Kinetics and Mechanisms of Reactions of ReO(κ^2-edt)(κ^2-edtMe):† Phosphane Displacement of the Thioether Group and Inversion of the Thioether Sulfur

Xiaopeng Shan and James H. Espenson*

Ames Laboratory and Department of Chemistry, Iowa State University, Ames, Iowa 50011

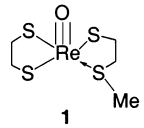
Received November 1, 2002

Phosphanes (PZ_3) convert ReO(κ^2-edt)(κ^2-edtMe) (**1**) into ReO(κ^2-edt)(κ^1-edtMe)(PZ_3) (**2**)[1,2] in equilibrium reactions that have been studied in benzene at 25.0 °C. The equilibrium constants and rate constants were evaluated by NMR spectroscopy and stopped-flow studies. The equilibrium constants were correlated by the Hammett equation, giving $\rho_K = -1.59$, which indicates an electronic effect on the equilibrium that is in agreement with reaction constants for the kinetics, $\rho_{for} = -0.07$ and $\rho_{rev} = 1.21$, for forward and reverse reactions, respectively. The small reaction constant for the forward reaction and large value for the reverse reaction can be explained by proposing an early transition state of the substitution reaction. In other words, the Re−P bond is not substantially made at the point where the Re−SMe bond is broken to a considerable extent. The kinetics of inversion of the thioether sulfur was investigated by determining the temperature profile of the NMR spectra, from which $\Delta H^{\ddagger} = 24 \pm 1$ kJ mol^{-1}. From the combination of results from the above two reactions, a planar intermediate mechanism is being proposed for the sulfur inversion.

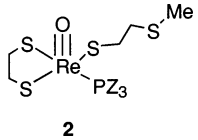
Introduction

Recent series of Re^V or Re^{VII} complexes catalyze oxygen atom transfer reactions that are analogous, stoichiometrically and to a great extent mechanistically, to those catalyzed by molybdenum enzymes.[3−9] Many of the rhenium compounds are prepared from reactions between methyltrioxorhenium(VII) (MTO) and alkane- or arenedithiols.[10−12] Usually the Re(VII) of MTO is reduced to lower valent Re(V) by oxidation of a dithiol to a disulfide. Recently we prepared an entirely new type of product from the reaction between MTO and 1,2-ethanedithiol ($edtH_2$). This gave rise to the Re^V compound **1**.[13] Compound **1** contains chelated 1,2-ethanedithiolate (edt) and the edtMe ligands. Although numerous transition-metal complexes with thiolate or thioether ligands have been synthesized and characterized,[14−19] only less commonly have mixed thiolate−thioether complexes been obtained.[20−22] Reaction of **1** with phosphanes gives rise to ReO(κ^2-edt)(κ^1-edtMe)PZ_3 (**2**),[1,2]

$$MeReO_3 + 2HS(CH_2)_2SH \rightarrow \underset{\mathbf{1}}{ReO(\kappa^2\text{-edt})(\kappa^2\text{-edtMe})} + 2H_2O \quad (1)$$



1



2

in which only the thiolate sulfur of edtMe is coordinated to rhenium and the thioether arm is not coordinated. This ligand displacement step is essential for catalytic oxygen atom transfer reactions catalyzed by oxorhenium(V) complexes,[3,5,23] because it allows the oxi-

* To whom correspondence should be addressed. E-mail: espenson@iastate.edu.

† The κ^n notation is used because η^n is restricted to carbocyclic ligands; see refs 1 and 2.

(1) *Nomenclature of Inorganic Chemistry: IUPAC Report*; Leigh, G., Ed.; Blackwell Scientific: London, 1990.
(2) Block, B. P.; Powell, W. H.; Fernelius, W. C. *Inorganic Chemical Nomenclature: Principles and Practice*; American Chemical Society: Washington, DC, 1990.
(3) Wang, Y.; Espenson, J. H. *Inorg. Chem.* **2002**, *41*, 2266−2274.
(4) Gangopadhyay, J.; Sengupta, S.; Bhattacharyya, S.; Chakraborty, I.; Chakravorty, A. *Inorg. Chem.* **2002**, *41*, 2616−2622.
(5) Arias, J.; Newlands, C. R.; Abu-Omar, M. M. *Inorg. Chem.* **2001**, *40*, 2185−2192.
(6) Bhattacharyya, S.; Chakraborty, I.; Dirghangi, B. K.; Chakravorty, A. *Inorg. Chem.* **2001**, *40*, 286−293.
(7) Bhattacharyya, S.; Chakraborty, I.; Dirghangi, B. K.; Chakravorty, A. *Chem. Commun.* **2000**, 1813−1814.
(8) Gable, K. P.; Brown, E. C. *Organometallics* **2000**, *19*, 944−946.
(9) Seymore, S. B.; Brown, S. N. *Inorg. Chem.* **2000**, *39*, 325−332.
(10) Espenson, J. H.; Shan, X.; Wang, Y.; Huang, R.; Lahti, D. W.; Dixon, J.; Lente, G.; Ellern, A.; Guzei, I. A. *Inorg. Chem.* **2002**, *41*, 2583−2591.
(11) Jacob, J.; Guzei, I. A.; Espenson, J. H. *Inorg. Chem.* **1999**, *38*, 1040−1041.
(12) Takacs, J.; Cook, M. R.; Kiprof, P.; Kuchler, J. G.; Herrmann, W. A. *Organometallics* **1991**, *10*, 316−320.
(13) Shan, X.-P.; Espenson, J. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 3870−3809.
(14) Stephan, D. W.; Nadasdi, T. T. *Coord. Chem. Rev.* **1996**, *147*, 147−208.
(15) Krebs, B.; Henkel, G. *Angew. Chem.* **1991**, *103*, 785−804 (See also *Angew. Chem., Int. Ed. Engl.* 1991, 1930 (1997), 1769−1988).
(16) Blower, P. J.; Dilworth, J. R. *Coord. Chem. Rev.* **1987**, *76*, 121−185.
(17) Sellmann, D.; Geipel, F.; Heinemann, F. W. *Eur. J. Inorg. Chem.* **2000**, 59−63.
(18) Zeltner, S.; Olk, R.-M.; Joerchel, P.; Sieler, J. *Z. Anorg. Allg. Chem.* **1999**, *625*, 368−373.
(19) Benson, I. B.; Knox, S. A. R.; Naish, P. J.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1981**, 2235−2244.
(20) Mullen, G. E. D.; Blower, P. J.; Price, D. J.; Powell, A. K.; Howard, M. J.; Went, M. J. *Inorg. Chem.* **2000**, *39*, 4093−4098.
(21) Al-Jeboori, M. J.; Dilworth, J. R.; Hiller, W. *Inorg. Chim. Acta* **1999**, *285*, 76−80.
(22) Zhuang, W.-W.; Hoffman, D. M.; Lappas, D.; Cohen, J. *Polyhedron* **1998**, *17*, 2583−2586.

10.1021/om0209071 CCC: $25.00
Publication on Web 01/25/2003

dant to access the rhenium atom and the product to depart.

Inversion of sulfur atoms of a coordinated thioether ligand has been widely discussed.[24−26] Transition metals in lower oxidation states with thioether ligands have been synthesized and studied.[27,28] In contrast, thioether ligands are rare with high-oxidation-state metals. Two mechanisms have been proposed for sulfur inversion: a planar-intermediate mechanism and a dissociation−recombination mechanism. On the basis of metal effects,[29−31] M−S bond influence,[32,33] and small activation entropies[34,35] of certain systems, the first mechanism appears more favorable, but the results remain controversial.[24,36]

In this paper, we report the kinetics and mechanism of phosphane displacement (eq 2) of the thioether ligand to generate a phosphane-rhenium(V) compound **2**. Also,

$$\underset{\mathbf{1}}{\mathrm{ReO}(\kappa^2\text{-edt})(\kappa^2\text{-edtMe})} + \mathrm{PZ_3} = \underset{\mathbf{2}}{\mathrm{ReO}(\kappa^2\text{-edt})(\kappa^1\text{-edtMe})(\mathrm{PZ_3})} \quad (2)$$

sulfur inversion of the thioether ligand has been studied and a mechanism proposed for it.

Experimental Section

Materials and Instrumentation. Compound **1** was synthesized from MTO and 1,2-ethanedithiol as reported previously.[13] The phosphanes were purchased from Aldrich or Strem and were used as received. Spectranalyzed benzene (Aldrich) was used as the solvent for UV−visible studies. d_8-Toluene and d_6-benzene were employed as solvents for NMR spectroscopy. An OLIS rapid-scan stopped-flow instrument was used to monitor reaction 2. A Bruker DRX 400 MHz spectrometer was used to record ^{1}H NMR spectra.

Kinetic Studies. An absorbance increase around 390 nm accompanies reaction 2. A typical repetitive scan is shown in Figure 1 for $P(C_6H_4\text{-}4\text{-}OMe)_3$.

An isosbestic point was found for this particular phosphane at 450 nm. The absorbance−time data at 415 nm were extracted from the repetitive scans. Because an excess of the phosphanes was used for the kinetic studies, the data could be fitted to eq 3, from which values of k_ψ were obtained. In eq

$$\mathrm{Abs}_t = \mathrm{Abs}_e + (\mathrm{Abs}_0 - \mathrm{Abs}_e)\exp(-k_\psi t) \quad (3)$$

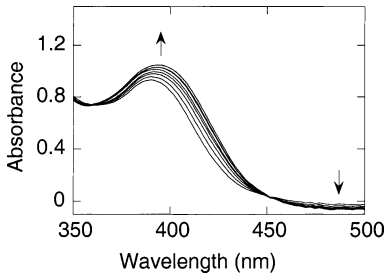


Figure 1. Repetitive scan data for the reaction between 0.1 mM ReO(κ²-edt)(κ²-edtMe) and 10 mM $P(p\text{-}MeOC_6H_4)_3$, showing spectra at 0.2 s intervals in benzene at 25.0 °C.

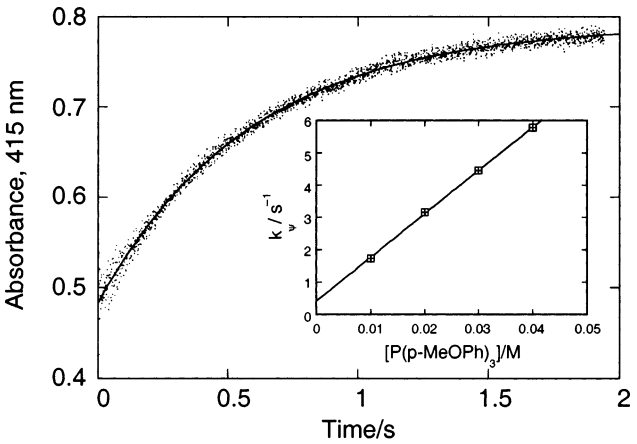


Figure 2. The absorbance-time data for reaction 2 follow pseudo-first-order kinetics with a large excess of phosphane, as in the illustrated case of $P(p\text{-}MeOC_6H_4)_3$. The inset shows a plot of k_ψ vs the concentration of $P(p\text{-}MeOC_6H_4)_3$, for reaction 2 in benzene at 25.0 °C, according to eq 4.

3, Abs_t stands for the absorbance of at time t, Abs_e for the absorbance at equilibrium, and Abs_0 for the initial absorbance. Figure 2 shows the plot of k_ψ against the concentration of this phosphane. Such plots for this and other phosphanes are linear, with slopes representing the second-order rate constants for the forward direction, k_{for}, and intercepts the first-order rate constant for the reverse direction, k_{rev}, as in eq 4.

$$k_\psi = k_{for}[\mathrm{PZ_3}] + k_{rev} \quad (4)$$

The kinetics of sulfur inversion was investigated by the lineshape change in NMR spectra from −40 °C to room temperature. The width at half-height ($W_{1/2}$) of the resonance peak at 1.94 and 7.00 ppm was measured by XPLOTED software from Bruker. The peak at 1.94 ppm is from the thioether methyl group of **1** and that at 7.00 ppm from the solvent. In comparison with the solvent peak, the methyl resonance at 1.94 ppm shows an obvious line-broadening effect when the temperature decreases (Figure 3). The values of $W_{1/2}$ are given in Table S-1 in the Supporting Information. Values of $W_{1/2}$ varied with the rate constant of inversion, k_{inv}, according to eq 5, where $\delta\nu$ is the difference between the chemical shift for the methyl group and W_0 is the half-width of the peak without inversion.

$$k_{inv} = \frac{\pi(\delta\nu)^2}{2(W_{1/2} - W_0)} \quad (5)$$

(23) Wang, Y.; Espenson, J. H. *Org. Lett.* **2000**, *2*, 3525−3526.
(24) Abel, E. W.; Moss, I.; Orrell, K. G.; Sik, V. *J. Organomet. Chem.* **1987**, *326*, 187−200.
(25) Abel, E. W.; Budgen, D. E.; Moss, I.; Orrell, K. G.; Sik, V. *J. Organomet. Chem.* **1989**, *362*, 105−115.
(26) Ascenso, J. R.; Carvalho, M. d. D.; Dias, A. R.; Romao, C. C.; Calhorda, M. J.; Veiros, L. F. *J. Organomet. Chem.* **1994**, *470*, 147−152.
(27) Abel, E. W.; Booth, M.; Orrell, K. G. *J. Chem. Soc., Dalton Trans.* **1980**, 1582−1592.
(28) Abel, E. W.; Long, N. J.; Orrell, K. G.; Osborne, A. G.; Sik, V.; Bates, P. A.; Hursthouse, M. B. *J. Organomet. Chem.* **1990**, *394*, 455−468.
(29) Abel, E. W.; Booth, M.; Orrell, K. G.; Pring, G. M. *J. Chem. Soc., Dalton Trans.* **1981**, 1944−1950.
(30) Hauptman, E.; Fagan, P. J.; Marshall, W. *Organometallics* **1999**, *18*, 2061−2073.
(31) Orrell, K. G.; Sik, V.; Brubaker, C. H., Jr.; McCulloch, B. *J. Organomet. Chem.* **1984**, *276*, 267−279.
(32) Abel, E. W.; Farrow, G. W.; Orrell, K. G.; Sik, V. *J. Chem. Soc., Dalton Trans.* **1977**, 42−46.
(33) Abel, E. W.; Bhargava, S. K.; Orrell, K. G.; Platt, A. W. G.; Sik, V.; Cameron, T. S. *J. Chem. Soc., Dalton Trans.* **1985**, 345−353.
(34) Toyota, S.; Yamada, Y.; Kaneyoshi, M.; Oki, M. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1509−1512.
(35) Toyota, S.; Oki, M. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1345−1351.
(36) Abel, E. W.; Orrell, K. G.; Poole, M. C.; Sik, V. *Polyhedron* **1999**, *18*, 1345−1353.

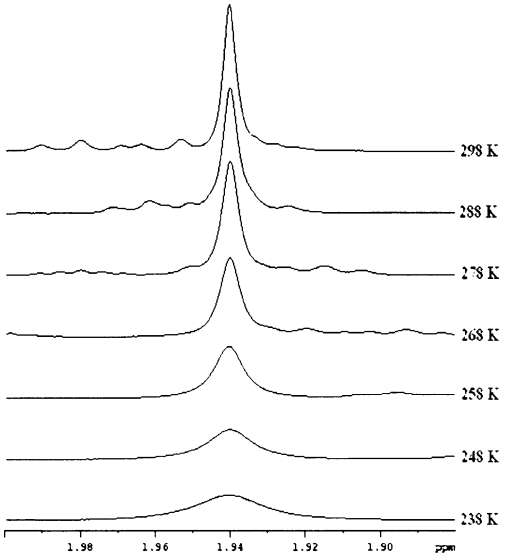


Figure 3. Line-broadening effects in the ^{1}H NMR spectrum of ReO(κ^2-edt)(κ^2-edtMe) (**1**) in d_8-toluene, which arises from inversion at sulfur.

Equilibrium Study. The equilibrium constants for reaction 2 were measured by NMR spectra of mixtures of **1** and phosphanes in d_6-benzene at 25 °C. Some of the equilibrium constants were calculated from kinetic data by $K = k_{for}/k_{rev}$.

Temperature Profiles. The temperature profile of reaction 2 was investigated by using a temperature-controlled water bath in conjunction with the OLIS rapid-scan instrument. Temperatures were varied from 15 to 40 °C and were controlled to within ±0.2 °C. An Eyring plot is depicted in Figure 4 and the rate constants were fitted by eq 6 to obtain values of the activation parameters. In eq 6, k stands for the rate constant, $\Delta S^{\ddagger}$ for the activation entropy, $\Delta H^{\ddagger}$ for the activation enthalpy.

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^{\ddagger}}{R} - \frac{\Delta H^{\ddagger}}{RT} \qquad (6)$$

The sulfur inversion process was studied by taking ^{1}H NMR spectra at temperatures between 233.7 and 298 K. An Eyring plot is given in Figure 5 and fitted by eq 7. Activation enthalpy was obtained from the slope. The activation entropy is not available because $\delta\nu$ is not known.

$$\ln[(W_{1/2} - W_0)T] = \ln\left(\frac{\pi(\delta\nu)^2}{2}\right) - \ln\left(\frac{k_B}{h}\right) - \frac{\Delta S^{\ddagger}}{R} + \frac{\Delta H^{\ddagger}}{RT} \qquad (7)$$

Results

Equilibrium of Thioether−Phosphane Substitution Reactions. A series of such reactions as in eq 2 with PZ_3 reagents have been explored. The equilibrium constants are given in Table 1. For the series with P(p-$XC_6H_4)_3$, K increases as electron-donating groups are placed on the aryl group.

The equilibrium constants were correlated by the Hammett equation against the substituent constants 3σ, affording $\rho_K = -1.59$, as shown in Figure 6. 3σ was used because of three identical substituents on phosphane. This indicates a substantial electronic effect on the equilibrium position of these reactions. The small increase of K_e from Cy_2PhP to $CyPh_2P$, compared with the 20-fold increase from Ph_3P to $CyPh_2P$, shows evidence of the different steric demands of this group of ligands. The reaction with the smallest and most electron-dense phosphane, PMe_2Ph, has the largest equilibrium constant, $K = 2580$.

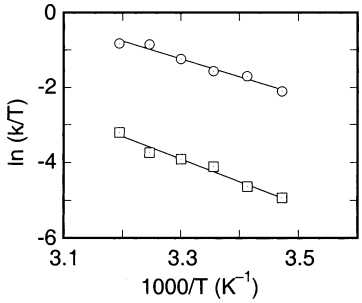


Figure 4. Analysis of kinetic data for the rate constants k_{for} (top) and k_{rev} (bottom) for the reaction ReO(κ^2-edt)(κ^2-edtMe) + PPh_3 ⇄ ReO(κ^2-edt)(κ^1-edtMe)(PPh_3) by the Eyring equation. Forward direction: $\Delta H^{\ddagger} = 40(4)$ kJ mol^{-1}; $\Delta S^{\ddagger} = -76(7)$ J K^{-1} mol^{-1}. Reverse direction: $\Delta H^{\ddagger} = 50(4)$ kJ mol^{-1}; $\Delta S^{\ddagger} = -66(7)$ J K^{-1} mol^{-1}.

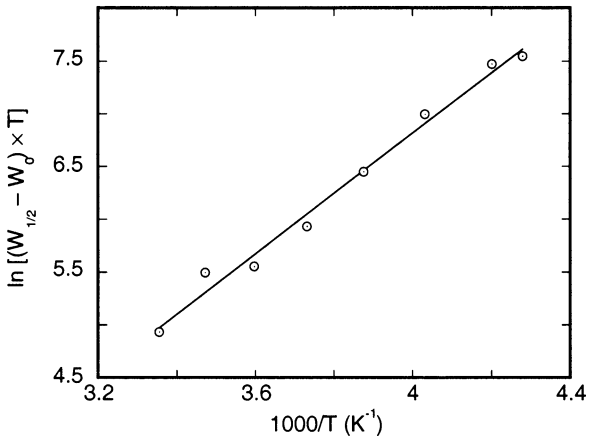


Figure 5. Plot of $\ln[(W_{1/2} - W_0)T]$ vs $1/T$ for compound **1** in d_8-toluene from 233.7 to 298 K.

Kinetics of Ligand Substitution. Values of k_{for} and k_{rev} are presented in Table 1. For the series with P(m- or p-$XC_6H_4)_3$, values of k_{for} increase slightly as electron-donating substituents are placed on the aryl group. In contrast, the values of k_{rev} decrease dramatically in the same series. Both series of rate constants could be correlated by the Hammett equation with the substituent constants 3σ, affording $\rho_{for} = -0.07$ and $\rho_{rev} = 1.21$, as shown in Figure 7. We conclude from this analysis that ligand substitution goes through an early transition state. That is, the Re−P bond is not substantially made at the point where the Re−SMe bond is broken to a considerable extent.

Temperature profiles of the forward and reverse rate constants were derived from the plots presented in Figure 4. Activation parameters for k_{for} and k_{rev} are summarized in Table 2 for the case of PPh_3. The activation enthalpy for the reverse direction is 10 kJ mol^{-1} greater than that of the forward direction, because of the stronger Re−P bond. Both directions have similar negative activation entropies indicative of an associative transition state, in agreement with early studies.[37,38]

Sulfur Inversion. Obvious line broadening of the ^{1}H resonance peak of the methyl group in **1** occurred as

(37) Espenson, J. H.; Shan, X.; Lahti, D. W.; Rockey, T. M.; Saha, B.; Ellern, A. *Inorg. Chem.* **2001**, *40*, 6717−6724.
(38) Lahti, D. W.; Espenson, J. H. *J. Am. Chem. Soc.* **2001**, *123*, 6014−6024.

Table 1. Equilibrium and Rate Constants for Phosphane Coordination to Re(κ¹-edt)(κ²-edtMe)[a]

phosphane	k_f/L mol^{-1} s^{-1} [b]	k_r/s^{-1} [b]	K kinetic[c]	K direct
$P(4\text{-}MeOC_6H_4)_3$	$(1.35 \pm 0.02) \times 10^2$	$(4.3 \pm 0.5) \times 10^{-1}$	$(3.1 \pm 0.4) \times 10^2$	$(3.2 \pm 0.3) \times 10^2$ [d]
$P(4\text{-}MeC_6H_4)_3$	$(7.61 \pm 0.07) \times 10^1$	1.30 ± 0.07	$(5.9 \pm 0.3) \times 10^1$	$(6.7 \pm 0.7) \times 10^1$ [d]
$P(3\text{-}MeC_6H_4)_3$	$(4.91 \pm 0.09) \times 10^1$	2.42 ± 0.03	$(2.03 \pm 0.04) \times 10^1$	$(3.2 \pm 0.5) \times 10^1$ [e]
PPh_3	$(6.20 \pm 0.09) \times 10^1$	4.86 ± 0.09	$(1.28 \pm 0.02) \times 10^1$	8.0 ± 0.8 [d]
$P(4\text{-}FC_6H_4)_3$	$(9.2 \pm 1.6) \times 10^1$	$(1.52 \pm 0.06) \times 10^1$	6 ± 1	3.5 ± 0.4 [d]
$P(3\text{-}MeOC_6H_4)_3$	$(1.06 \pm 0.03) \times 10^2$	7.54 ± 0.08	$(1.41 \pm 0.04) \times 10^1$	$(1.12 \pm 0.05) \times 10^1$ [e]
$P(4\text{-}ClC_6H_4)_3$				$(7.8 \pm 0.8) \times 10^{-1}$ [d]
$PMePh_2$	$(8.1 \pm 0.3) \times 10^2$			$(2.58 \pm 0.09) \times 10^3$ [e]
$P(c\text{-}C_6H_{11})Ph_2$	$(8.1 \pm 0.3) \times 10^1$	$(4.3 \pm 0.7) \times 10^{-1}$	$(1.9 \pm 0.3) \times 10^2$	
$P(c\text{-}C_6H_{11})_2Ph$	$(1.10 \pm 0.02) \times 10^1$	$(5.4 \pm 0.4) \times 10^{-2}$	$(2.0 \pm 0.2) \times 10^2$	

[a] In benzene at 25.0 °C. [b] From eq 3. $k_{obsd} = k_f[PZ_3] + k_r$. [c] From k_f/k_r. [d] From NMR integration. [e] From UV/vis titration.

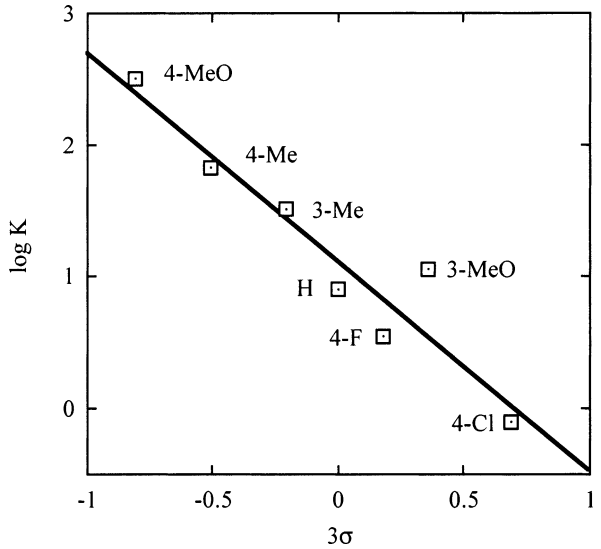


Figure 6. Hammett correlation of the equilibrium constants for reaction 2 with PAr_3 reagents against the substituent constants.

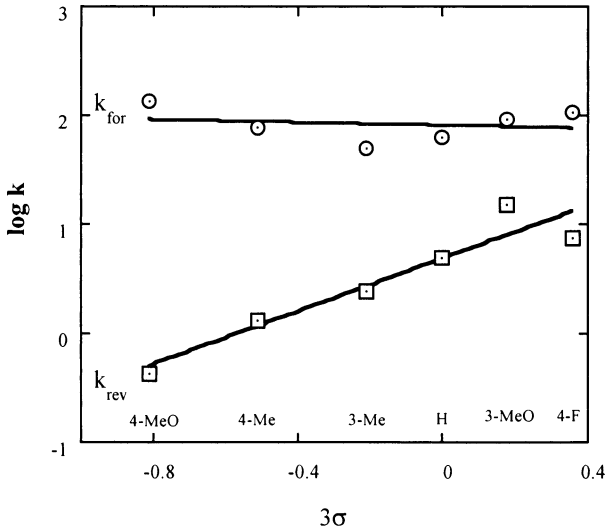


Figure 7. Hammett analysis of the rate constants k_{for} and k_{rev} for the reaction ReO(κ²-edt)(κ²-edtMe) + PAr_3 ⇄ ReO(κ²-edt)(κ¹-edtMe)(PAr_3).

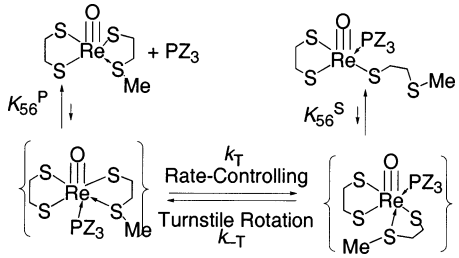
the temperature was decreased from 298 to 233.7 K. This line-shape change is caused by rapid inversion of the thioether sulfur.[27,28,32,33,39] The activation enthalpy has been obtained from Figure 5, fitted by eq 7 and

(39) Abel, E. W.; Bhargava, S. K.; Orrell, K. G.; Sik, V. *Inorg. Chim. Acta* **1981**, *49*, 25−30.

Table 2. Activation Energy Parameters for Ligand Substitution and Sulfur Inversion Reactions of 1 in Benzene

	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
k_{for}	40(4)	−76(7)
k_{rev}	50(4)	−66(7)
k_{inv}	24(1)	

Scheme 1. Competitive and Reversible Coordination of Phosphane and Thioether



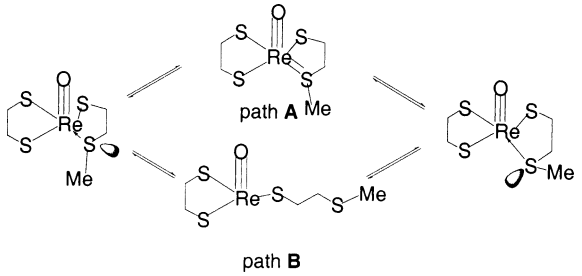
listed in Table 2. It is smaller than the activation enthalpy of Re−S ligand substitution. Because $\delta\nu$ is not known, the rate constant and activation entropy for sulfur inversion cannot be determined.

Discussion

Mechanism of Ligand Substitution. Reaction 2 does not occur in a single step. Indeed it cannot, because of restrictions imposed by the principle of microscopic reversibility that require a mechanism that is symmetric in the forward and reverse directions. The new donor atoms, P in one direction and thioether S in the other, enter axially, and each must leave from that same site. Building on our earlier work,[37,38] we propose the mechanism given in Scheme 1.

According to Scheme 1, $k_{for} = K_{56}{}^{P}k_T$ and $k_{rev} = K_{56}{}^{S}k_{-T}$ where "56" stands for the equilibrium step in which the coordination number of rhenium changes from 5 to 6. Both values of K_{56} are ≪1, and no six-coordinate intermediate attains a concentration that would permit its detection. Values of k_{for} in the series of P(*m*- or *p*-$XC_6H_4)_3$ reactants show relatively little variation, because k_{for} includes the contribution of $K_{56}{}^{P}$, such that little discrimination among the PZ_3 reagents will be seen, owning to the labile attachment of PZ_3 on Re. Furthermore, with k_T attributed to a reaction with an early transition state, the influence of PZ_3 will not be great. In contrast, significant changes in k_{rev} were recorded. They simply reflect the significant extent of Re−P bond cleavage at the same transition state. As with k_{for}, little variation of k_{rev} arises from variations in $K_{56}{}^{S}$.

Scheme 2. Pyramidal Sulfur Inversion of 1



The turnstile rotation in Scheme 1 is a Bailar twist combined with formation of the Re−P bond and cleavage of the Re−S bond. The energy barrier of ligand displacement, which arises mainly from the rotation step, is smaller than that of the Bailar twist in the literature,[40,41] because the Re−P and Re−S bond distances in transition state are longer than regular bonds.

Mechanism of Sulfur Inversion. Two mechanisms have been proposed in the literature for sulfur inversion in thioether-coordinated transition-metal complexes. The alternative pathways are presented in Scheme 2.[19,26,36,39,42] Pathway A involves a planar intermediate with a (p−d)π conjugation, which is favored by a stronger metal−sulfur interaction. In contrast, pathway B with a dissociation−recombination step prefers a weak Re−S bond. Re(V), as a high-oxidation-state metal, readily accepts electron density from the thioether sulfur and gives rise to strong Re−S interaction. Thus the activation enthalpy, 24(1) kJ mol^{-1}, is smaller than values previously reported.[29] The NMR spectrum of **1** displays a unique resonance for each hydrogen on the edt ligand, indicating no position exchange of thiolato and thioether sulfurs in edtMe, indirectly ruling out pathway B.[43]

Indeed, the value of k_{for} for the ligand displacement of thioether sulfur, in which the Re−S bond is breaking as in pathway A, showed an activation enthalpy that is much larger than that of sulfur inversion. Thus, pathway A with the planar intermediate appears more likely in this case than the dissociation−recombination pathway B.

Acknowledgment. This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract W-7405-Eng-82.

Supporting Information Available: Table and plots of kinetic data to illustrate agreement to selected mathematical forms and to evaluate numerical parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0209071

(40) Gromova, M.; Jarjayes, O.; Hamman, S.; Nardin, R.; Beguin, C.; Willem, R. *Eur. J. Inorg. Chem.* **2000**, 545−550.
(41) Murray, S. G.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 365−414.
(42) Abel, E. W.; Farrow, G. W.; Orrell, K. G. *J. Chem. Soc., Dalton Trans.* **1976**, 1160−1163.

(43) We are grateful to a reviewer for this observation.