_4$ .<sup>18</sup>

## Oxygen atom transfer from DMSO

Oxygen atom transfer from DMSO to a metal complex has been shown to be a thermodynamically favorable process.<sup>19</sup> The complex  $\text{MeReO}_2(\text{O}_2\text{C}_6\text{H}_4)(\text{DMSO})$  appears to act as an oxygen atom transfer catalyst between DMSO and triphenylphosphine ( $\text{PPh}_3$ ) as determined by GC/MS. The addition of a catalytic amount of  $\text{MeReO}_2(\text{O}_2\text{C}_6\text{H}_4)(\text{DMSO})$ , 0.5 mM, to a toluene solution of DMSO and  $\text{PPh}_3$  causes the transfer of an oxygen atom from DMSO to  $\text{PPh}_3$  to form  $\text{O}=\text{PPh}_3$  and  $\text{Me}_2\text{S}$  (Equation 4). In the absence of any catalyst, DMSO and  $\text{PPh}_3$  do not react for at least one hour at  $189^\circ\text{C}$ .<sup>20</sup>



The  $\text{PPh}_3$  was completely converted to  $\text{O}=\text{PPh}_3$ , as analyzed by GC/MS. The formation of  $\text{Me}_2\text{S}$  was observed by passing an argon stream from the reaction flask through an aqueous solution of  $\text{Hg}(\text{II})\text{Cl}_2$  to form a precipitate of  $(\text{Me}_2\text{S})_2 \cdot 3\text{HgCl}_2$ .<sup>20</sup> A similar reaction occurs upon the addition of a catalytic amount of  $\text{MeReO}_2(\text{O}_2\text{C}_6\text{H}_4)(\text{pyridine-N-oxide})$  to a toluene solution of DMSO and  $\text{PPh}_3$ . Both of these reactions are rapid, and proceed through at least 200 turnovers.

A number of other compounds can catalyze similar reactions.<sup>19,21-24</sup> A notable example is the  $\text{MO}_2(\text{LNS})$  (LNS = 2,6-bis(2,2-diphenyl-2-mercaptoethyl)pyridine) system of Berg and Holm.<sup>25-27</sup>

The technetium (III) complex  $\text{TcO}(\text{tmbt})_3(\text{pyridine})$  ( $\text{tmbt} = 2,3,5,6$ -tetramethylbenzenethiolate) also catalytically transfers an oxygen atom from DMSO to  $\text{PPh}_3$ .<sup>28,29</sup> This catalyst cycles between the Tc(III) complex and the oxidized Tc(V) complex, and is still active through 450 turnovers.

## Reactions with norbornadiene

In order to investigate oxygen atom transfer from a *cis*-dioxo rhenium(VII) complex, a series of complexes was heated with bicyclo[2.2.1]heptadiene (norbornadiene). A sample of the metal complex dissolved in  $d_6$ -benzene or  $d_8$ -toluene was heated in a sealed tube with the strained diene to between 80°C and 120°C, following the methodology of Gable and Phan. Gable and Phan have observed the reversible addition of bicyclo[2.2.1]heptene (norbornene) and norbornadiene to  $\text{Cp}^*\text{ReO}_3$  at 120°C.<sup>30</sup> In the case of the complexes synthesized here, no reaction other than decomposition of the starting complex to insoluble material was observed either with proton NMR spectroscopy or with gas chromatography/mass spectroscopy (GC/MS), precluding the study of oxygen transfer reactions to alkenes.

## Conclusion

A number of new rhenium(VII) catechol complexes have been synthesized and characterized. This work shows that at least two of the different types of ligands on these complexes can be varied. The complexes synthesized are all moisture sensitive. Unfortunately, the complexes all decompose above 100°C in solution to uncharacterized black products.

None of the complexes display oxygen atom transfer to alkenes below the temperature at which they decompose. Several of these complexes appear to be oxygen atom transfer catalysts, transferring an oxygen from DMSO to  $\text{PPh}_3$ . This reactivity has not been fully explored, but may be a fruitful area of future research.

## Experimental

All work has been performed on a high vacuum line using Schlenk techniques or in a drybox.  $\text{Me}_3\text{SiOReO}_3$ ,  $\text{Ph}_3\text{SiOReO}_3$ ,<sup>31</sup>  $\text{ClReO}_3$ ,<sup>32</sup> and  $\text{MeReO}_3$ <sup>33</sup> have been synthesized by previously published procedures. Hexanes, tetrahydrofuran (THF), and toluene were distilled over sodium benzophenone ketal under nitrogen. All other reagent were purchased from Aldrich Chemical Company. Proton nuclear magnetic resonance (NMR) spectra were recorded using a Bruker AC250, a Varian 300XL, a Varian Unity 300, or a Varian VXR500 spectrometer. IR spectra were recorded as KBr pellets on a Perkin Elmer 1600 Series FTIR. The elemental analyses were performed by Atlantic Microlab, Norcross, GA. X-ray crystallography data was collected with a Siemens R3m/V CCD detector.

### Preparation of *Cis*-methylrheniumdioxotetrachlorocatechol pyridine, $\text{Re}(\text{O})_2\text{Me}(\text{O}_2\text{C}_6\text{Cl}_4)(\text{NC}_5\text{H}_5)$

$\text{MeReO}_3$  (0.200 g, 0.802 mmol), tetrachlorocatechol (0.213 g, 0.802 mmol), and 10 mL toluene were added to a dry 50 mL Schlenk flask under argon. The solution immediately turned dark purple and was stirred for 10 minutes. Dry pyridine (0.6 mL, 0.802 mmol) was added via syringe, and a dark blue-purple precipitate formed. To remove the water by azeotropic

distillation, 5 mL of toluene were removed *in vacuo*. Dry hexanes (5 mL) were added *via* syringe, and the flask was cooled to -20°C. The precipitate was filtered *via* cannula, washed with hexanes, and dried *in vacuo*. Yield 0.283 g (63%).

Anal. calc. for C<sub>12</sub>H<sub>8</sub>Cl<sub>4</sub>NO<sub>4</sub>Re: C 25.83; H 1.44; N 2.51 Cl, 25.40.

Found: C 25.90; H 1.56; N 2.52; Cl 25.31.

<sup>1</sup>H NMR:(CD<sub>2</sub>Cl<sub>2</sub>) δ(ppm): 8.8(d,2H), 8.54(t,1H), 8.02(d,2H), 2.7(s,3H).

IR:(KBr) (cm<sup>-1</sup>) (νRe=O): 958(s), 919(s).

### **Preparation of *Cis*-methylrheniumdioxocatechol pyridine-N-oxide, Re(O)<sub>2</sub>Me(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(O-NC<sub>5</sub>H<sub>5</sub>)**

MeReO<sub>3</sub> (0.067 g, 0.27mmol), catechol (0.029 g, 0.27mmol), and 15 mL dry toluene were added to a dry 50 mL Schlenk flask under argon. The solution slowly turned dark purple and was stirred for 30 minutes. Pyridine-N-oxide (0.025 g, 0.27 mmol) was added, and the solution immediately turned dark blue-purple. Upon cooling to -20°C, a dark microcrystalline powder precipitated and was isolated in the glovebox. Recrystallization from pentane/benzene produced X-ray quality crystals.

Anal. calc. for C<sub>12</sub>H<sub>12</sub>NO<sub>5</sub>Re: C 33.03; H 2.77; N 3.21.

Found: C 33.08; H 2.73; N 3.21.

<sup>1</sup>H NMR:(C<sub>6</sub>D<sub>6</sub>) δ(ppm): 7.4(d,2H), 6.95(dd,2H), 6.35(dd,2H), 6.05(t,1H), 5.8(t,2H), 1.5(s,3H).

IR:(KBr) (cm<sup>-1</sup>): 1472 (m), 1198(m)(νN-O), 1175(m), 954(vs)(νRe=O), 921(vs)(νRe=O), 830(m)(δN-O), 754(m)(γC-H).

### **Reaction of Re(O)<sub>2</sub>Me(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(O-NC<sub>5</sub>H<sub>5</sub>) with DMSO and PPh<sub>3</sub>**



$\text{Re}(\text{O})_2\text{Me}(\text{O}_2\text{C}_6\text{H}_4)(\text{OS}(\text{CH}_3)_2)$  (2.8 mg, 6.4  $\mu\text{mol}$ ), DMSO (0.046 mL, 0.64 mmol),  $\text{PPh}_3$  (0.168 g, 0.64 mmol), and dry toluene (10 mL) were added to a dry 50 mL Schlenk flask under argon. The blue solution was heated to reflux for 30 minutes. An aliquot of the reaction was taken for GC/MS analysis. A single peak in GC analyzed as 277 ( $m/z$ ).

**Preparation of *Cis*-methylrheniumdioxocatechol dimethylsulfoxide,  $\text{Re}(\text{O})_2\text{Me}(\text{O}_2\text{C}_6\text{H}_4)(\text{OS}(\text{CH}_3)_2)$**

$\text{MeReO}_3$  (0.113 g, 0.45 mmol), catechol (0.05 g, 0.45 mmol), and 15 mL dry toluene were added to a dry 50 mL Schlenk flask under argon. The solution slowly turned dark purple and was stirred for 30 minutes. Dimethylsulfoxide (0.032 mL, 0.45 mmol) was added, and the solution turned dark blue-purple. Toluene (5 mL) was removed *in vacuo*, and 10 mL dry hexanes were added. Upon cooling to  $-20^\circ\text{C}$ , a dark microcrystalline powder precipitated, and was isolated in the glovebox. Recrystallization from pentane/toluene produced X-ray quality crystals. The dark blue solid was recrystallized from benzene/pentane.

Anal. calc. for  $\text{C}_9\text{H}_{13}\text{O}_5\text{ReS}$ : C 25.77; H 3.12; S 7.64.

Found: C 25.89; H 3.18; S 7.67.

$^1\text{H}$  NMR:( $\text{C}_6\text{D}_6$ )  $\delta$ (ppm): 7.05(AA'BB',2H), 6.4(AA'BB',2H), 1.6(s,3H), 1.4(s,6H).

IR:(KBr) ( $\text{cm}^{-1}$ ) 1325(w), 1270(w), 1210(w), 1142(w), 988(w), 948(vs)( $\nu\text{Re}=\text{O}$ ), 916(vs)( $\nu\text{Re}=\text{O}$ ), 830(w), 744(s), 608(m), 549(m).

**X-ray crystal determination of  $\text{Re}(\text{O})_2\text{Me}(\text{O}_2\text{C}_6\text{H}_4)(\text{OS}(\text{CH}_3)_2)$**

Crystal data are presented in Tables 1.I-1.III. X-ray quality crystals were grown from pentane/toluene. The crystal dimensions were 0.18 mm x 0.10 mm x 0.10 mm. Data collection was carried out using a Siemens

R3m/V CCD X-ray diffractometer at room temperature. The scan mode used was  $\omega$ - $2\theta$ , with a maximum  $2\theta$  of  $23.3^\circ$ . A total of 4749 unique reflections were collected, of which 1730 were of  $I > 3\sigma(I)$  and were used in the final structure refinement. The rhenium atom was located using direct methods and refined using full-matrix least-squares refinement on  $F^2$ . No absorption correction was used. All atoms except hydrogens were refined anisotropically.

#### **Reaction of $\text{Re}(\text{O})_2\text{Me}(\text{O}_2\text{C}_6\text{H}_4)(\text{OS}(\text{CH}_3)_2)$ with DMSO and $\text{PPh}_3$**

$\text{Re}(\text{O})_2\text{Me}(\text{O}_2\text{C}_6\text{H}_4)(\text{OS}(\text{CH}_3)_2)$  (2.3 mg,  $5.5 \mu\text{mol}$ ), DMSO (0.07 mL, 1.0 mmol),  $\text{PPh}_3$  (0.23 g, 0.9 mmol), and dry toluene (10 mL) were added to a dry 50 mL Schlenk flask under argon. The blue solution was refluxed for 3 hours. An aliquot of the reaction was taken for GC/MS analysis. Single peak in GC analyzed as 277 ( $m/z$ ). The stream of argon from the reaction was bubbled through an aqueous solution of  $\text{HgCl}_2$ . The resulting precipitate of  $(\text{Me}_2\text{S})_2 \cdot 3\text{HgCl}_2$  was filtered from the solution and dried.<sup>20</sup>

#### **Reactions of metal complexes with norbornadiene**

The appropriate metal complex was dissolved in  $\text{C}_6\text{D}_6$  or  $\text{C}_7\text{D}_8$  in an NMR tube. Several equivalents of dry norbornadiene were added and the NMR tube was sealed under vacuum. The NMR tubes were heated on an oil bath, and the courses of the reactions followed by  $^1\text{H}$  NMR.

## References

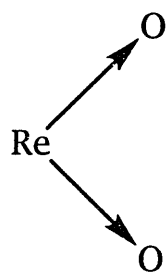
- (1) Takacs, J.; Kiprof, P.; Riede, J.; Herrmann, W. A. *Organometallics* **1990**, *9*, 782.
- (2) deLearie, L. A.; Haltiwanger, R. C.; Pierpont, C. G. *Inorg. Chem.* **1987**, *26*, 817.
- (3) Edwards, C. F.; Griffith, W. P.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1992**, 957.
- (4) Kettler, P. B.; Chang, Y.; Zubieta, J.; Abrams, M. J. *Inorg. Chim. Acta* **1994**, *218*, 157.
- (5) Dilworth, J. R.; Ibrahim, S. K.; Khan, S. R.; Hursthouse, M. B.; Karaulov, A. A. *Polyhedron* **1990**, *9*, 1323.
- (6) Brown, S. M.; Mayer, J. M. *Inorg. Chem.* **1992**, *31*, 4091.
- (7) Takacs, J.; Cook, M. R.; Kiprof, P.; Kuchler, J. G.; Herrmann, W. A. *Organometallics* **1991**, *10*, 316.
- (8) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley & Sons: New York, 1988.
- (9) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; John Wiley & Sons: New York, 1978, pp 344-346.
- (10) DuMez, D. D.; M., M. J. *Inorg. Chem.* **1995**, *34*, 6396.
- (11) Furukawa, N.; Fujihara, H. In *The Chemistry of Sulfoxes and Sulfoxides*; S. Patai, Z. Rappoport and C. J. M. Stirling, Eds.; John Wiley & Sons: New York, 1988; pp 541-581.
- (12) Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1979**, 409.
- (13) Horner, S. M.; Tyree, S. Y. *Inorg. Chem.* **1962**, *1*, 122.

- (14) Karayannis, N. M.; Pytlewski, L. L.; Mikulski, C. M. *Coord. Chem. Rev.* **1973**, *11*, 93.
- (15) Garvey, R. G.; Nelson, J. H.; Ragsdale, R. O. *Coord. Chem. Rev.* **1968**, *3*, 375.
- (16) Schmidt, M.; Schmidbaur, H. *Chem. Ber.* **1959**, *92*, 2667.
- (17) Schmidt, M.; Schmidbaur, H. *Inorg. Syn.* **9**, 149.
- (18) Danopoulos, A. A.; Wong, A. C. C.; Wilkinson, G.; Hursthouse, M. B.; Hussain, B. *J. Chem. Soc., Dalton Trans.* **1990**, 315.
- (19) Holm, R. H. *Chem. Rev.* **1988**, *88*, 1401.
- (20) Szmant, H. E.; Cox, O. *J. Org. Chem.* **1966**, *31*, 1595.
- (21) Bhattacharjee, S.; Bhattacharyya, R. *J. Chem. Soc., Dalton Trans.* **1993**, 1151.
- (22) Cervilla, A.; Llopis, E.; Ribera, A.; Doménech, A.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1994**, 3511.
- (23) Arzoumanian, H.; Lopez, R.; Agrifoglio, G. *Inorg. Chem.* **1994**, *33*, 3177.
- (24) Gheller, S. F.; Schultz, B. E.; Scott, M. J.; Holm, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 6934.
- (25) Berg, J. M.; Holm, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 917.
- (26) Berg, J. M.; Holm, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 925.
- (27) Harlan, E. W.; Berg, J. M.; Holm, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 6992.
- (28) de Vries, N. Ph.D. Thesis, Massachusetts Institute of Technology, 1988.
- (29) de Vries, N.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1989**, *28*, 3728.
- (30) Gable, K. P. P., T. N. *J. Am. Chem. Soc.* **1993**, *115*, 3036-3037.

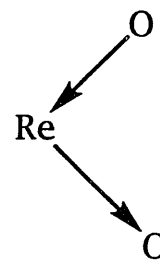
- (31) Schoop, T.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G.  
*Organometallics* **1993**, *12*, 571.
- (32) Herrmann, W. A.; Kühn, F. E.; Romão, C. C.; Kleine, M.; Mink, J. *Chem. Ber.* **1994**, *127*, 47.
- (33) Herrmann, W. A.; Thiel, W. R.; Kühn, F. E.; Fischer, R. W.; Kleine, M.; Herdtweck, E.; Scherer, W. *Inorg. Chem.* **1993**, *32*, 5188.

Figure 1.1 Rhenium *cis*-dioxo infrared stretches and a portion of the IR spectrum from  $\text{MeReO}_2(\text{O}_2\text{C}_6\text{H}_4)(\text{O-NC}_5\text{H}_5)$  taken in KBr.

IR stretches:



$\nu$ Re-O Symmetric



$\nu$ Re-O Asymmetric

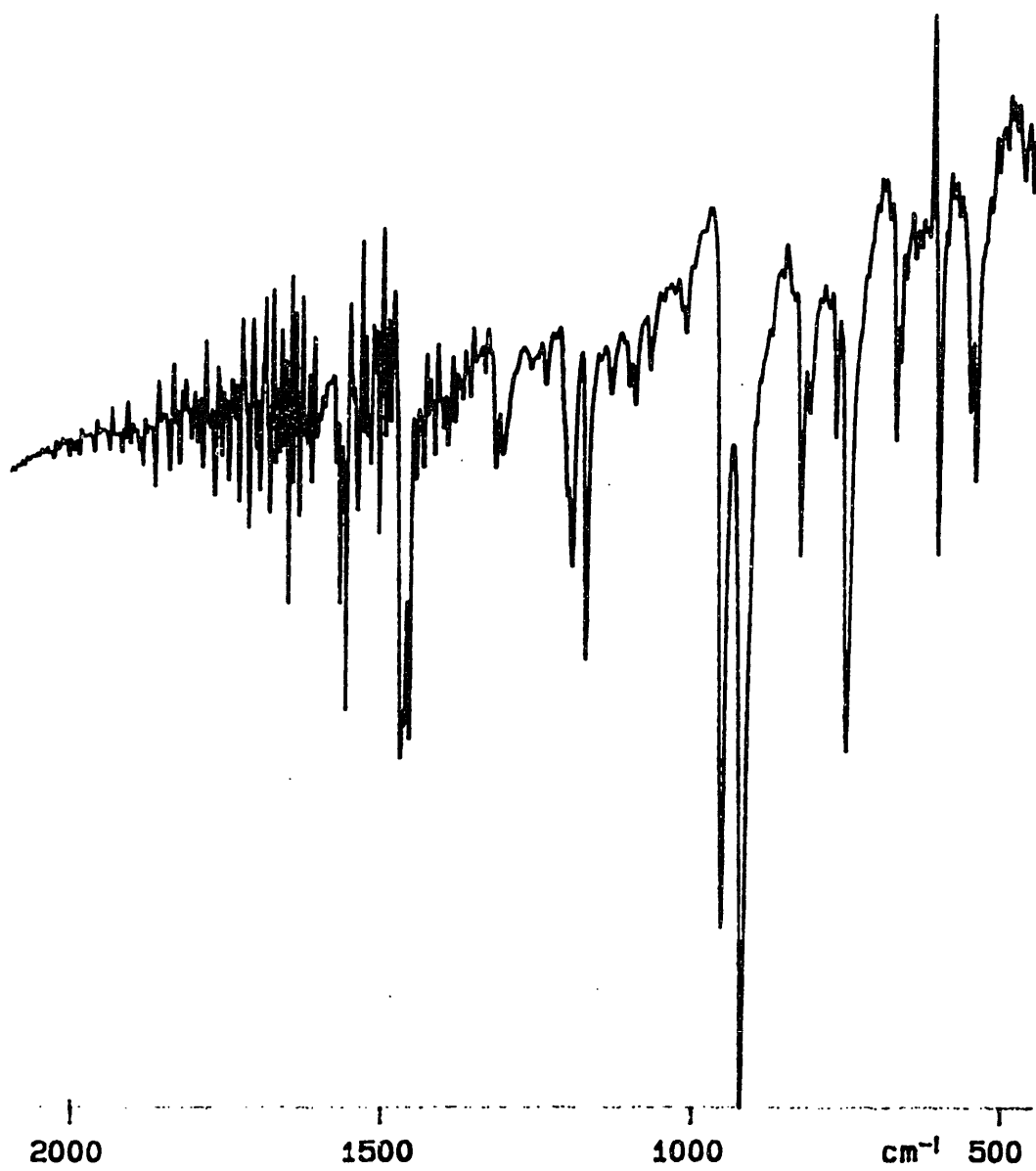
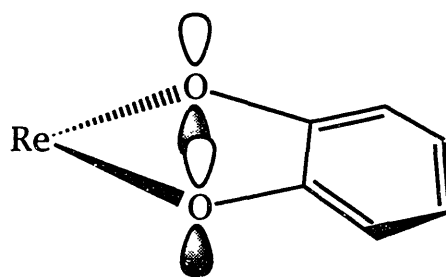
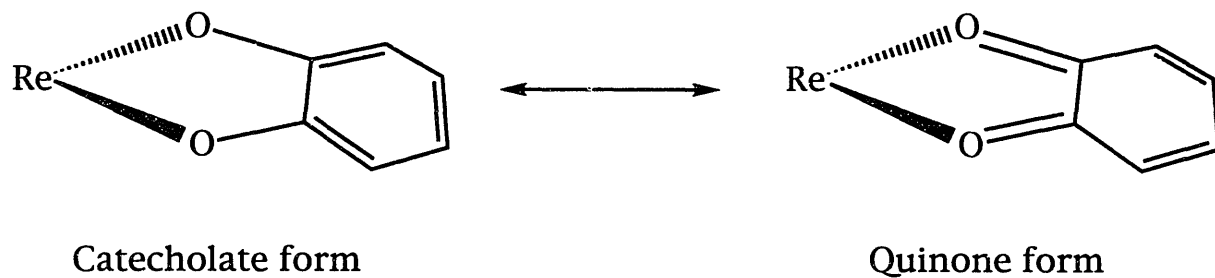


Figure 1.2 Catecholate ligand resonance forms and oxygen  $\pi$  donation.





$\pi$  donation from oxygen p orbitals  
to Re  $d_{\pi}$  orbitals

Figure 1.3 ORTEP diagram of  $\text{MeReO}_2(\text{O}_2\text{C}_6\text{H}_4)(\text{DMSO})$

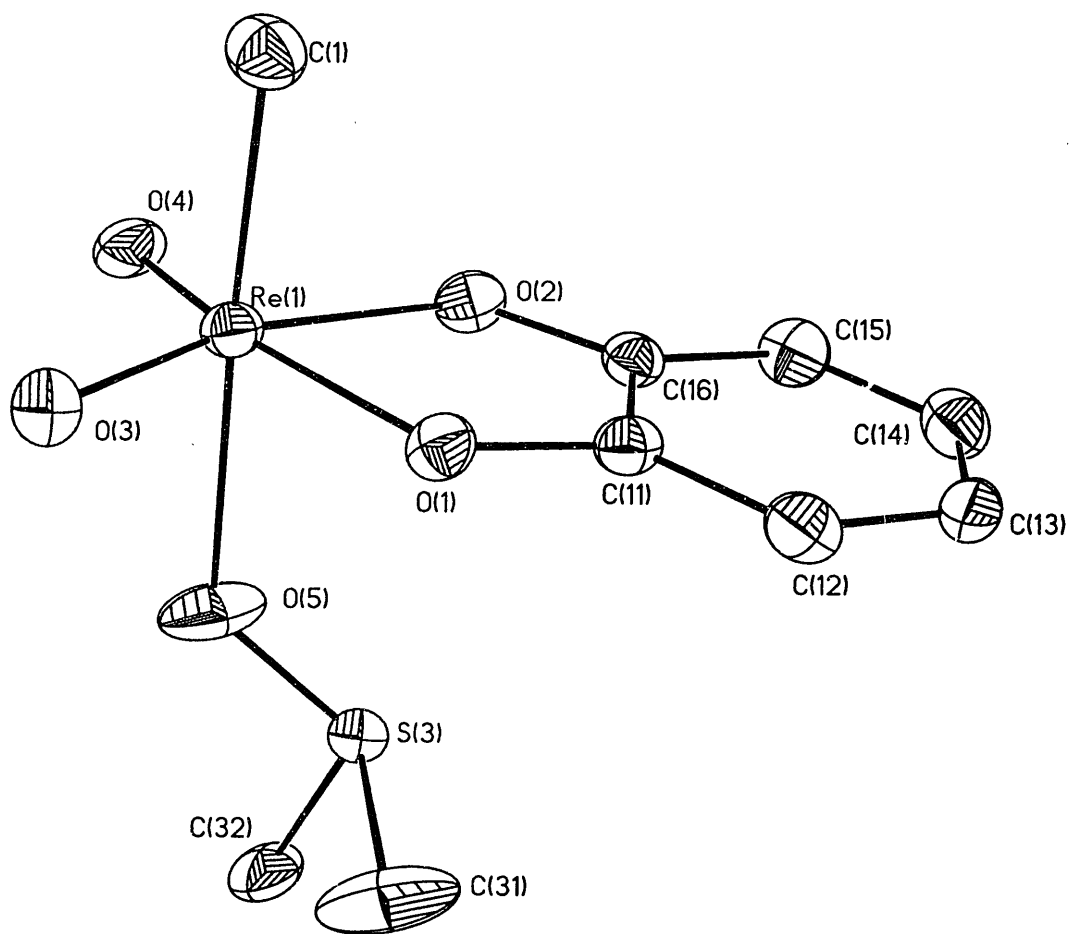


Table 1. I X-ray data for the structure determination of  
 $\text{MeReO}_2(\text{O}_2\text{C}_6\text{H}_4)(\text{DMSO})$

Empirical Formula	C <sub>9</sub> H <sub>13</sub> O <sub>5</sub> ReS
Formula Weight (g mol <sup>-1</sup> )	419.45
Crystal color, habit	blue-black, prism
Temperature (K)	163(2)
Diffractometer	Siemens R3m/V
Wavelength (Å)	MoKα (0.71073)
Crystal System	Monoclinic
Space Group	P2 <sub>1</sub> /n
<i>a</i> (Å)	7.92595(5)
<i>b</i> (Å)	11.9276(8)
<i>c</i> (Å)	12.8964(8)
β (°)	95.7890(10)
<i>V</i> (Å <sup>3</sup> )	1213.52(13)
<i>Z</i>	4
<i>D</i> (calc.) (mg m <sup>-3</sup> )	2.296
Absorption coefficient (mm <sup>-1</sup> )	10.187
Crystal Dimensions (mm)	0.18 x 0.10 x 0.10
Theta range (°)	2.33 to 23.29
Limiting indices	-8 ≤ <i>h</i> ≤ 6, -13 ≤ <i>k</i> ≤ 10, -14 ≤ <i>l</i> ≤ 13
Reflections collected	4749
Independent reflections	1730 (R <sub>int</sub> =0.0441)
Absorption correction	None
Refinement method	Full-matrix least squares on F <sup>2</sup>
Data/restraints/parameters	1730/0/156
Goodness-of-fit on F <sup>2</sup>	1.140
Final R indices [ <i>I</i> > 2σ( <i>I</i> )]	R <sub>1</sub> =0.0275, wR <sub>2</sub> =0.0660
R indices (all data)	R <sub>1</sub> =0.0310, wR <sub>2</sub> =0.0678

Table 1.I Continued

Extinction coefficient	0.0025(2)
Max. difference peak ( $\text{e}\text{\AA}^{-3}$ )	0.840
Min. difference peak ( $\text{e}\text{\AA}^{-3}$ )	-0.556

**Table 1.II. Bond lengths (Å) and angles (°) for MeReO<sub>2</sub>(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(DMSO)**

### Bond lengths (Å)

Re(1)-O(4)	1.701(5)	Re(1)-O(3)	1.701(5)
Re(1)-O(2)	2.002(5)	Re(1)-O(1)	2.006(5)
Re(1)-C(1)	2.109(7)	Re(1)-O(5)	2.282(5)
O(2)-C(16)	1.327(8)	O(1)-C(11)	1.344(8)
O(5)-S(3)	1.463(6)	C(12)-C(13)	1.378(10)
C(12)-C(11)	1.395(10)	C(15)-C(14)	1.367(11)
C(15)-C(16)	1.388(9)	C(16)-C(11)	1.407(9)
C(13)-C(14)	1.389(11)	C(32)-S(3)	1.767(8)
C(31)-S(3)	1.784(9)		

### Bond angles (°)

O(4)-Re(1)-O(3)	108.7(3)	O(4)-Re(1)-O(2)	86.4(2)
O(3)-Re(1)-O(2)	163.2(2)	O(4)-Re(1)-O(1)	161.3(2)
O(3)-Re(1)-O(1)	88.6(2)	O(2)-Re(1)-O(1)	75.6(2)
O(4)-Re(1)-C(1)	95.5(3)	O(3)-Re(1)-C(1)	93.7(3)
O(2)-Re(1)-C(1)	92.1(2)	O(1)-Re(1)-C(1)	90.1(3)
O(4)-Re(1)-O(5)	89.0(2)	O(3)-Re(1)-O(5)	85.4(2)
O(2)-Re(1)-O(5)	87.6(2)	O(1)-Re(1)-O(5)	85.4(2)
C(1)-Re(1)-O(5)	175.4(3)	C(16)-O(2)-Re(1)	119.4(4)
C(11)-O(1)-Re(1)	118.8(4)	S(3)-O(5)-Re(1)	127.9(4)
C(13)-C(12)-C(11)	117.0(7)	C(14)-C(15)-C(16)	117.8(7)
O(2)-C(16)-C(15)	126.3(6)	O(2)-C(16)-C(11)	113.4(6)
C(15)-C(16)-C(11)	120.3(7)	C(12)-C(13)-C(14)	121.3(7)
C(15)-C(14)-C(13)	122.2(7)	O(1)-C(11)-C(12)	125.7(6)
O(1)-C(11)-C(16)	112.9(6)	C(12)-C(11)-C(16)	121.4(6)
O(5)-S(3)-C(32)	105.4(4)	O(5)-S(3)-C(31)	109.3(4)
C(32)-S(3)-C(31)	98.7(5)		



**Table 1.III. Atomic Coordinates [x10] and equivalent isotropic displacement parameters [ $\text{\AA}^2 \times 10^3$ ] for MeReO<sub>2</sub>(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(DMSO). U(eq) is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.**

Atom	x	y	z	U(eq)
Re(1)	2099(1)	7410(1)	4558(1)	2S(1)
O(2)	1461(6)	7290(4)	6016(4)	34(1)
O(3)	3123(7)	7277(5)	3467(4)	45(1)
O(1)	3354(6)	6055(4)	5144(3)	32(1)
O(4)	979(6)	8629(4)	4480(4)	41(1)
O(5)	4434(7)	8391(5)	5219(5)	60(2)
C(12)	3977(9)	4838(6)	6653(6)	36(2)
C(15)	1793(9)	6273(7)	7650(5)	38(2)
C(16)	2086(8)	6458(5)	6621(5)	28(2)
C(13)	3647(9)	4667(6)	7670(6)	37(2)
C(14)	2586(10)	5381(7)	8155(6)	41(2)
C(11)	3180(8)	5748(6)	6130(5)	30(2)
C(1)	53(9)	6385(7)	3973(6)	41(2)
C(32)	6781(10)	9391(8)	6401(7)	58(2)
C(31)	7160(12)	7215(10)	5912(9)	76(4)
S(3)	5530(3)	8172(2)	6180(2)	30(1)
S(3')	6118(10)	8088(9)	5386(6)	39(3)

**CHAPTER 2**  
**Synthesis and Characterization**  
**of Rhenium bis(*o*-hydroxyphenyl)phenylphosphine oxide**  
**Complexes**

## Introduction

The rhenium *cis*-dioxo moiety is constrained by electronic reasons to exist mainly in the  $d^0$  state, i.e. rhenium (VII).<sup>1</sup> There are exceptions, as previously noted, but this holds true for majority of the known rhenium *cis*-dioxo complexes. To achieve a six-coordinate heptavalent metal center with two oxo ligands it is necessary to also have three uninegative ligands and a fourth neutral donor. Ideally, the ligands would be 'hard,' less easily ionized donors. The potentially tridentate, dinegative ligand bis(*ortho*-hydroxyphenyl)phenylphosphine oxide ( $H_2bipo$ ) provides part of such a ligand environment.

This ligand was first synthesized in 1956 by Kenndey *et al.* as part of a study of organic complexing compounds.<sup>2</sup> Very little data on the ligand was reported. Crabtree and coworkers have utilized  $H_2bipo$  as an oxygen donor ligand for ruthenium, demonstrating the tridentate nature of the ligand with an X-ray crystallographic analysis of  $(\eta^6\text{-cymene})Ru(\eta^3\text{-[PhP(O)(C}_6\text{H}_4\text{O)}_2])$ .<sup>3</sup>

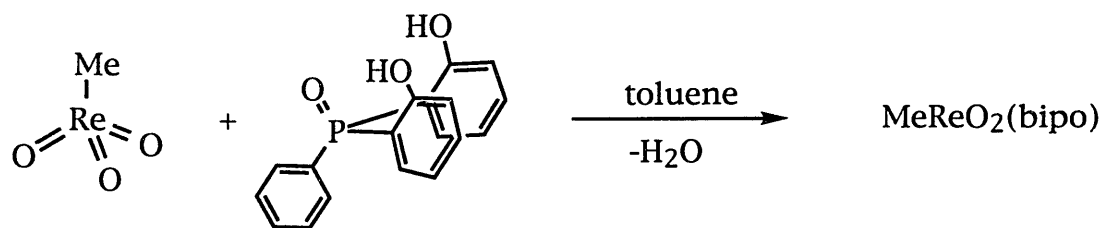
## Results and Discussion

The published synthesis of the  $H_2bipo$  ligand is a multistep procedure starting from 2-bromoanisole.<sup>2</sup> The formation of a Grignard reagent at  $0^\circ\text{C}$  is followed by addition of phenylphosphonic dichloride. The methyl protection is difficult to undo, necessitating refluxing with aluminum trichloride. The protecting group is not completely removed even after prolonged reaction times, and may also attack the phosphine oxide moiety. In order to circumvent these problems, a new synthesis of

H<sub>2</sub>bipo has been developed, following the methods of Orvig *et al.* in the synthesis of bis(*o*-hydroxyphenyl)phenylphosphine.<sup>4</sup>

In the place of methyl ether, the methoxymethyl ('mom') group is used to protect the phenol. The 'mom' group is easily cleaved with mineral acids, affording the desired alcohol under mild conditions.<sup>5</sup> The mom-protected phenol can be *ortho*-lithiated, and then reacted with phenylphosphonic dichloride to produce the mom-protected intermediate (Figure 2.1). After treatment with anhydrous HCl gas or concentrated HCl in methanol, the expected ligand H<sub>2</sub>bipo can be isolated. The ligand prepared *via* the alternative route has the same melting point, phosphorus-31, and proton NMR spectra as a sample produced via the original route.

H<sub>2</sub>bipo reacts with MeReO<sub>3</sub> in toluene to form a complex identified as *cis*-MeReO<sub>2</sub>(bipo) (Equation 1).



Equation 1

This reaction is similar to that observed between MeReO<sub>3</sub> and catechols, although more forcing conditions are necessary. The toluene must be refluxed and the water produced in the reaction removed in an azeotropic distillation with toluene by means of a Dean-Stark trap. After filtration, the remaining solution can be evaporated to leave a red-purple solid.

IR spectroscopy is an essential technique in the identification of metal *cis*-dioxo complexes. MeReO<sub>2</sub>(bipo) exhibits two strong bands at 969 cm<sup>-1</sup> and 938 cm<sup>-1</sup>, indicative of a *cis*-dioxo complex. The P=O stretch ( $\nu$ P=O) of the ligand shifts very slightly from 1128 cm<sup>-1</sup> to 1127 cm<sup>-1</sup>. This suggests that the phosphine oxide oxygen atom is coordinating to the metal center, decreasing the electron density of the P-O bond. This band shift is not diagnostic of tridentate coordination because the magnitude of the shift is small. Crabtree *et al.* have observed a shift of 8 cm<sup>-1</sup> between the free ligand and the ruthenium bipo complex.

Proton NMR spectra of MeReO<sub>2</sub>(bipo) exhibit a resonance at 2.6 ppm, corresponding to the three protons of the methyl group bound directly to the metal. The phenolic proton resonances observed in the free ligand at 10.5 ppm are not present, indicating that the phenolate oxygens are coordinated to the metal. One set of ligand resonances are shifted upfield by approximately -0.5 ppm on coordination to 6.4 ppm. This resonance probably belongs to the protons *ortho* to the phenolate oxygens, an assignment supported by a similar shift observed by Crabtree *et al.*

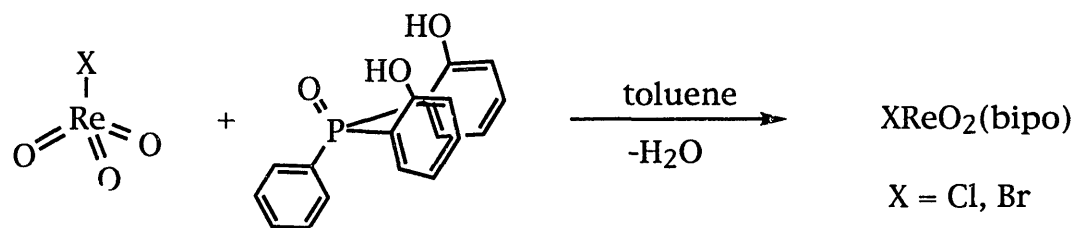
Phosphorus-31 NMR spectra of MeReO<sub>2</sub>(bipo) exhibit a resonance at 46.6 ppm, referenced to H<sub>2</sub>PO<sub>4</sub> in D<sub>2</sub>O. This is an upfield shift of about 2.3 ppm relative to the free ligand at 48.9 ppm, indicating that the phosphorus atom is in a different chemical environment. This shift is less than the -6 ppm shift observed by Crabtree *et al.*<sup>3</sup> This data, in concert with the IR data, suggests that the ligand is tridentate.

The electron impact mass spectrum (EI(+))MS) exhibits the correct isotope distribution pattern for MeReO<sub>2</sub>(bipo) (C<sub>19</sub>H<sub>16</sub>O<sub>5</sub>PRe) appears around 542 mass units (*m/z*). A set of peaks corresponding to the loss of CH<sub>3</sub> is centered at 527 mass units (Figure 2.2).

Crystallization of  $\text{MeReO}_2(\text{bipo})$  for X-ray analysis has not been successful. The product is extremely moisture sensitive, and all manipulations must be carried out in the absence of air. Although several sets of crystals have been grown and mounted on the X-ray diffractometer, all the crystals have failed to produce data sets suitable for refinement.

Several other  $\text{Re(VII)}$  trioxo compounds react with  $\text{H}_2\text{bipo}$  in a manner similar to the reaction of  $\text{MeReO}_3$ . The halogen complexes  $\text{ClReO}_3$  and  $\text{BrReO}_3$  may be prepared from dirhenium heptoxide,  $\text{Re}_2\text{O}_7$ , and the appropriate trimethylsilyl halogen reagent.<sup>6</sup> *Ab initio* calculations show that the X-Re bonds in these complexes are polarized opposite to normal X-Re bonds due to the strong electron accepting nature of the  $[\text{ReO}_3]$  unit.<sup>7</sup> This suggests that these bonds should be relatively strong, and the halide non-labile.

By refluxing the appropriate complex  $\text{XReO}_3$  in toluene and removing the water formed in the reaction *via* azeotropic distillation, it is possible to synthesize the complexes  $\text{XReO}_2(\text{bipo})$ ,  $\text{X} = \text{Cl}, \text{Br}$  (Equation 2). The complexes are isolated from the purple solutions after filtration and concentration of the toluene solutions *in vacuo*.



Equation 2

These complexes can be characterized in the same fashion as  $\text{MeReO}_2(\text{bipo})$ . Proton NMR spectra show a pattern similar to that seen for

the methyl analogue. The lack of phenolate proton resonances argues strongly for the coordination of the ligand to the metal.

The phosphorus-31 NMR spectra of the halogen complexes exhibit downfield shifts from that of the free ligand. These shifts are +5.9 ppm and +2.4 ppm for the chlorine and bromine analogues, respectively. This downfield shift corresponds to a deshielded phosphorus, indicating that the electron deficient metal center is withdrawing electron density from the phosphine oxide. In comparison to the slight upfield shift observed in the methyl complex, this data suggests that there is a stronger electron withdrawing effect from a halogen attached to the metal.

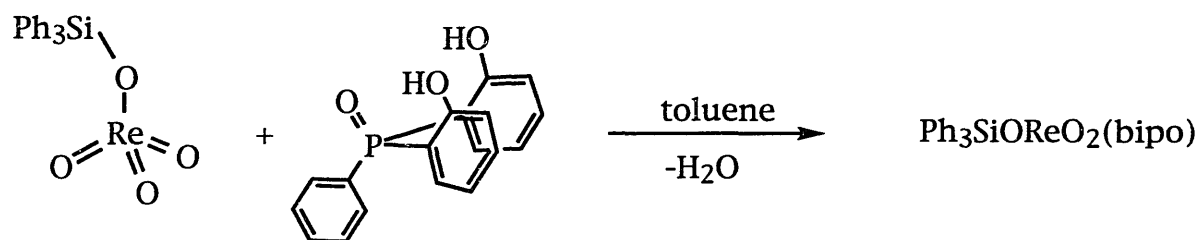
The increased electrophilicity of the metal-halogen complexes is supported by the IR data. The decreased electron density on the phosphine oxide is due to a stronger electron withdrawing effect of the metal fragment. The decrease in electron density is reflected by the decrease in the IR band assigned to the P=O stretch ( $\nu_{\text{P=O}}$ ). The  $\nu_{\text{P=O}}$  band appears at 1119  $\text{cm}^{-1}$  in both the chlorine complex and the bromine complex. The shift of 8  $\text{cm}^{-1}$  is much greater than the 1  $\text{cm}^{-1}$  shift observed in the case of  $\text{MeReO}_2(\text{bipo})$ , due to the difference between the high electronegativity of the halogens versus the electron donating ability of the methyl group.

The presence of a *cis*-dioxo unit is indicated by the strong  $\nu_{\text{Re=O}}$  bands present at 973  $\text{cm}^{-1}$  and 907  $\text{cm}^{-1}$  for the chlorine complex and 973  $\text{cm}^{-1}$  and 873  $\text{cm}^{-1}$  for the bromine complex.

The complex *cis*- $\text{ReO}_2[\text{OSiPh}_3](\text{bipo})$  may be prepared from a third type of trioxorhenium complex.  $\text{Ph}_3\text{SiOReO}_3$  is easily prepared from  $\text{Ph}_3\text{SiOH}$  and  $\text{Re}_2\text{O}_7$  in toluene at 25°C.<sup>8</sup>  $\text{Ph}_3\text{SiOReO}_3$  reacts with  $\text{H}_2\text{bipo}$  in refluxing toluene to produce a purple solution from which  $\text{ReO}_2[\text{OSiPh}_3](\text{bipo})$  can be isolated (Equation 3). The water produced in the



reaction is removed by means of an azeotropic distillation with toluene, as previously noted.



Equation 3

This complex exhibits similar spectroscopic characteristics as the previously synthesized complexes. The IR spectrum exhibits bands at 973  $\text{cm}^{-1}$  and 909  $\text{cm}^{-1}$  assigned to the  $\nu\text{Re}=\text{O}$  symmetric and asymmetric stretches. The  $\nu\text{P}=\text{O}$  stretch appears at 1118  $\text{cm}^{-1}$ , shifted by about 10  $\text{cm}^{-1}$  from the free ligand.

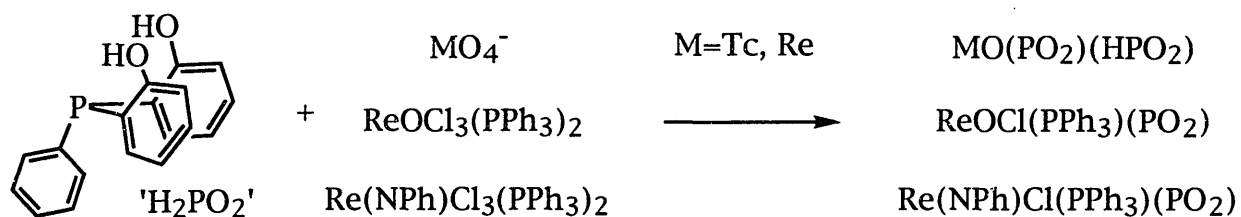
Proton NMR spectroscopic studies of the complex show that the phenolate proton resonances are missing, indicating probable coordination of the phenolate oxygens to the metal center. The phosphorus-31 NMR spectrum exhibits only one resonance, at 51.7 ppm. This is shifted downfield, in a similar fashion to the halogen derivatives. The downfield shift indicates deshielding of the phosphorus atom, implying that triphenylsilyloxy is more electron-withdrawing than the methyl group, but less so than the halogens. This result is in line with simple electronegativity differences, but is also probably due to  $\pi$  bonding between the  $d^0$  metal center and the oxygen atom attached to the silicon.

Mass spectrometry results (EI(+))MS support the other spectroscopic analyses. A molecular ion cluster is evident, centered around 802 mass

numbers ( $m/z$ ). The isotopic ratios are in approximately the correct distribution as calculated for  $\text{ReO}_2[\text{OSiPh}_3](\text{bipo})$ .

The trioxorhenium complex  $\text{Me}_3\text{SiOReO}_3$  is structurally similar to  $\text{Ph}_3\text{SiOReO}_3$ .  $\text{Me}_3\text{SiOReO}_3$  is synthesized by refluxing  $\text{Re}_2\text{O}_7$  in neat  $(\text{Me}_3\text{Si})_2\text{O}$  and crystallizing the product directly from the solution.<sup>9</sup> However, it appears to be more hydrolytically unstable than the triphenyl derivative. A mixture of unidentified products resulted from the reaction of  $\text{Me}_3\text{SiOReO}_3$  with  $\text{H}_2\text{bipo}$  in refluxing toluene. This may be due to the hydrolysis of the trimethylsiloxide to  $\text{Me}_3\text{SiOH}$ ,  $\text{H}^+$ , and  $\text{ReO}_4^-$ , followed by further reactions. This hydrolysis is proposed by Wilkinson, Hursthouse *et al.* to be the cause of the loss of the trimethylsiloxide ligand during the reaction of  $\text{Me}_3\text{SiOReO}_3$  with 1,2- $(\text{NH}_2)_2\text{C}_6\text{H}_4$ .<sup>10</sup>

Orvig *et al.* have prepared a set of Re(V) and Tc(V) complexes using a tridentate ligand similar to the one used here.<sup>4</sup> The ligand bis(*o*-hydroxyphenyl)phenylphosphine ( $\text{PO}_2$  in the notation of Orvig *et al.*) reacts with  $\text{ReOCl}_3(\text{PPh}_3)_2$ ,  $\text{Re}(\text{NPh})\text{Cl}_3(\text{PPh}_3)_2$ , and  $\text{NH}_4\text{ReO}_4$  and their technetium analogues (Equation 4).



Equation 4

A variety of Re(V) and Tc(V) products were characterized, including *fac-cis*-(P,P)Re(NPh)Cl(PPh<sub>3</sub>)(PO<sub>2</sub>)·2CHCl<sub>3</sub>. The PO<sub>2</sub> ligand is tridentate, bonding through the phosphorus and the two phenolate oxygens to form two five-

membered rings. This structure is confirmed by two different X-ray crystal structures, including one of the phenylimido complex.

Unlike the substituted phenylphosphine ligand of Orvig *et al.*, the phenylphosphine oxide ligand H<sub>2</sub>bipo does not react with ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>, NH<sub>4</sub>ReO<sub>4</sub>, NaReO<sub>4</sub>, or with [N(Bu)<sub>4</sub>][ReOBr<sub>4</sub>] under a variety of conditions. In each case, unreacted starting material is recovered. There are two possible reasons for this lack of reactivity. The phosphine oxide moiety may be too weak a donor to form an adduct with the metal complex, although the chelate effect from the reaction of the phenols should overcome this weak basicity. Alternatively, the formation of a six-membered ring as opposed to a five-membered ring formed by the phosphine ligand may be unfavorable. Simple molecular modeling (Chem3D Pro)<sup>11</sup> supports this theory.

## Reactions with norbornadiene

Crabtree *et al.* have noted that despite the tridentate nature of this ligand, it can be readily cleaved from the metal.<sup>3,12</sup> They observed the decomposition of ruthenium complexes of bipo upon reaction with CO and H<sub>2</sub>O<sub>2</sub>, as well as with electrophiles. During the course of this study, all the complexes synthesized were observed to be extremely hydrolytically unstable, decomposing to the original diol within minutes of exposure to air while in solution and days in the solid state. More importantly in terms of oxygen atom transfer, high valent rhenium complexes with bipo as a ligand are thermally unstable above 100°C, decomposing to insoluble black solids. This thermal instability precluded observation of oxygen atom

transfer, as previous oxygen atom transfer to olefins has only been observed for rhenium(VII) at temperatures above 100°C.<sup>13</sup>

## Conclusion

The ligand H<sub>2</sub>bipo reacts with several trioxorhenium(VII) complexes to form XReO<sub>2</sub>(bipo) (X = Me, Cl, Br, Ph<sub>3</sub>SiO). These complexes have been characterized by a variety of methods, including mass spectrometry. These complexes are all extremely moisture sensitive, and decompose in solution above 100°C to uncharacterizable black solids. The thermal decomposition has prevented the study of oxygen atom transfer to alkenes using these complexes. The ligand H<sub>2</sub>bipo does not react with several common Re(VII) and Re(V). This reactivity stands in contrast to previously published work on a triarylphosphine ligand containing two *ortho*-phenolate groups published by Orvig *et al.*<sup>4</sup>

## Experimental

All work has been done on a high vacuum line using Schlenk techniques or in a drybox. Me<sub>3</sub>SiOReO<sub>3</sub>,<sup>9</sup> Ph<sub>3</sub>SiOReO<sub>3</sub>,<sup>8</sup> ClReO<sub>3</sub>,<sup>6</sup> BrReO<sub>3</sub>,<sup>6</sup> MeReO<sub>3</sub>,<sup>14</sup> bis(*o*-hydroxyphenyl)phenylphosphine oxide,<sup>2</sup> and methoxymethylphenyl ether<sup>5</sup> have been synthesized by previously published procedures. Hexanes, tetrahydrofuran (THF), and toluene were distilled over sodium benzophenone under nitrogen. All other reagent were purchased from Aldrich Chemical Company. Proton and phosphorus-31 NMR spectra were recorded using a Bruker AC250, a Varian XL300, a Varian Unity 300, or a Varian VXR500 spectrometer. IR spectra were

recorded as KBr pellets on a Perkin Elmer 1600 Series FTIR. Gas-chromatograph-mass spectra (GC-MS) have been recorded on a Hewlett Packard 5890. Other mass spectra (EI-MS) have been recorded on a Finnigan Mat 8200. The elemental analyses were performed by Atlantic Microlab, Norcross, GA.

### **Bis(*o*-methoxymethylphenyl ether)phenylphosphine oxide**

Methoxymethylphenyl ether (8.98 g, 0.065 mol) and dry hexanes (125 mL) were added to a dry 500 mL Schlenk flask under argon. The solution was cooled to 0°C over an ice bath. A cold (0°C) suspension of dry tetramethylenediamine (9.8 mL, 0.065 mol), 2.5 M *n*-butyl lithium in hexanes (32 mL, 0.078 mol), and 50 mL dry hexanes was transferred into the Schlenk flask using a cannula. The cloudy yellow-orange suspension was stirred overnight at room temperature, warmed to 40°C for 1 hour, and cooled to 0°C on an ice bath. Phenylphosphonic dichloride (4.61 mL, 0.0325 mol) was added dropwise. The resulting suspension was stirred overnight at room temperature. Sodium hydrogen phosphate (200 mL of a 0.1M solution in water) was added to the solution. The aqueous layer was separated, washed with dichloromethane and ether, the organic fractions were combined, dried, and evaporated on a rotary evaporator. Ether was added to the red oil produced, and the product precipitated after standing overnight in a freezer.

### **Bis(*o*-hydroxyphenyl)phenylphosphine oxide**

#### **Method (a):**

Magnesium turnings (1.5 g, 0.064 mol) and ether (30 mL) were added to a dry 300 mL three necked flask equipped with two dropping funnels, a

condenser, and a stir bar. To one dropping funnel was added *o*-bromoanisole (12.7 mL, 0.068 mol) and to the other dropping funnel was added phenylphosphonic dichloride (4.82 mL, 0.034 mol) in ether (25 mL). A crystal of iodine was added to the magnesium turnings to initiate the Grignard reaction. The *o*-bromoanisole was added dropwise over a period of 20 minutes, maintaining a slight ether reflux. The green reaction mixture was stirred for 2.5 hours, and cooled on an ice bath. The phenylphosphonic dichloride was added dropwise over a period of 20 minutes, forming a white solid. Acidified water (100 mL) was added, and the solution was allowed to stir overnight. Dichloromethane was added, the aqueous layer was separated and washed with dichloromethane and all the organic fractions were combined and dried with magnesium sulfate. The organic solvents were removed *in vacuo*, to leave a yellow-white solid. The yellow solid was dissolved in toluene (60 mL) and anhydrous aluminum chloride (7.2 g, 0.054 mol) was added. The reaction was refluxed for 5 hours, acidified with 2N HCl (100 mL), and stirred overnight. The solvents were removed using a rotary evaporator until a precipitate formed. The precipitate was filtered from the solution and washed with ether and hexanes. Overall yield is 3.8 g (39%).

#### **Method (b):**

Bis(*o*-methoxymethylphenyl ether)phenylphosphine oxide was dissolved in methanol (50 mL) and anhydrous HCl was bubbled through the solution for 6 hours. Yield was quantitative.

$^1\text{H}$  NMR:( $\text{CD}_2\text{Cl}_2$ )  $\delta$ (ppm): 10.5 (s,2H), 7.6(m,7H), 7.1(m,6H).

$^{31}\text{P}$  NMR:( $\text{CD}_2\text{Cl}_2$ )  $\delta$ (ppm): 48.9

IR:(KBr) ( $\text{cm}^{-1}$ ) 3056(s), 1577(s), 1458(s), 1375(m), 1301(s), 1241(s), 1128(s) ( $\nu_{\text{P=O}}$ ), 1084(s), 1063(s), 1033(w), 833(w), 766(s), 697(s).

**Preparation of *Cis*-methylrheniumdioxo[bis(*o*-hydroxyphenyl)phenylphosphine oxide],  $\text{Re}(\text{O})_2(\text{CH}_3)(\text{bipo})$**

$\text{MeReO}_3$  (0.200 g, 0.802 mmol),  $\text{H}_2\text{bipo}$  (0.249 g, 0.802 mmol), and dry toluene (15 mL) were added to a dry 50 mL Schlenk flask under argon equipped with a Dean-Stark trap and a water cooled reflux condenser. The solution was refluxed until 6 mL of solvent had been removed *via* the Dean-Stark trap (2.5 hours). The solution was filtered and the remaining solvent was removed *in vacuo*.

$^1\text{H}$  NMR:( $\text{C}_6\text{D}_6$ )  $\delta$ (ppm): 7.65(dd,2H), 6.9(m,7H), 6.4(dq,2H), 2.5(s,3H).

$^{31}\text{P}$  NMR:( $\text{d}_6$ -acetone)  $\delta$ (ppm): 46.6

IR:(KBr) ( $\text{cm}^{-1}$ ) ( $\nu_{\text{P=O}}$ ): 1127(m); ( $\nu_{\text{Re=O}}$ ): 969(s), 938(s).

EI(+) $\text{MS}$ :  $m/z = 542$  ( $\text{M}^+$ )

**Preparation of *Cis*-rheniumdioxo(triphenylsiloxy)[bis(*o*-hydroxyphenyl)phenylphosphine oxide],  $\text{Re}(\text{O})_2[\text{OSi}(\text{C}_6\text{H}_5)_3](\text{bipo})$**

$\text{Ph}_3\text{SiORE}(\text{O})_3$  (0.20 g, 0.39 mmol),  $\text{H}_2\text{bipo}$  (0.12g, 0.39 mmol), and toluene (15 mL) were added to a dry 50 mL Schlenk flask under argon equipped with a water cooled reflux condenser. The solution was refluxed for 3 hours, and the toluene was filtered *via* cannula from the dark purple precipitate. The solid was dried *in vacuo*. Yield is 0.183 g (58%).

$^1\text{H}$  NMR:( $\text{d}_6$ -acetone)  $\delta$ (ppm): 7.8(m,4H), 7.64(m,6H), 7.42(m,8H), 7.28(m,3H), 7.1(m,7H).

$^{31}\text{P}$  NMR:( $\text{d}_6$ -acetone)  $\delta$ (ppm): 51.7 ppm

IR:(KBr) ( $\text{cm}^{-1}$ ) ( $\nu_{\text{P=O}}$ ): 1118(m); ( $\nu_{\text{Re=O}}$ ): 974(s), 929(s).

EI(+)MS:  $m/z = 801$  (M+)

**Preparation of *Cis*-chlororheniumdioxo[bis(*o*-hydroxyphenyl)phenylphosphine oxide],  $\text{Re}(\text{O})_2(\text{Cl})(\text{bipo})$**

$\text{Re}_2\text{O}_7$  (0.200 g, 0.413 mmol) and THF (3 mL) were added to a dry 50 mL Schlenk flask under argon.  $\text{ClSiMe}_3$  (0.105 mL, 0.826 mmol) was syringed into the flask, and the solution was stirred for 5 minutes.  $\text{H}_2\text{bipo}$  (0.256 g, 0.826 mmol) and 10 mL toluene were added to the flask; a Dean Starke trap and a water cooled reflux condenser were attached. The solution was refluxed until approximately 6 mL of solvent had been removed *via* the Dean-Stark trap (30 min.). The dark purple precipitate was filtered and washed with hexanes. The solid was dried *in vacuo*. Yield is 0.365g (78%).

$^1\text{H}$  NMR:( $\text{d}_6$ -acetone)  $\delta$ (ppm): 7.6(m,7H), 7.1(m,6H)

$^{31}\text{P}$  NMR:( $\text{d}_6$ -acetone)  $\delta$ (ppm): 54.8

IR:(KBr) ( $\text{cm}^{-1}$ ) ( $\nu\text{P}=\text{O}$ ): 1119(m); ( $\nu\text{Re}=\text{O}$ ): 973(s), 907(s).

**Preparation of *Cis*-bromorheniumdioxo[bis(*o*-hydroxyphenyl)phenylphosphine oxide],  $\text{Re}(\text{O})_2(\text{Br})(\text{bipo})$**

$\text{Re}_2\text{O}_7$  (0.300 g, 0.619 mmol) and THF(3 mL) were added to a dry 50 mL Schlenk flask under argon.  $\text{BrSiMe}_3$  (0.163 mL, 1.238 mmol) was syringed into the flask, and the solution was stirred for 10 minutes.  $\text{H}_2\text{bipo}$  (0.384 g, 1.238 mmol) and toluene (8 mL) were added to the flask, and a Dean-Stark trap and a water cooled reflux condenser were attached. The solution was refluxed until approximately 7 mL of solvent had been removed *via* the Dean-Stark trap. The dark purple precipitate was filtered



from the solution and washed with hexanes. The solid was dried *in vacuo*.

Yield is 0.583 g (77%).

$^1\text{H}$  NMR:( $\text{CD}_2\text{Cl}_2$ )  $\delta$ (ppm): 7.75(m,1H), 7.65(m,3H), 7.5(m,3H), 7.1(m,2H), 7.0(m,2H), 6.9(m,2H).

$^{31}\text{P}$  NMR:( $\text{CD}_2\text{Cl}_2$ )  $\delta$ (ppm): 51.3, ( $\text{d}^6$ -acetone): 48.3

IR:(KBr) ( $\text{cm}^{-1}$ ) : 1437 (s), 1299 (m), 1264(m), 1231(m), 1119(m) ( $\nu\text{P}=\text{O}$ ), 1082(m), 973(s)( $\nu\text{Re}=\text{O}$ ), 9874(s) ( $\nu\text{Re}=\text{O}$ ), 753(s).

### **Reactions of metal complexes with norbornadiene**

The appropriate metal complex was dissolved in  $\text{C}_6\text{D}_6$  or  $\text{C}_7\text{D}_8$  in an NMR tube. Several equivalents of dry norbornadiene were added and the NMR tube was sealed under vacuum. The NMR tubes were heated on an oil bath, and the courses of the reactions followed by  $^1\text{H}$  NMR.

## References

- (1) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley & Sons: New York, 1988.
- (2) Kennedy, J.; Lane, E. S.; Willans, J. L. *J. Chem. Soc.* **1956**, 4670.
- (3) Tanke, R. S.; Holt, E. M.; Crabtree, R. H. *Inorg. Chem.* **1991**, *30*, 1714.
- (4) Luo, H.; Setyawati, I.; Rettig, S. J.; Orvig, C. *Inorg. Chem.* **1995**, *34*, 2287.
- (5) Yardley, J. P.; Fletcher, H. *Synthesis* **1976**, 244.
- (6) Herrmann, W. A.; Kühn, F. E.; Romão, C. C.; Kleine, M.; Mink, J. *Chem. Ber.* **1994**, *127*, 47.
- (7) Weist, R.; Leininger, T.; Jeung, G.-H.; Bénard, M. *J. Phys. Chem.* **1992**, *96*, 10800.
- (8) Schoop, T.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Organometallics* **1993**, *12*, 571.
- (9) Schmidt, M.; Schmidbaur, H. *Inorg. Syn.* **9**, 149.
- (10) Danopoulos, A. A.; Wong, A. C. C.; Wilkinson, G.; Hursthouse, M. B.; Hussain, B. *J. Chem. Soc., Dalton Trans.* **1990**, 315.
- (11) CambridgeSoft Corporation, Copyright 1985-1995.
- (12) Crabtree, R. H., personal communication, 1995.
- (13) Gable, K. P. P., T. N. *J. Am. Chem. Soc.* **1993**, *115*, 3036-3037.
- (14) Herrmann, W. A.; Thiel, W. R.; Kühn, F. E.; Fischer, R. W.; Kleine, M.; Herdtweck, E.; Scherer, W. *Inorg. Chem.* **1993**, *32*, 5188.

Figure 2.1 New *bis*-(*o*-hydroxyphenyl)phenylphosphine oxide synthesis.

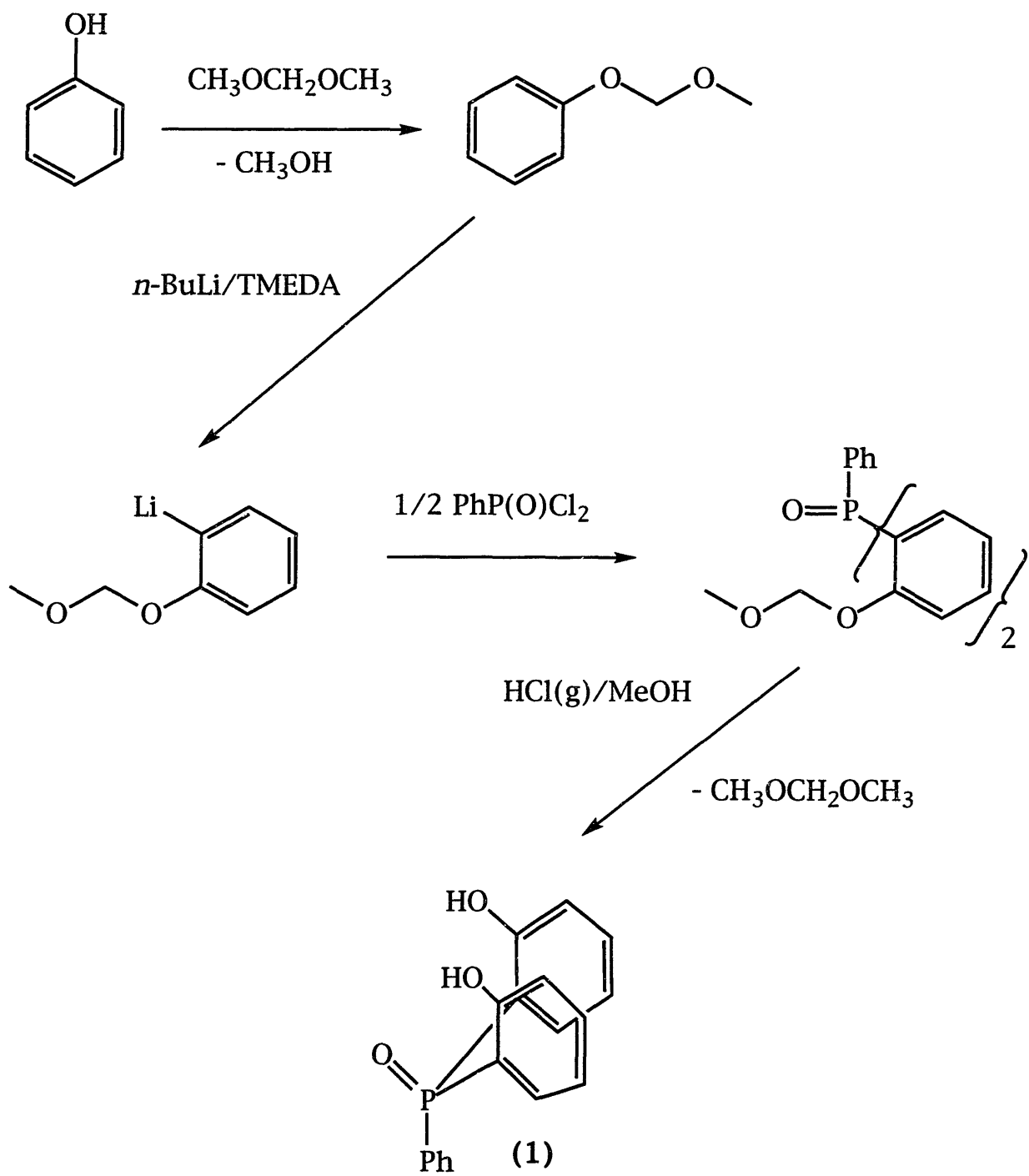
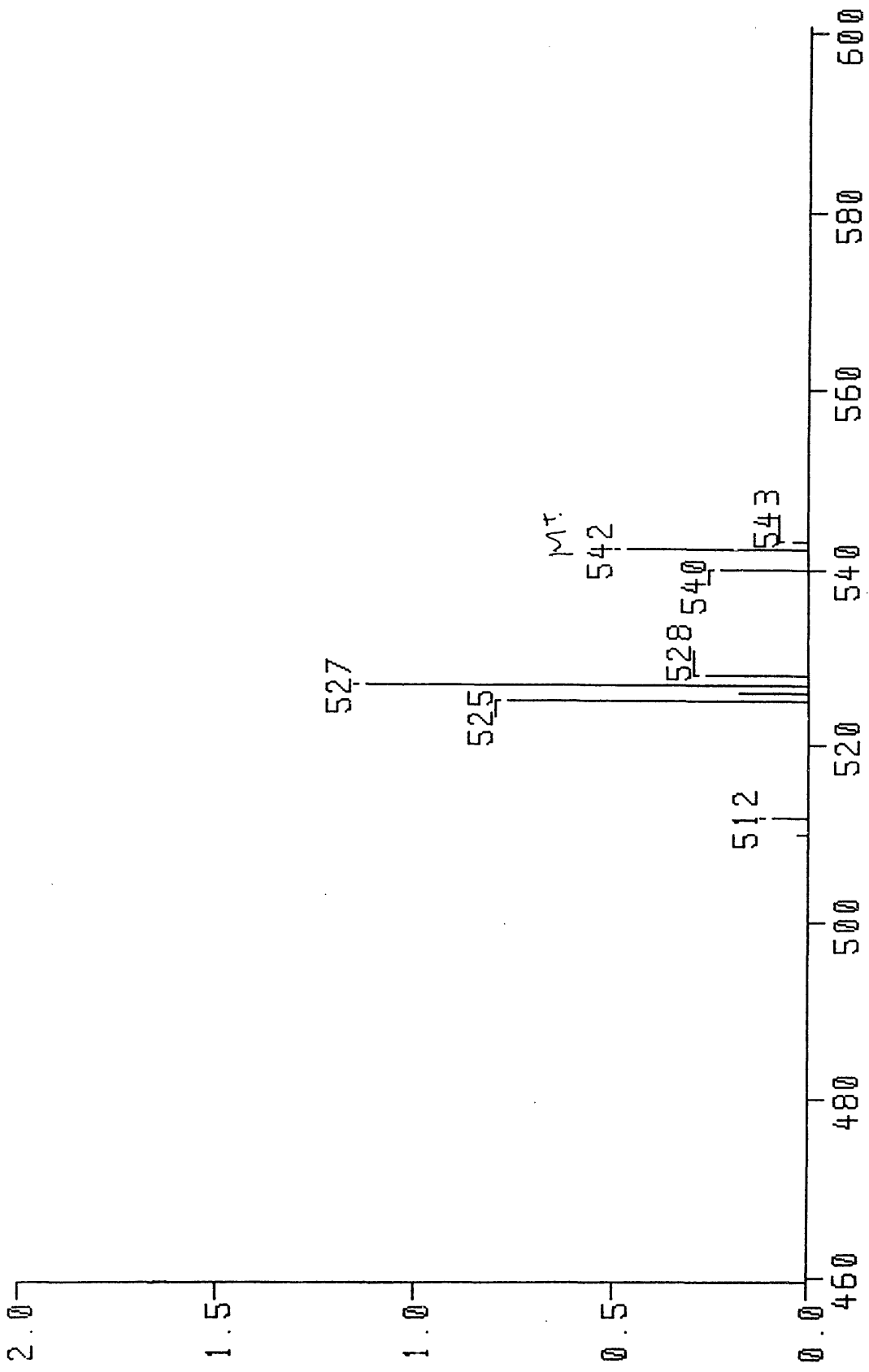


Figure 2.2 Portion of an electron impact mass spectrum (EI(+))MS) of MeReO<sub>2</sub>(bipo). The molecular ion is at 542 mass units.



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## **Biographical Note**

The author was born on December 8, 1971 in Washington, D.C. to Donald E. and Martha W. Goldstone. He graduated from the Maret School in Washington D.C. in 1989 and attended Yale University. While at Yale, he worked for Professor Robert Crabtree for several years. He managed to spend a semester in Antarctica studying marine biology, and received a B.S. in Chemistry in May 1993. He entered MIT in the fall of the same year, and joined the research group of Alan Davison. After receiving his degree, he intends to find a job, with the eventual goal of attending graduate school in chemical oceanography.



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