

Kinetics and Mechanism of Oxygen Atom Transfer from Methyl Phenyl Sulfoxide to Triarylphosphines Catalyzed by an Oxorhenium(V) Dimer

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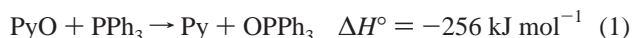
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An oxorhenium(V) dimer, $\{\text{MeReO}(\text{mtp})\}_2$, **D**, where mtpH_2 is 2-(mercaptomethyl)thiophenol, catalyzes oxygen atom transfer reaction from methyl phenyl sulfoxide to triarylphosphines. Kinetic studies in benzene- d_6 at 23 °C indicate that the reaction takes place through the formation of an adduct between **D** and sulfoxide. The equilibrium constants, K_{DL} , for adduct formation were determined by spectrophotometric titration, and the values of K_{DL} for $\text{MeS}(\text{O})\text{C}_6\text{H}_4\text{-4-R}$ were obtained as 14.1(2), 5.7(1), and 2.1(1) for $\text{R} = \text{Me}, \text{H},$ and Br , respectively. Following sulfoxide binding, oxygen atom transfer occurs with either internal or external nucleophilic assistance. Because $\{\text{MeReO}(\text{mtp})\}_2$ is a much more reactive catalyst than its monomerized form, $\text{MeReO}(\text{mtp})\text{PPh}_3$, loss of the active catalyst during the time course of the reaction must be taken into account as a part of the kinetic analysis. As it happens, sulfoxide catalyzes monomerization. Monomerization by triarylphosphines was also studied in the presence of sulfoxide, and a mechanism for that reaction was also proposed. Both the phosphine-assisted monomerization and the phosphine-assisted pathway for oxygen atom transfer involve transition states with ternary components, **D**, sulfoxide, and phosphine, which we suggest are structural isomers of one another.

Introduction

Oxygen atom transfer (OAT) catalyzed by $\text{Re}(\text{V}/\text{VII})$ compounds has been studied actively in the past decade.^{1–4} Triphenylphosphine is a good oxygen acceptor, which is reflected by the large O–P bond dissociation energy (557 kJ mol^{-1}) of OPPh_3 .⁵ Therefore, OAT from pyridine *N*-oxide or dimethyl sulfoxide to triphenylphosphine is spontaneous. These equations show the reactions and the values of ΔH° ; given the symmetry of these reactions of large molecules, $\Delta S^\circ \sim 0$, and so $\Delta G^\circ \sim \Delta H^\circ$.



Despite that, reactions 1 and 2 do not take place under ordinary conditions; only at high temperatures or with acid

or metal complex catalysts will they proceed.^{6–8} Methyltrioxorhenium (MTO) can also catalyze certain other OAT reactions when triphenylphosphine is the oxygen acceptor.^{3,9}

Two rhenium compounds are the focus of this study: $\{\text{MeReO}(\text{mtp})\}_2$, **D**, and $\text{MeReO}(\text{mtp})\text{L}$, **M–L**, where mtpH_2 is 2-(mercaptomethyl)thiophenol and L represents a Lewis base such as PPh_3 or Py, Chart 1.^{10–13} Our previous study of reaction 1 catalyzed by **M–PPh**₃ established that reaction 1 proceeds only with nucleophilic assistance from a Lewis base such as pyridine *N*-oxide, halide ions, or pyridine.¹²

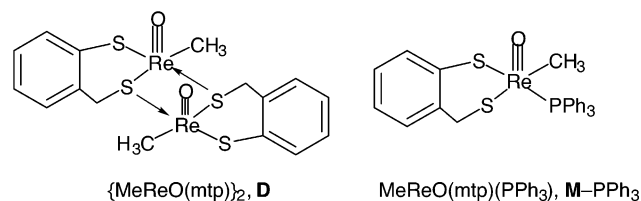
We also noted that **D** catalyzes reaction 1 ca. 90 times faster than **M–PPh**₃ does, but we have not yet resolved the mechanism in detail.¹⁴ We have now undertaken a study of

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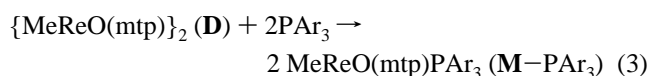
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Chart 1



reaction 2, catalyzed by **D**, with two important goals. First, we wished to understand why **D** is so reactive compared to **M-L**, and second, we wished to resolve the issue of nucleophilic assistance. As it turns out, two pathways have been found, both requiring a nucleophile, one with an external nucleophilic center, the other an internal one.

Complicating the kinetic analysis is the fact that **D** is converted to **M-PAr₃** over the time scale of the OAT reaction, eq 3. Ordinarily, eq 3 is much slower than reaction 2, but it turns out that sulfoxide serves as a monomerization catalyst. This developed into a further significant result, because the mechanism for sulfoxide-catalyzed monomerization of **D** resembles that for the **D**-catalyzed OAT reaction of eq 2.



Experimental Section

$\{\text{MeReO(mtp)}\}_2$, **D**, and MeReO(mtp)PPh_3 , **M-PPh₃**, were synthesized by the reported procedures.¹⁵ Other reagents except $\text{MeS(O)C}_6\text{H}_4\text{-4-Br}$ were obtained from commercial sources and used without further purification. $\text{MeS(O)C}_6\text{H}_4\text{-4-Br}$ was synthesized from methyl 4-bromophenyl sulfide by its MTO-catalyzed oxidation with hydrogen peroxide.¹⁶ The crude product was dissolved in small amount of CH_2Cl_2 and then purified by column chromatography on a silica gel column prepared in ethyl acetate, which was also used as the eluting solution. The product was obtained by recrystallization from acetonitrile, and its purity was confirmed by its ¹H NMR spectrum. Benzene-*d*₆ (CIL) was used as the solvent; the ¹H chemical shifts were measured relative to its residual proton resonance at δ 7.16 ppm. Both ¹H and ³¹P NMR spectra were recorded at 23 °C by a Bruker DRX 400 MHz spectrometer. For the quantitative determination of concentrations, a known concentration of triphenylmethane was added as an internal standard; the integrated resonance of Ph_3CH was used for the calculation of concentrations. A Shimadzu 2501 spectrophotometer was used to record UV-vis spectra. Nonlinear least-squares analyses were carried out with the programs KaleidaGraph, Scientist for Windows (MicroMath Scientific Software, Inc.), and a local program written in N88-BASIC.¹⁷

Results

OAT by Dimer versus Monomer. As was reported previously,¹⁴ the reactivity of **D** is 90 times higher than that

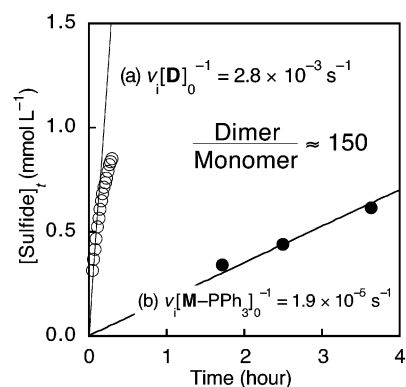


Figure 1. Comparison of two rhenium catalysts for OAT from MeS(O)Ph to PPh_3 in C_6D_6 at 23 °C, with these initial concentrations: (a) 0.5 mmol L^{-1} of **D**, 19 mmol L^{-1} of MeS(O)Ph , and 22 mmol L^{-1} of PPh_3 ; (b) 2.6 mmol L^{-1} of **M-PPh₃**, 26 mmol L^{-1} of MeS(O)Ph , and 28 mmol L^{-1} of PPh_3 .

of **M-PPh₃** in OAT from 2-Me-4- NO_2 -pyridine *N*-oxide to phosphine. To compare their reactivities in OAT from MeS(O)Ph to PPh_3 , we prepared two solutions, one contained 0.5 mmol L^{-1} of **D** and the other 2.6 mmol L^{-1} of **M-PPh₃**, and we monitored the increase of $[\text{MeSPh}]$ by ¹H NMR. Figure 1 shows the comparative data in terms of the increase of $[\text{MeSPh}]$ as catalyzed by **D** or **M-PPh₃**. Because the monomer catalyzed reaction is so slow, initial rate methods were used to compare the two.¹⁸ The initial rates were normalized to unit catalyst concentration; the rate constants so obtained are $2.8 \times 10^{-3} \text{ s}^{-1}$ for **D** and $1.9 \times 10^{-5} \text{ s}^{-1}$ for **M-PPh₃**. Therefore, **D** is more effective than **M-PPh₃** by a factor of ca. 150. Interestingly, this difference is nearly the same as the factor of 90 by which **D** is favored over **M-PPh₃** in the reaction of 2-Me-4- NO_2 -pyridine *N*-oxide, from which we infer a common mechanistic change.

The OAT reaction of MeS(O)Ph is, however, ca. 400 times slower than that of 2-Me-4- NO_2 -pyridine *N*-oxide. The reason for this arises from the difference in bond dissociation energy (BDE) for S-O and N-O bonds; X-O BDEs in MeS(O)Ph and 4- NO_2 -pyridine *N*-oxide are 360 and 259 kJ mol^{-1} , respectively.^{5,19,20} An advantage of using sulfoxide as the substrate is that **D** is not monomerized by sulfoxide itself,²¹ which allowed us to study the mechanism of the **D**-catalyzed OAT without this complication. However, the monomerization of **D** by PPh_3 takes place contemporaneously with OAT. This causes depletion of the active catalyst, which is the reason that the latter part of the **D**-catalyzed reaction in Figure 1 deviates from linearity, even though only the first few percent of the reaction was followed. We will consider the loss of **D** during the reaction in a later section.

Observation of OAT Reaction Catalyzed by $\{\text{MeReO(mtp)}\}_2$. Figure 2 shows a set of ¹H NMR spectra taken

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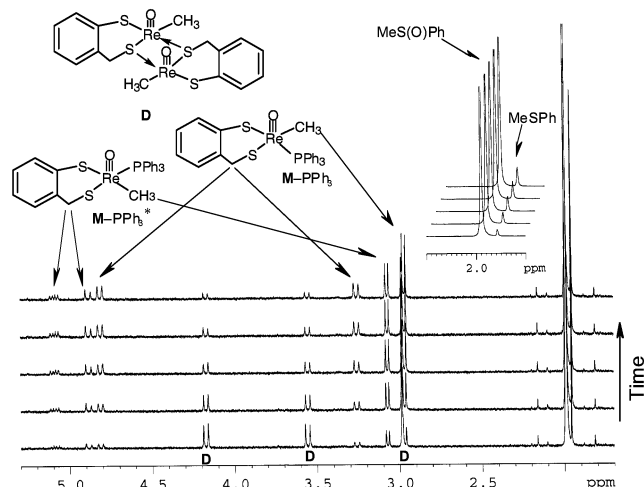


Figure 2. Stacked ^1H NMR spectra of the solution which contained 1.4 mmol L^{-1} of **D**, 20.2 mmol L^{-1} of MeS(O)Ph , and 23.7 mmol L^{-1} of PPh_3 in C_6D_6 at 23°C . The spectra were recorded at 2 min intervals.

during the course of a reaction with 20.2 mmol L^{-1} of MeS(O)Ph and 23.7 mmol L^{-1} of PPh_3 in a solution that contained 1.4 mmol L^{-1} of **D** at 23°C . The formation of MeSPh was indicated by the gradual growth of a small resonance at 1.96 ppm .

Although **D** is not monomerized by MeS(O)Ph , it is monomerized by PPh_3 and produces M-PPh_3 and its geometrical isomer, M-PPh_3^* , a kinetic product.²² During the period of the OAT reaction, therefore, only a limited amount of MeSPh was produced, ca. 2 mmol L^{-1} , because of the concurrent loss of the catalyst according to eq 3. In the same period, formation of 2 mmol L^{-1} of Ph_3PO was also confirmed by ^{31}P NMR spectroscopy.

We previously reported that **D** is monomerized by Lewis bases such as triphenylphosphine and pyridine.^{21,23} The rate law for the monomerization in the absence of sulfoxide is expressed by eq 4.

$$-\frac{d[\mathbf{D}]}{dt} = (k_a[\text{PPh}_3] + k_b[\text{PPh}_3]^2)[\mathbf{D}] \quad (4)$$

The rate constants are $k_a = 1.57 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$ and $k_b = 5.1 \times 10^{-2} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$,²³ from which one expects to find a pseudo-first-order rate constant from eq 4 is $4.0 \times 10^{-4} \text{ s}^{-1}$ at 23.7 mmol L^{-1} of PPh_3 . In fact, the observed rate constant measured by ^1H NMR directly was a great deal larger, $3.4 \times 10^{-3} \text{ s}^{-1}$, which shows that monomerization of **D** is catalyzed by MeS(O)Ph . Although the monomerization of **D** by PPh_3 takes place slowly, the reaction is known to be accelerated by weaker ligands such as pyridine. The pyridine mechanism involves formation of M-Py and is not directly pertinent to the sulfoxide case.²³ Therefore, although it is not unreasonable that sulfoxide also assists the monomerization of **D**, it does not do so by first forming M-OSR_2 . We succeeded in obtaining rate constants for the sulfoxide-catalyzed monomerization of **D** by monitoring the decrease

of **D** in the ^1H NMR spectra. Here, we use k_m to designate the pseudo-first-order rate constant at given phosphine and sulfoxide concentrations, and will discuss the mechanism in a later section.

Speciation of D. During the course of catalysis, it was found that the chemical shifts of **D** are slightly displaced from those measured for **D** alone.¹⁵ Values of δ are as follows, for **D** during reaction (and **D** alone): 2.99 (2.91, s, 6H); 3.56 (3.53, d, 2H); 4.18 (4.05, d, 2H). The displacements are consistent with formation of the adduct **D-OS(Me)Ph**. The principal support for the existence of such an adduct comes from the existence of the crystallographically characterized compound **D-OSMe**.²¹

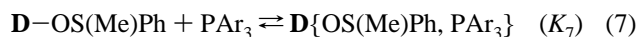


To evaluate the equilibrium constant for the reaction between **D** and MeS(O)Ph , eq 5, a spectrophotometric titration was carried out. The absorbance changes in UV-vis spectra were analyzed by nonlinear least-squares fitting according to eq 6, which gave $K_{\text{DL}} = 5.7(1) \text{ L mol}^{-1}$ in benzene at 23°C (Figures S1–2).

$$\text{absorbance} = \left\{ \frac{\epsilon_{\text{D}} + \epsilon_{\text{DL}}K_{\text{DL}}[\text{L}]}{1 + K_{\text{DL}}[\text{L}]} \right\} [\mathbf{D}]_{\text{T}} \quad (6)$$

Here, ϵ_{D} and ϵ_{DL} are molar absorptivities for **D** and **D-L** species at the corresponding wavelength, $[\text{L}]$ is the concentration of sulfoxide, and $[\mathbf{D}]_{\text{T}}$ is the total concentration of **D** and **D-L** in the solution. Similar determinations for $\text{MeS(O)-C}_6\text{H}_4\text{-4-R}$ gave $K_{\text{DL}} = 14.1(2)$ and $2.1(1) \text{ L mol}^{-1}$ for $\text{R} = \text{CH}_3$ and Br , respectively. Correlation of the three values by the Hammett equation gave $\rho = -2.1(1)$, consistent with **L** acting as a Lewis base. The K_{DL} value of 5.7 L mol^{-1} for MeS(O)Ph can be compared with $120(6) \text{ L mol}^{-1}$ for $\text{Me}_2\text{-SO}$.²¹ The difference is reasonable, considering the relative Lewis basicities and steric demands of the two sulfoxides. We also note K_{DL} for $\text{L} = 4\text{-picoline } N\text{-oxide}$ is $4.1(3) \times 10^3 \text{ L mol}^{-1}$,²³ indicating that it is a stronger Lewis base toward rhenium(V) than sulfoxide.

In addition, it proved possible to determine by a kinetic analysis the equilibrium constants for the further association of **D-OS(Me)Ph** with phosphines:



From the kinetic analysis given later in this report, values of K_7 for $\text{L} = \text{P}(\text{C}_6\text{H}_4\text{-4-R})_3$, $\text{R} = \text{H}$, F , and Cl , could also be determined. Table 1 summarizes the association constants.

Kinetics of the $\{\text{MeReO}(\text{mtp})\}_2$ -Catalyzed OAT Reaction. To analyze the kinetic data for this reaction, we presumed that the product is formed exclusively from the dimer catalyst; that is, mononuclear forms of the catalyst were taken to be unreactive on this time scale. Figure 1 provides justification for this approach: **D** is 150 times more reactive than M-PPh_3 . Therefore, the catalytic rate will be proportional to $[\mathbf{D}]_{\text{T},t}$ ($[\mathbf{D}]_{\text{T}}$ is made up of **D** and **D-OS(Me)Ph**; the second subscript emphasizes that it is not a static value). This expression contains an apparent rate constant

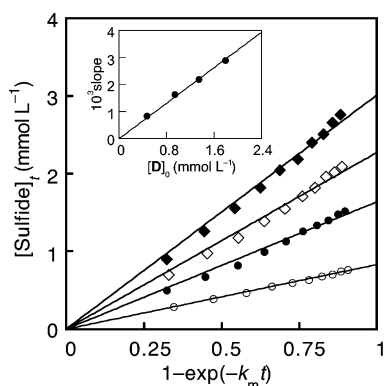
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Table 1. Equilibrium Constants for the 1:1 Association of {MeReO(mtp)}₂ with Different Lewis Bases in Benzene at 23 °C

Association of D and Lewis Bases		
Lewis base	$K_{DL}/L \text{ mol}^{-1}$	ref
4-Me-C ₅ H ₄ NO	$4.1(3) \times 10^3$	25 °C, ref 23
Me ₂ SO	120(6)	25 °C, ref 21
MeS(O)C ₆ H ₄ -4-Me	14.1(2)	this work ^{a,b}
MeS(O)Ph	5.7(1)	this work ^{a,b}
<i>N,N</i> -dimethylformamide	7.6(1)	this work ^a
MeS(O)C ₆ H ₄ -4-Br	2.1(1)	this work ^{a,b}
Association of D –OS(Me)Ph with Phosphines ^{c,d}		
phosphine	$K_7/L \text{ mol}^{-1}$	note
PPh ₃	38(2)	this work
P(C ₆ H ₄ -4-F) ₃	11(8)	this work
P(C ₆ H ₄ -4-Cl) ₃	~0.4	this work

^a From direct measurement by absorbance changes. ^b For this series MeS(O)C₆H₄-4-R, Hammett's $\rho = -2.1(1)$. ^c For eq 7. ^d From kinetic fitting.

**Figure 3.** Plots according to eq 10 for four experiments with constant [MeS(O)Ph] = 20.2 mmol L⁻¹ and constant [PPh₃] = 23.7 mmol L⁻¹ at different concentrations of catalyst **D** in the range 0.46–1.8 mmol L⁻¹ in C₆D₆ at 23 °C. The inset shows the dependence of slopes in the four experiments on the initial concentration of **D**.

for catalysis, k_{ψ} , with dependences on other reagents that remain to be determined subsequently. The rate of sulfide formation is therefore expressed by eq 8.

$$\frac{d[\text{sulfide}]}{dt} = k_{\psi}[\mathbf{D}]_{T,t} = k_{\psi}[\mathbf{D}]_0 \exp(-k_m t) \quad (8)$$

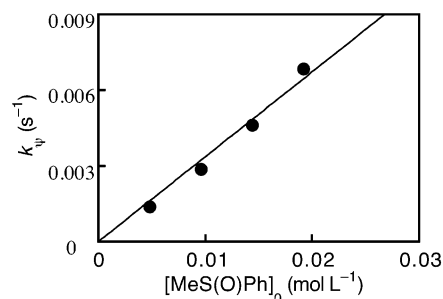
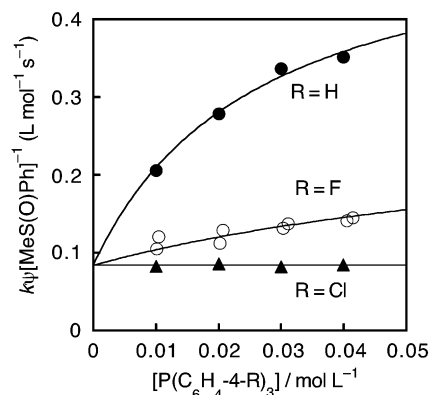
Solution of this equation yields a form that can be used for the data analysis:

$$\int_0^t d[\text{sulfide}] = \int_0^t \{k_{\psi}[\mathbf{D}]_0 \exp(-k_m t)\} dt \quad (9)$$

$$[\text{sulfide}]_t = \frac{k_{\psi}[\mathbf{D}]_0}{k_m} \{1 - \exp(-k_m t)\} \quad (10)$$

According to eq 10, a plot of the sulfide concentrations at particular times against the quantity $\{1 - \exp(-k_m t)\}$ should give a straight line that passes through the origin with a slope equal $k_{\psi}[\mathbf{D}]_0/k_m$. Figure 3 shows such plots for a series of four experiments in which $[\mathbf{D}]_0$ was varied in the range 0.47–1.80 mmol L⁻¹ with constant concentrations of MeS(O)Ph and PPh₃.

The data do agree with the model. It should be noted that the OAT reaction slows down, simply because under these

**Figure 4.** Plot of k_{ψ} vs [MeS(O)Ph]₀ in a series of experiments with 0.49 mmol L⁻¹ of **D** and 21.7 mmol L⁻¹ of PPh₃ in C₆D₆ at 23 °C.**Figure 5.** Dependence of $k_{\psi}[\text{MeS(O)Ph}]^{-1}$ on $[\text{P}(\text{C}_6\text{H}_4\text{-4-R})_3]$ for OAT reactions in C₆D₆ at 23 °C.

conditions **D** is being converted to **M**–PPh₃ and **M**–PPh₃* fairly rapidly in comparison with catalysis. One can see from the extrapolated limit of [sulfide]_t in eq 10 as $t \rightarrow \infty$, which is $k_{\psi}[\mathbf{D}]_0/k_m$. The slopes obtained from the main part of Figure 3 are a linear function of $[\mathbf{D}]_0$, as shown in the inset. This is consistent with eq 10. The slope allows the evaluation of k_{ψ} by use of the values of k_m which were determined from the decrease of **D**.

We investigated the dependence of k_{ψ} on [MeS(O)Ph]₀. As shown in Figure 4, k_{ψ} varies linearly with [MeS(O)Ph]₀.

It remains to determine the influence of the phosphine concentration on the catalytic rate. The kinetic dependences on $[\text{P}(\text{C}_6\text{H}_4\text{-4-R})_3]$ are more complex, as illustrated in Figure 5. Three cases were explored, $\text{P}(\text{C}_6\text{H}_4\text{-4-R})_3$, with R = H, F, and Cl. All three plots of $k_{\psi}[\text{MeS(O)Ph}]^{-1}$ against $[\text{P}(\text{C}_6\text{H}_4\text{-4-R})_3]$ extrapolate to the same value at $[\text{PAR}_3] = 0$. That for R = Cl stays nearly constant over the concentration range, whereas $k_{\psi}[\text{MeS(O)Ph}]^{-1}$ values for R = H and F rise hyperbolically to different limiting values.

The full rate law for the catalytic conversion of MeS(O)Ph to MeSPh takes this form:

$$v = \left(\frac{A + BK_7[\text{PAR}_3]}{1 + K_7[\text{PAR}_3]} \right) \left(\frac{K_{DL}[\text{MeS(O)Ph}]}{1 + K_{DL}[\text{MeS(O)Ph}]} \right) [\mathbf{D}]_{T,t} \quad (11)$$

The highest sulfoxide concentration used for kinetics was 20 mM. With $K_{DL} = 5.7 \text{ L mol}^{-1}$, the denominator $(1 + K_{DL}[\text{MeS(O)Ph}])$ reduces to unity. The resulting equation is

$$v = \left(\frac{A + BK_7[\text{PAR}_3]}{1 + K_7[\text{PAR}_3]} \right) K_{DL}[\text{MeS(O)Ph}][\mathbf{D}]_{T,t} \quad (12)$$

Table 2. Kinetic Parameters and K_7 for $P(C_6H_4-4-R)_3$ from Fitting to Equation 13^{a,b}

R	$A/10^{-2} s^{-1}$	$B/10^{-2} s^{-1}$	$K_7/L mol^{-1}$
H	1.5(0.2)	9.5(0.4)	38(2)
F	1.5(0.2)	5.0(0.2)	11(8)
Cl	1.5(0.2)	~0.1	~0.4

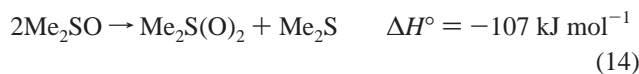
^a At 23 °C in C_6D_6 . ^b Unified multivariate fit was done for all three sets of data simultaneously. This resulted in a single value of A and individual values of B .²⁴

which gives the following expression for k_{ψ} :

$$k_{\psi} = \left(\frac{A + BK_7[PAR_3]}{1 + K_7[PAR_3]} \right) K_{DL}[MeS(O)Ph] \quad (13)$$

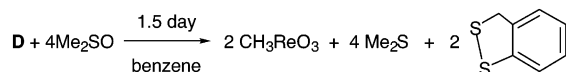
Parameter K_7 represents the association constant for reaction 7. Table 2 summarizes the results of the nonlinear least-squares fitting of the data to eq 13. Unified multivariate fit was done for all three sets of data simultaneously. This resulted in a single value of A and individual values of B .²⁴ It gives the values of A (which proved independent of the phosphine used) and B summarized in Table 2. The reaction scheme subsequently presented will identify parameters A and B in terms of individual rate and equilibrium constants.

Because sulfoxide disproportionation is thermodynamically favorable, one might wonder whether this reaction produces sulfone:^{5,19}



However, PPh_3 is a much better oxygen acceptor than sulfoxide, which is reflected in the difference of reaction enthalpies; ΔH° in eq 2 is -195 kJ mol^{-1} . Moreover, a reaction of PPh_3 with dioxo species to form $OPPh_3$ is kinetically more favorable than that of sulfoxide to sulfone.²⁵ In our experiments, no sulfone was observed in 1H NMR spectra.

It should be noted that the reaction takes a different course when phosphine is absent. The mixture of **D** and Me_2SO eventually decomposes to $MeReO_3$ and $RS-SR$, the disulfide coupling product from mtp.¹⁵

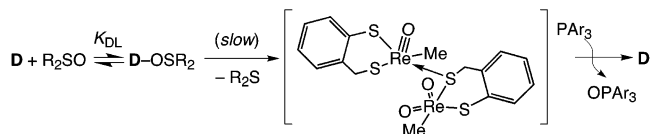


In the present work, the prior association of **D** and sulfoxide has been demonstrated. On the basis of this reaction and the independently studied chemistry of dioxorhenium(VII), which lies along the OAT pathway, it is proposed that the associated form between **D** and sulfoxide slowly produces

(24) This calculation was done with the following settings: (i) the reactions with $P(C_6H_4-4-R)$ give the same A value, and (ii) the values of K_7 were floated to keep a correlation based on Hammett's constants; $\sigma(F) = 0.06$ and $\sigma(Cl) = 0.23$. The K_7 values give Hammett's ρ value as -2.9 .

(25) Reynolds, M. S.; Berg, J. M.; Holm, R. H. *Inorg. Chem.* **1984**, *23*, 3057–3062.

a dioxorhenium species, which in turn quickly reacts with phosphine to produce phosphine oxide.

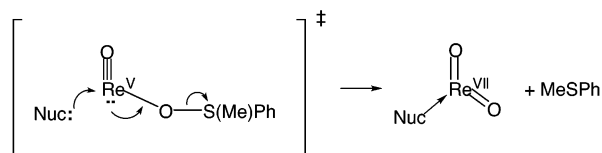


Interpretation and Discussion

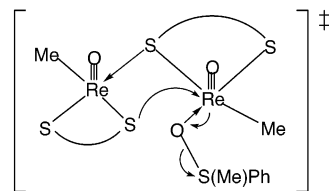
Reaction Scheme of OAT Reaction. During the OAT reaction, it was found that a significant concentration of **D** was being diverted concurrently to $M-PPh_3$, and to its geometrical isomer $M-PPh_3^*$.²² The monomeric complexes are ineffective in catalyzing the OAT reaction in comparison with **D**; therefore, their contributions during the reaction time can be disregarded in their own right, provided one allows for the extent to which they deplete the concentration of the active form **D**. One can rewrite the rate law in terms of the participating chemical species:

$$v = A[D-OS(Me)Ph] + k_B[D\{OS(Me)Ph, PAr_3\}] \quad (15)$$

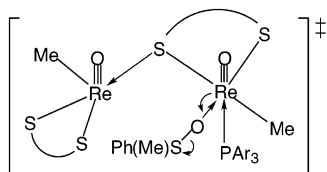
where k_B , according to eq 12, is related to B , K_7 , and K_{DL} . On the basis of earlier research on oxorhenium catalysis,^{12,14} the key step along each pathway is the formation of a dioxorhenium(VII) intermediate that results from the O–X bond breaking step. The two rate-controlling steps implied by eq 15 involve the transformation of a $ORe^V-OS(Me)Ph$ species to $Re^{VII}(O)_2 + MeSPh$. This reaction has always required nucleophilic assistance.¹² The role of the nucleophile is to assist in the oxidation of rhenium and in the severing of the covalent O–X bond. The transition state suggested in this case can be diagrammed as follows:



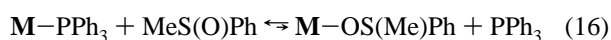
In the case at hand, either of two nucleophiles plays a role in parallel pathways. The nucleophilic groups are the coordinated sulfur atom of an mtp ligand in one transition state and an exogenous phosphine in the other. The first transition state contains only the entities present in $D-OS(Me)Ph$, because the rate constant A is independent of $[P(C_6H_4-4-Cl)]$, and for the other phosphines the values extrapolate to A as $[PAR_3] \rightarrow 0$. Our interpretation of this pathway is that a lone pair of the thiolate coordinated to one rhenium acts as the nucleophile toward the other rhenium. This can be represented as transition state $[A]^\ddagger$.



The parallel pathway in eq 15 shows phosphine involvement. The transition state is shown as $[B]^\ddagger$. This type of nucleophilic assistance was observed in the reaction between pyridine *N*-oxide and PPh_3 catalyzed by $M-PPh_3$.¹²



Catalysis by **D** offers an intramolecular pathway that is not available to the slower-reacting catalysts based on $M-PPh_3$. Furthermore, the reactivity of **D** is not impeded by one of the major kinetic barriers that $MeReO(mtp)PPh_3$ experiences, namely the need to displace the bulky and tightly bound phosphine.



The PPh_3 ligand of the mononuclear catalyst must be displaced by sulfoxide, which is thermodynamically unfavorable. This equilibrium constant is too small to be determined experimentally; however, we estimate the value should be $<10^{-3}$ by considering the difference in basicities of pyridine *N*-oxide and $MeS(O)Ph$ (Table 1).¹² In the $M-PPh_3$ catalyzed OAT, the strongly coordinating phosphine must be replaced by an oxygen source such as $MeS(O)Ph$ to avoid formation of a *trans*-dioxorhenium(VII) intermediate, which is the electronically disfavored isomer. Most reported dioxo- $Re(VII)$ species adopt a *cis* geometry.^{14,26–30} The ligand displacement is the primary cause of the ca. 150-fold difference in catalytic reactivity shown in Figure 1, because phosphine displacement is not involved in the reaction catalyzed by **D**.

Monomerization of $\{MeReO(mtp)\}_2$ by PAR_3 in the Presence of $MeS(O)Ph$. Our initial aim in this study was simply to make allowance for the depletion of the dimer catalyst. We noticed, however, that monomerization of **D** in the presence of $MeS(O)Ph$ is ca. 10 times faster than that in its absence. As this aspect progressed, however, it was realized that catalyzed monomerization and OAT have mechanistic features in common, and that became the factor underlying further study.

To investigate this effect in detail, we performed some additional experiments and found that the rate of monomerization is given by eq 16.

$$-\frac{d[D]}{dt} = \left\{ k_a [PPh_3] + k_b [PPh_3]^2 + \frac{k_{mp} K_{DL} [L] [PAR_3]}{1 + K_{DL} [L]} \right\} [D] \quad (17)$$

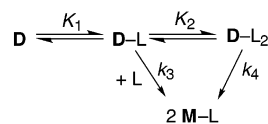
- (26) Brown, S. N.; Mayer, J. M. *J. Am. Chem. Soc.* **1996**, *118*, 12119–12133.
 (27) Takacs, J.; Kiprof, P.; Riede, J.; Herrmann, W. A. *Organometallics* **1990**, *9*, 782–787.
 (28) Dilworth, J. R.; Ibrahim, S. K.; Khan, S. R.; Hursthouse, M. B.; Karaulov, A. A. *Polyhedron* **1990**, *9*, 1323–1329.
 (29) Cai, S.; Hoffmann, D. M.; Wierda, D. A. *Organometallics* **1988**, *7*, 2069–2070.
 (30) Cai, S.; Hoffmann, D. M.; Wierda, D. A. *J. Chem. Soc., Chem. Commun.* **1988**, 313–315.

After allowance for the noncatalyzed k_a and k_b terms, the catalyzed component is given by

$$k_m = \frac{k_{mp} K_{DL} [L] [PAR_3]}{1 + K_{DL} [L]} \quad (18)$$

where k_m is the pseudo-first-order rate constant for the catalyzed component of the monomerization, k_{mp} is the rate constant for the reaction between **D**-L and PAR_3 , and L is the concentration of weak base such as sulfoxide or DMF.

As shown in Figure S7, k_m is first-order with respect to $[PPh_3]$. On the other hand, the dependences of k_m on $[L]$ show saturation kinetics as depicted in Figure S8a,b. Fixing K_{DL} at 5.7 L mol⁻¹ for $MeS(O)Ph$ and at 7.6 L mol⁻¹ for DMF, as determined independently, we found the values $k_{mp} = 1.2(1)$ L mol⁻¹ s⁻¹ for $MeS(O)Ph$ and 0.29(1) L mol⁻¹ s⁻¹ DMF at 23 °C in benzene.³¹ We also analyzed the monomerization by a series of $P(C_6H_4-4-R)_3$ species in the presence of $MeS(O)Ph$ and obtained the Hammett reaction constant (ρ) as $-1.2(1)$ as shown in Figure S9. Our previous study of the monomerization of **D** by PAR_3 in the absence of $MeS(O)Ph$ gave $\rho = -1.89$ for k_b .²³ The observed pathway in the present study can be compared with the k_b pathway ($=K_1 K_2 k_4$ in ref 14), where K_{DL} represents K_1 and k_{mp} represents $K_2 k_4$.



We obtained $\rho = -2.1(1)$ for K_{DL} (Table 1) and $-1.2(1)$ for k_{mp} . Therefore, total contributions from K_{DL} and k_{mp} could lead to a more negative ρ value overall. Thus, our observation in this monomerization reaction is consistent with the previously proposed monomerization mechanism. In this study, we found that sulfoxide accelerates the monomerization of **D** by triarylphosphine, mainly because a sulfoxide is much smaller molecule than triarylphosphine. Such a small molecule easily coordinates to one of the rhenium(V) centers on **D** and provides enough space for the second attack by triarylphosphine.

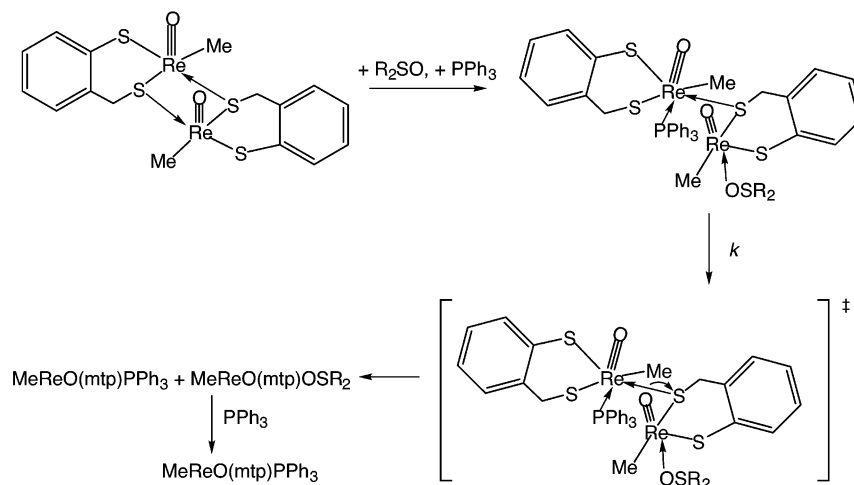
Chemical Mechanisms. It should be noted that different mechanisms operate for monomerization of **D** by PPh_3 with and without $MeS(O)Ph$. In the absence of $MeS(O)Ph$, PPh_3 itself monomerizes **D**, which takes place quite slowly according to eqs 3–4.

Sulfoxides, on the other hand, do not monomerize **D**; instead, they give **D**- OSR_2 , as in eq 5. With both R_2SO and PPh_3 present, however, each ligand is coordinated with a measurable formation constant K_7 , eq 7. This signifies an important interaction because when only PPh_3 is present, **D**- PPh_3 never attains a measurable concentration. This seeming anomaly can be resolved if one postulates that the ternary complex assumes a structure in which one (only) of

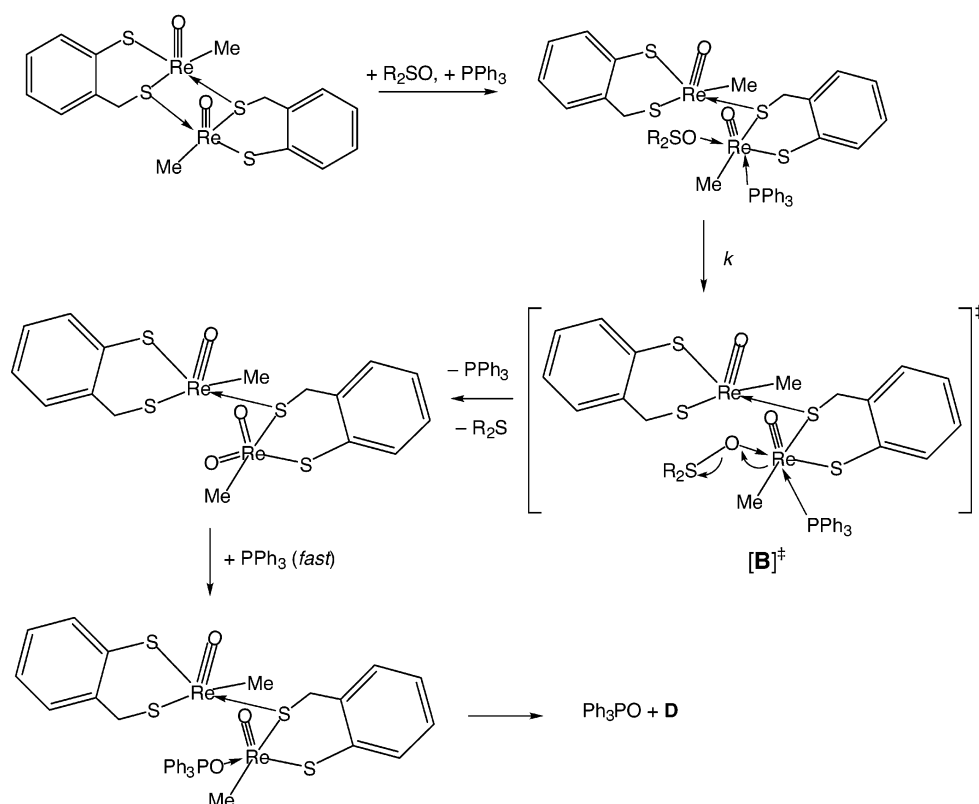
- (31) The correlation for $MeS(O)Ph$ is poor probably because the OAT reaction also took place, and $[MeS(O)Ph]$ changed during the reaction.

Oxorhenium(V) Dimer Catalyzed Oxygen Atom Transfer

Scheme 1. Proposed Mechanism for the Sulfoxide-Catalyzed Monomerization Reaction



Scheme 2. Proposed Mechanism for OAT from Sulfoxide to Phosphine



the coordinate $S \rightarrow \text{Re}$ bonds of the central core has been broken. Speculatively, then, rotation about the remaining $S \rightarrow \text{Re}$ bond of the central core appears to allow coordination not only by R_2SO but also by the sterically encumbered PPh_3 . Without this proposed half-opening of the dimer core, the large PPh_3 by itself is too large to coordinate to rhenium to any measurable extent. We estimate $K_{\text{DL}} < 10^{-2} \text{ L mol}^{-1}$ for $\text{L} = \text{PPh}_3$.

In the structure of the proposed ternary intermediate, the coordination numbers of rhenium would be five and six. We further hypothesize that this ternary interaction generates two structural isomers, one of which lies on the path to monomerization and the other on the path to OAT. The distinction lies in whether both ligands are bound to a single rhenium

atom of **D**, or one ligand to each rhenium atom. In the formulation we present, the first intermediate leads to OAT, the second to the sulfoxide-catalyzed monomerization reaction.

This important distinction is governed by two factors. The first is the strong tendency of oxorhenium compounds not to exist with coordination numbers less than five: four-coordinate $\text{MeReO}(\text{mtp})$ has never been detected. The second factor is the way in which each ternary structure facilitates the subsequent reaction it will undergo. For monomerization of **D** to $\text{M}-\text{PPh}_3$, the sequence can be diagrammed as shown in Scheme 1.

Scheme 1 depicts the suggested pathway for sulfoxide-assisted monomerization from an interpretation of the kinetics

and other aspects of the chemistry of the parent dimer. Note that PPh_3 attacks at one Re atom and OSR_2 at the other. One might ask whether this scheme can also accomplish OAT, but the answer is negative. Instead, we suggest for OAT a different sequence, as shown in Scheme 2. Note that the form of the ternary complex along this pathway is a structural isomer of that in Scheme 1.

The subsequent rapid step is phosphine attack on an oxo group by phosphine. This step takes place rapidly, as demonstrated for a related dioxo rhenium complex.³² Phosphine approaches the oxygen atom on Re(VII) ; the $\text{Re}=\text{O}$ π^* orbital interacts with the lone pair on the phosphorus atom.^{33,34} This event promotes electron flow into the rhenium d-orbital. Then, an O–P bond is formed, giving Re(V) weakly coordinated by OPAr_3 . Phosphine oxide coordinated in this fashion was seen in the recently isolated molybdenum-(IV) compound, $\text{Mo}^{\text{IV}}\text{O}(\text{OPPh}_3)$.³⁵ Finally, the phosphine oxide is released, and the original **D** regenerates.

A key feature of the pathway for OAT is that it *must not* lead to a monomeric structure, for such would rapidly be transformed to the most stable species, $\text{M}-\text{PPh}_3$, which is not catalytically active.

Conclusions. The fascinating aspects of this system can be summarized as follows: (a) The binary complex $\text{D}-\text{OS}-\text{Me}_2$ has been crystallographically characterized. It is sufficiently stable with respect to its constituents that a 50:50 mixture of it and **D** is present when $[\text{Me}_2\text{SO}]_{\text{eq}} = 8 \text{ mM}$. (b)

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R_2SO does not convert **D** to $\text{M}-\text{OSR}_2$ to any detectable extent, unlike ligands such as Py, PZ_3 , and even Me_2S which (rapidly or slowly, with varying equilibrium constants)²³ form equilibrium mixtures of **D** and $\text{M}-\text{L}$. (c) The otherwise slow but favored conversion $\text{D} + 2\text{PAR}_3 \rightarrow 2\text{M}-\text{PAR}_3$ is catalyzed by R_2SO . Kinetic studies showed that a ternary intermediate, $\text{D}(\text{OSR}_2)(\text{PAR}_3)$, lies along the reaction pathway. The plausible structure of the transition state has one ligand on each rhenium, $[\text{R}_2\text{SO}-\text{Re}, \text{Re}-\text{PAR}_3]^\ddagger$. (d) The OAT reaction, $\text{R}_2\text{SO} + \text{PAR}_3 \rightarrow \text{R}_2\text{S} + \text{Ar}_3\text{PO}$, is catalyzed by **D** along parallel pathways, one of which also proceeds by a ternary complex. For OAT, however, the plausible transition state is the structural isomer $[\text{Re}, \text{Re}(-\text{OSR}_2)(-\text{PAR}_3)]^\ddagger$, in which the role of phosphine is to provide nucleophilic assistance for the step $\text{Re}^{\text{V}}-\text{OSR}_2 \rightarrow \text{Re}^{\text{VII}}(\text{O})_2 + \text{R}_2\text{S}$. (e) Concurrent with this, a second pathway for OAT operates in parallel. It lacks phosphine involvement in the transition state, as revealed by the form of the rate law. Here, too, there is nucleophilic assistance for sulfide formation, but now it is provided by a sulfur atom of the chelating dithiolate ligand.

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Supporting Information Available: Figures detailing UV–vis spectral changes accompanying the formation of $\text{D}-\text{OS}(\text{Me})-\text{Ph}$, its analyzed data set to obtain K_{DL} , plots of $[\text{sulfide}]$, against $\{1 - \exp(-k_{\text{mt}}t)\}$ at different concentrations, and kinetic data for monomerization of **D**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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