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Oxygen Atom Transfer Reactions from Dioxygen to Phosphines via a Bridging Sulfur Dioxide in a Trinuclear Cluster Complex of Rhenium, $[(Ph_3P)_2N][Re_3(\mu_3\text{-}S)(\mu\text{-}S)_2(\mu\text{-}SO_2)Cl_6(PMe_2Ph)_3]$

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A trinuclear rhenium sulfide cluster complex, $[(Ph_3P)_2N][Re_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_6(PMe_2Ph)_3]$, synthesized from $Re_3S_7Cl_7$, dimethylphenylphosphine, and $[(Ph_3P)_2N]Cl$ is readily converted to a bridging SO_2 complex, $[(Ph_3P)_2N][Re_3(\mu_3\text{-}S)(\mu\text{-}S)_2(\mu\text{-}SO_2)Cl_6(PMe_2Ph)_3]$, by reaction with O_2. The oxygen atoms on the SO_2 ligand react with phosphines or phosphites to form phosphine oxides or phosphates, and the original cluster complex is recovered. The reaction course has been monitored by ^{31}P NMR as well as by UV–vis spectroscopy. The catalytic oxygenation of $PMePh_2$ in the presence of the SO_2 complex shows that turnovers are 8 per hour at 23 °C in $CDCl_3$. The X-ray structures of the cluster complexes are described.

Introduction

Oxygen atom transfer (OAT) reactions are one of the most important reactions in bioinorganic chemistry,[1] and it is well-known that various metal complexes are involved in these reactions. Most of them are metal-centered, and metal oxo species play a catalytic role in the oxygen atom transfer.[2,3] Rhenium oxo complexes are extensively studied as the catalysts and intermediates for OAT reactions.[4−6] There are many kinds of oxygen atom donors and acceptors, and a thermodynamic scale for the reaction $X + {}^{1}/_{2}O_2 \rightarrow XO$ has been discussed.[5] Tertiary phosphines or phosphites are moderately reactive toward oxygen, and it is convenient to use them as oxygen atom acceptors in model reactions,[6] even though they may not participate in biological reactions.

Cluster sulfide chemistry of rhenium is still in the early stage of development compared with those of molybdenum and tungsten.[7−13] A number of hexanuclear rhenium chalcogenide cluster compounds have been synthesized, and their chemistry and photochemistry have been studied extensively.[14] Rhenium cluster chalcogenide compounds of other nuclearity are not numerous,[15] and one of the interesting features is the reaction of bridging sulfur ligands with dioxygen to form bridging SO_2 complexes. Early examples are the synthesis of $[Re_4S_2(SO_2)_4(CN)_{10}]^{8-}$ from a reaction intermediate, $[Re_4S_6(CN)_{10}]^{8-}$, in the cyanolysis of either $[NH_4]_4[Re_4S_4(S_3)_6]$ or Re_2S_7.[16] Sokolov and others reported that an attempt to prepare $[Et_4N][Re_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_6(PEt_3)_3]$ resulted in the formation of $[Et_4N][Re_3(\mu_3\text{-}S)(\mu\text{-}S)_2(\mu\text{-}SO_2)Cl_6(PEt_3)_3]$.[17] These reactions suggest that a bridging sulfur

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ligand in the high-oxidation-state rhenium clusters is very reactive with dioxygen.

The purposes of the present study are to isolate the well-characterized rhenium sulfide cluster complexes that undergo oxygenation upon exposure to dioxygen to form bridging SO_2 cluster complexes, and to study the reactivity of the oxygen atoms on the SO_2 ligand toward oxophilic compounds such as tertiary phosphines or phosphites. Although OAT reactions mediated by rhenium oxo species have been intensively studied,[6] oxygenation catalysis via a SO_2 ligand presents novel chemistry.

Experimental Section

General Experimetal Procedures. Rhenium metal powder, trimethylphosphine (PMe_3), dimethylphenylphosphine (PMe_2Ph), methyldiphenylphosphine ($PMePh_2$), triphenylphosphine (PPh_3), and bis(triphenylphosphinylidene)ammonium chloride ($[(Ph_3P)_2N]Cl$) were purchased from Aldrich and the other chemicals from Wako Chemicals. Solvents were dried and distilled by general methods. $Re_3S_7Cl_7$ was prepared according to the literature.[18] Most of the handlings were carried out under dinitrogen using standard Shlenk techniques unless otherwise stated.

Physical Measurements. ^{1}H and ^{31}P NMR spectra were measured by a JEOL GX400 or a JEOL ECP500 spectrometer, UV−vis spectra were recorded on a JASCO V-570 spectrophotometer, and cyclic voltammograms were recorded on a BAS 620A electrochemical analyzer.

$[(Ph_3P)_2N][Re_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_6(PMe_2Ph)_3]\cdot 3CH_2Cl_2$ (1). $Re_3S_7Cl_7$ (1.03 g, 1.00 mmol) and PMe_2Ph (0.97 g, 7.02 mmol) were stirred in CH_2Cl_2 (30 mL) at room temperature under dinitrogen for 3 days. The reaction mixture was filtered, and the solvent and volatile materials were removed from the filtrate under reduced pressure to give a solid. The solid was washed with Et_2O twice, dried, and dissolved in CH_2Cl_2 (10 mL). $[(Ph_3P)_2N]Cl$ (0.70 g, 1.21 mmol) was dissolved in the solution, and Et_2O was layered on it. The mixture was allowed to stand for 3 days to produce black crystals in 66% yield. Anal. Calcd for $C_{63}H_{69}Cl_{12}NP_5Re_3S_4$: C, 35.91; H, 3.07; N, 0.66. Found: C, 36.02; H, 3.07; N, 0.70. UV−vis (CH_2Cl_2): λ_{max}, nm (ϵ) 439 (3534). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.16 (d, J(P−H) = 10.7 Hz) ($P(CH_3)_2Ph$). ^{31}P NMR (161.7 MHz, $CDCl_3$, 15% H_3PO_4): δ −48.33 ($P(CH_3)_2Ph$), 21.56 ($(Ph_3P)_2N^+$).

$[(Ph_3P)_2N][Re_3(\mu_3\text{-}S)(\mu\text{-}S)_2(\mu\text{-}SO_2)Cl_6(PMe_2Ph)_3]\cdot 3CH_2Cl_2$ (2). Cluster compound **1** (1.39 g, 0.66 mmol) was dissolved in CH_2Cl_2 (10 mL) and the resulting solution stirred for 3 days in air. The color of the solution changed from dark brown to dark yellow. Et_2O (30 mL) was layered on the solution, and black crystals of **2** formed after a few days in 84% yield based on **1**. Anal. Calcd for $C_{63}H_{69}Cl_{12}NO_2P_5Re_3S_4$: C, 35.37; H, 3.25; N, 0.66. Found: C, 35.42; H, 3.31; N, 0.63. UV−vis (CH_2Cl_2): λ_{max}, nm (ϵ) 447 (3070), 663 (1047), 873 (966). IR (KBr): ν(S−O) 1039, 1182 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.34 (d, J(P−H) = 11.0 Hz), 2.45 (d, J(P−H) = 11.5 Hz) ($P(CH_3)_2Ph$). ^{31}P NMR (161.7 MHz, $CDCl_3$): δ −40.89, −39.93 ($P(CH_3)_2Ph$), 21.53 ($(Ph_3P)_2N^+$).

Cyclic Voltammetry. The redox potentials of **1** and **2** were determined by cyclic voltammetry using a conventional three-electrode system. Platinum wires were used as the working electrode and the counter electrode. A Ag/AgCl electrode was used as the reference. Tetra-*n*-butylammonium perchlorate (TBAP) was used as supporting electrolyte. (*Caution: One of the reviewers of this Article advised us to abolish the use of this perchlorate salt as the electrolyte because of possible fatal accidents!*) The experiments were carried out in dried CH_2Cl_2 solutions under a dinitrogen atmosphere at room temperature.

Table 1. Crystallographic Data for **1** and **2**

	1	2
emprical formula[a]	$C_{63}H_{69}Cl_{12}NP_5Re_3S_4$	$C_{63}H_{69}Cl_{12}NO_2P_5Re_3S_4$
fw	2107.28	2139.28
cryst color	black	black
cryst size (mm^3)	0.36 × 0.08 × 0.06	0.50 × 0.10 × 0.10
space group	$P\bar{1}$	$P\bar{1}$
unit cell dimensions		
a (Å)	11.0850(5)	11.1304(5)
b (Å)	13.3607(6)	13.5270(6)
c (Å)	27.3106(12)	27.1809(11)
α (deg)	93.354(1)	92.684(1)
β (deg)	100.763(1)	99.322(1)
γ (deg)	110.345(1)	110.833(1)
V ($Å^3$)	3692.1(3)	3750.0(3)
Z	2	2
T (°C)	−100	−50
radiation (Mo Kα)	0.71069	0.71069
ρ_{calcd} (g cm^{-3})	1.895	1.895
μ (mm^{-1})	5.601	5.518
θ range (deg)	0.77−18.28	0.76−28.31
hkl index ranges	−14/+13 −17/+17 −33/+36	−13/+14 −17/+18 −36/+34
GOF on F^2	0.982	1.013
R1[b]/wR2[c] [$I > 2\sigma(I)$]	R1 = 0.0433, wR2 = 0.0897	R1 = 0.0297, wR2 = 0.0684
R (all data)	R1 = 0.0637, wR2 = 0.1014	R1 = 0.0391, wR2 = 0.0757
largest diff peak and hole	2.150 and −1.184	1.443 and −1.355

[a] Including solvate molecules. [b] $R1 = \sum||F_o| - |F_c||/\sum F_o$. [c] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

X-ray Crystal Structure Determination. Data were collected at low temperatures on a Bruker Smart Apex CCD system equipped with a graphite-monochromated Mo Kα radiation source. The intensity data were corrected for Lorentz and polarization effects. Absorption corrections were applied using the SADABS empirical method. Data were treated by the Bruker SAINT software, and structures were solved using SHELXTL.[19] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added at calculated positions and included in the final refinement. The crystallographic data for **1** and **2** are given in Table 1.

Oxygenation of Tertiary Phosphines. 1. NMR Spectra. Complex **2** was dissolved in $CDCl_3$, and 5 molar equivalents of $PMePh_2$ was added to the solution. ^{31}P NMR spectra (JEOL GX400) were measured either in a dinitrogen atmosphere or in air to monitor the following: a decrease of the ^{31}P signals of **2** (−40.88 ppm, septet, −39.93 ppm, septet) and free $PMePh_2$ (−24.91 ppm, singlet), and an increase in those of complex **1** (−48.33 ppm, singlet) and $O{=}PMePh_2$ (30.00 ppm, quartet).

Methyldiphenylphosphine (2×10^{-3} mol) and **2** (10^{-5} mol) in $CDCl_3$ (20 mL) were reacted at 23 °C for 6 h in a three-necked flask connected to a gas (O_2) buret, and the ratio of methyldiphenylphosphine and methyldiphenylphosphine oxide during the oxygenation of methyldiphenylphosphine was measured by ^{31}P NMR spectroscopy (JEOL ECP500) at 1 h intervals. Control measurements were carried out without complex **2**.

2. Visible Spectra. Complex **2** (10 mg, 0.005 mmol) was dissolved in dichloromethane (5 mL) under N_2, and a phosphine or a phosphite was added to the solution at 23 °C. The reaction was monitored by the spectral features at 447, 663, and 873 nm.

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Table 2. Selected Interatomic Distances (Å) and Angles (deg) for Compounds **1** and **2**

	1	**2**		**1**	**2**
		Distances			
Re1−Re3	2.7008(3)	2.7671(2)	P1−Re1	2.5387(16)	2.5304(10)
Re1−Re2	2.7081(3)	2.7890(2)	P2−Re2	2.5293(16)	2.5219(10)
Re2−Re3	2.7046(3)	2.7828(2)	P3−Re3	2.5332(16)	2.5416(10)
Re1−S1	2.2818(14)	2.2431(10)	Cl1−Re1	2.4264(15)	2.3939(9)
Re1−S3	2.2850(15)	2.3445(9)	Cl2−Re1	2.4284(15)	2.4526(9)
Re1−S4	2.3407(15)	2.3394(9)	Cl3−Re2	2.4363(15)	2.4328(9)
Re2−S1	2.2859(15)	2.2464(9)	Cl4−Re2	2.4244(15)	2.4320(9)
Re2−S2	2.2956(15)	2.2524(9)	Cl5−Re3	2.4386(16)	2.4087(10)
Re2−S4	2.3321(15)	2.3623(10)	Cl6−Re3	2.4278(14)	2.4407(9)
Re3−S3	2.2895(15)	2.3358(9)	O1−S3		1.471(3)
Re3−S2	2.3034(15)	2.2463(10)	O2−S3		1.468(3)
Re3−S4	2.3254(12)	2.3310(9)	N1−P5	1.574(5)	1.590(3)
			N1−P4	1.594(5)	1.578(3)
		Angles			
Re3−Re1−Re2	60.004(9)	60.111(5)	Cl1−Re1−P1	78.52(5)	78.86(4)
Re3−Re2−Re1	59.865(9)	59.554(5)	Cl1−Re1−Cl2	83.83(5)	84.09(4)
Re1−Re3−Re2	60.131(9)	60.334(6)	Cl1−Re1−Re3	96.74(4)	98.94(3)
Re1−S3−Re3	72.37(4)	72.49(3)	S4−Re1−P1	165.30(5)	167.01(3)
S3−Re3−Re1	53.74(4)	53.90(2)	S1−Re1−Cl1	161.84(6)	161.94(4)
Re2−S4−Re1	70.83(4)	72.77(3)	O2−S3−O1		111.59(18)
S4−Re2−Re1	54.74(4)	53.24(2)	O2−S3−Re3		116.29(12)
P1−Re1−Re3	135.99(4)	136.71(2)	O1−S3−Re3		118.11(13)
			O2−S3−Re3		115.43(13)
			O1−S3−Re1		117.99(13)

Results and Discussion

Synthesis and Characterization. Treatment of $Re_3S_7Cl_7$ with dimethylphenylphosphine followed by addition of bis(triphenylphosphinylidene)ammonium chloride ($[(Ph_3P)_2N]Cl$) in a dinitrogen atmosphere formed a trinuclear rhenium cluster complex, **1**, in moderate yield. As this complex is very air-sensitive even in the solid state, every operation should be carried out under dinitrogen. The features of the UV−vis spectra are not very distinctive, but absence of the bands at 663 and 873 nm is informative in judging if the complex is contaminated by the SO_2 complex **2**. The ^1H NMR spectra indicate a doublet of methyl protons of PMe_2Ph (δ 2.16) together with multiplets of phenyl protons of PMe_2Ph (δ 7.2−7.5) and $(Ph_3P)_2N^+$ (δ 7.5−7.7). The ^{31}P NMR spectra show a broad singlet (δ −48.33) of PMe_2Ph and a singlet (δ 21.56) of $(Ph_3P)_2N^+$. When a dichloromethane solution of the cluster complex **1** was stirred in air, the color of the solution gradually changed from dark brown to yellow brown. Addition of diethyl ether to the solution formed a cluster SO_2 complex, **2**, in 84% yield. The UV−vis spectra have bands at 447, 663, and 873 nm. The band at 873 nm is especially distinctive and can be used as a marker for the formation of **2**.

The IR spectrum has two bands assignable to ν(S−O) at 1039 and 1182 cm^{-1}. The ^1H NMR spectra indicate doublets of methyl protons of PMe_2Ph (δ 2.34 and 2.45) in a 2:1 intensity ratio together with multiplets of phenyl protons of PMe_2Ph (δ 7.1−7.4) and $(Ph_3P)_2N^+$ (δ 7.5−7.7). The ^{31}P NMR spectra show septets (δ −40.89, −39.93, J(P−H) = 10.8 Hz) of PMe_2Ph in a 2:1 intensity ratio and a singlet (δ 21.53) of $(Ph_3P)_2N^+$. The intensity ratio of 2:1 in both ^1H and ^{31}P spectra suggests that two PMe_2Ph ligands are coordinated to two rhenium atoms bridged by the μ-SO_2 ligand and the third phosphine is coordinated to the other rhenium atom. The results show that only one μ-S atom in **1** among three reacts with O_2 under ambient conditions. There is a brief report that three μ-S atoms are oxygenated during the transformation of the Re_3S_7 core to the Re_3S_4 core.[20]

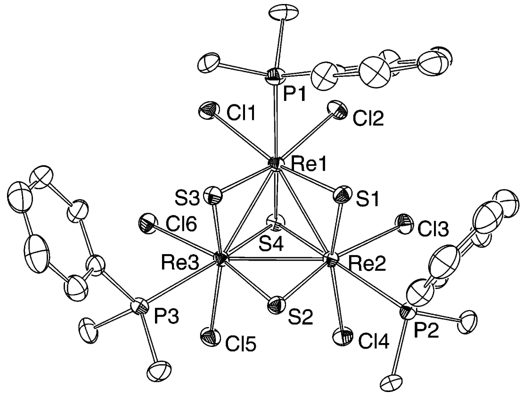

Figure 1. ORTEP (50%) structure of $[Re_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_6(PMe_2Ph)_3]^-$. Hydrogen atoms are omitted for clarity.

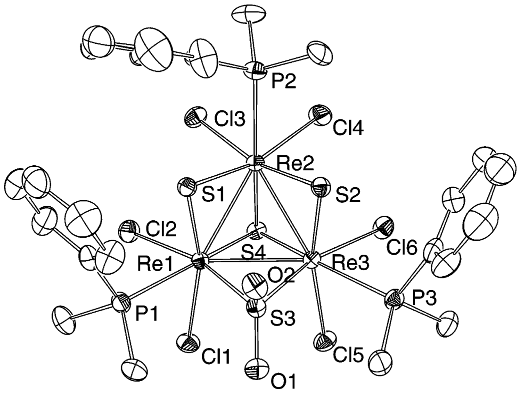

Figure 2. ORTEP (50%) structure of $[Re_3(\mu_3\text{-}S)(\mu\text{-}S)_2(\mu\text{-}SO_2)Cl_6(PMe_2Ph)_3]^-$. Hydrogen atoms are omitted for clarity.

Structures. Interatomic distances and angles for **1** and **2** are given in Table 2. The cluster anion structures of **1** and **2** are illustrated in Figures 1 and 2, respectively. Complex **1** consists of three rhenium atoms forming almost an equilateral triangle with an average Re−Re distance of 2.705 Å. The Re_3 triangle is bridged by one μ_3-S atom and three μ-S atoms with a μ_3-S−Re distance of 2.33 Å (av), about 0.04 Å longer than the μ-S−Re distance of 2.29 Å (av). Each rhenium atom is coordinated by two chlorine atoms and one dimethylphenylphosphine ligand. The mean Re−Cl distance is 2.43 Å. All the phosphines are in the orientations trans to the capping μ_3-S atom with an average Re−P distance of 2.53 Å. The structure is similar to that of $[PEt_3H][Re_3S_4Cl_6(PEt_3)_3]$, which has a mean Re−Re distance of 2.719 Å, a Re−Cl distance of 2.42 Å, and a Re−P distance of 2.56 Å.[21] Thus, the difference of phosphines and cations has little influence on the structure. The structure of bis(triphenylphosphinylidene)ammonium cation ($(Ph_3P)_2N^+$) is not remarkable, and its size is as large as that of the cluster anion, giving enough voids to accommodate three CH_2Cl_2 molecules in an asymmetric unit.

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Table 3. Redox Potentials in the Cyclic Voltammograms of **1** and **2**

	$E_{1/2}$/V vs Ag/AgCl (CH_2Cl_2)	
	$-1/-2^a$	$0/-1^a$
$[(Ph_3P)_2N][Re_3S_4Cl_6(PMe_2Ph)_3]$ (**1**)	−0.84	0.48
$[(Ph_3P)_2N][Re_3S_3(SO_2)Cl_6(PMe_2Ph)_3]$ (**2**)	−0.26	1.07

[a] −1 refers to cluster monoanions.

Complex **2** has almost an isosceles triangle of three rhenium atoms with Re−Re distances of 2.767, 2.789, and 2.783 Å, the shortest one being bridged by a μ-SO_2 ligand. It is noteworthy that these distances are considerably longer than those in **1**. The mean μ_3-S−Re distance is 2.34 Å, and that of μ-S−Re is 2.25 Å. The Re−S distances for the μ-SO_2 ligand are 2.34 Å. The mean Re−Cl distance is 2.43 Å, and that of Re−P is 2.53 Å. Three phosphines are directed trans to the capping μ_3-S atom, and this contrasts with those in $[Et_4N][Re_3S_3(SO_2)(PEt_3)_3]$ in which one of the three phosphines is directed cis to μ_3-S.[17] The complex shows ν(S−O) at 1039 and 1182 cm^{-1} which are normal for a μ-SO_2 complex.[22] The S−O distance of 1.47 Å is almost the same as that in the triethylphosphine derivative, while the O−S−O angle of 111.6° is a little smaller than that (113.8°) in the same compound. The Re−S(O_2)−Re angle is 72.5°, and this value is not very different from that (72.4°) of Re−S−Re in **1**. For $[Re_4S_2(SO_2)_4(CN)_{10}]^{8-}$, the S−O distance is 1.49 Å, the O−S−O angle is 108.2°, and the angle Re−S(O_2)−S is 74.2 Å.[16] Thus, the structural features around the μ-SO_2 ligand in **2** are not exceptional among several rhenium sulfur dioxide complexes with a μ-SO_2 ligand, and oxygenation of the μ-S atom seems to form a normal μ-SO_2 complex.[22,23]

Cyclic Voltammetry. The oxidation state of SO_2 ligands is usually treated as neutral for electron counting purposes,[22] but it seems better to regard the present bridging SO_2 as dinegative from its bond angles.[17] On this basis, we assign identical formal oxidation states for **1** and **2**. Redox potentials of **1** and **2** are given in Table 3. These potentials correspond to changes of the formal rhenium oxidation state $Re^{V}Re^{IV}Re^{IV}$ of **1** and **2** to $Re^{V}Re^{V}Re^{IV}$ on one-electron oxidation (0/−1) and to $Re^{IV}Re^{IV}Re^{IV}$ on one-electron reduction (−1/−2). They indicate that the oxidation potential of **2** is higher than that of **1**, which reflects the decrease of the electron density of the cluster system in going from **1** to **2**. It is conceivable that reduction of the electron density in the Re_3 cluster system of **2** by bonding of two electronegative oxygen atoms to the bridging sulfur results in the inertness to oxidation, and hence in a higher oxidation potential. A decrease of the bonding interaction between Re atoms as judged by longer Re−Re distances in **2** may also be explainable by higher repulsion between rhenium atoms due to lower electron density.

Oxygen Atom Transfer Reactions. The reaction chemistry of the μ-SO_2 ligand has received little attention,[22] and we have been interested in the reactivity of μ-SO_2 in complex **2** with oxygen acceptors. We considered that oxygenation

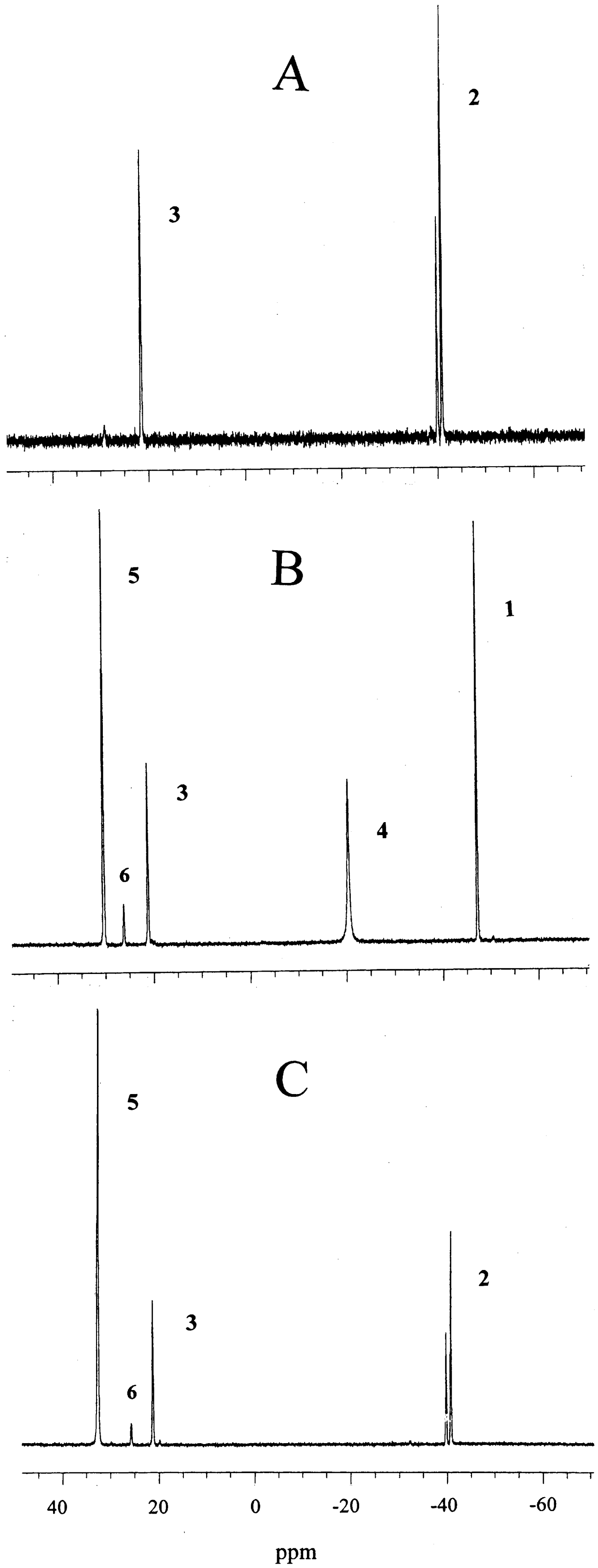

Figure 3. (A) ^{31}P NMR spectra of $[(Ph_3P)_2N][Re_3S_3(SO_2)Cl_6(PMe_2Ph)_3]$. (B) After reaction with $PMePh_2$ (1:5 molar ratio) in $CDCl_3$ at room temperature in N_2. (C) After reaction with $PMePh_2$ (1:5 molar ratio) in $CDCl_3$ at room temperature in air. Key: 1, *P*Me_2Ph of **1**; 2, *P*Me_2Ph of **2**; 3, $(Ph_3P)_2N^+$; 4, *P*$MePh_2$ (ca. 6 ppm downfield shifted); 5, O=*P*$MePh_2$; 6, an impurity contained in $PMePh_2$ from the start of the measurements.

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of complex **1** was so smooth that reverse oxygen atom abstraction by oxygen atom acceptors may construct a good catalytic system for OAT reactions. We first examined stoichiometric reactions by NMR and UV−vis spectroscopies and found catalytic oxygenation of phosphines or phosphites.

^{31}P NMR spectra of the $CDCl_3$ solutions of the reaction mixture of complex **2** and $PMePh_2$ in a 1:5 molar ratio in dinitrogen or air (Figure 3) showed a notable difference. Spectrum B in dinitrogen shows that all of complex **2** reacted to give **1** and 2 equiv of methyldiphenylphosphine oxide. The chemical shift of the unreacted phosphine is ca. 6 ppm downfield shifted presumably by an interaction with the bridging sulfur atom. Only 2 mol $O{=}PMePh_2$ should be formed from 1 mol of **2**, and this is apparent from spectrum B. However, spectrum C of the reaction in air showed that all the added phosphine was converted to methyldiphenylphosphine oxide. The fact that more than 2 equiv of $O{=}PMePh_2$ formed in air indicates the catalytic nature of the reaction. Namely, methyldiphenylphosphine was oxygenated catalytically in the presence of complex **2**, and complex **2** was regenerated after all the added $PMePh_2$ was converted to $O{=}PMePh_2$.

Oxygenation of methyldiphenylphosphine (2×10^{-3} mol) was measured by ^{31}P NMR spectra at 23 °C in the presence (10^{-5} mol) and absence of complex **2**. The reactions were carried out in $CDCl_3$ solutions (20 mL), and NMR samples drawn from the reaction flask were subjected to NMR measurements. After 6 h, 25% of methyldiphenylphosphine was oxygenated to methyldiphenylphosphine oxide in the presence of **2**, indicating turnovers of 8 per hour. Although 6% of methyldiphenylphosphine was also oxygenated in the absence of **2** under similar conditions, **2** promotes remarkably the oxygenation of methyldiphenylphosphine. Measurements on the oxygenation of $PMePh_2$ and other phosphines using a volumetric method have so far not given very satisfactory reproducibility, and further experiments will be published in future papers.

UV−vis spectra of complex **2** have characteristic bands at 663 and 873 nm, and on addition of a tertiary phosphine or a phosphite in a N_2 atmosphere, absorption of these bands decreases while a new band at 447 nm due to complex **1** increases. When the sample solutions were contacted with air, the absorptions due to the SO_2 complex recovered rapidly. The rate of oxygen atom transfer reaction from the SO_2 ligand in **2** to a phosphine or phosphite has been measured by the change of absorbance of the band at 873 nm of **2** in dichloromethane at 23 °C. The spectra were measured at intervals appropriate for the reaction rate of each phosphine or phosphite. Figure 4 illustrates the change of the bands when 2 equiv of $PMePh_2$ was added to the dichloromethane solution of **2**.

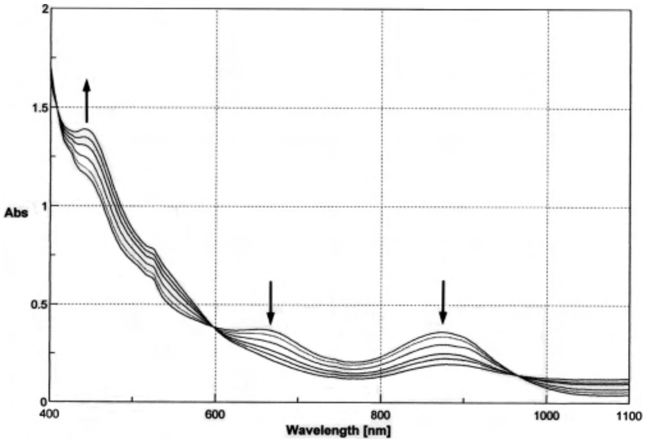

Figure 4. UV−vis spectra of the reaction mixture of $[(Ph_3P)_2N][Re_3S_3(SO_2)Cl_6(PMe_2Ph)_3]$ (**2**) with $PMePh_2$ (1:2 molar ratio) in CH_2Cl_2 at room temperature. Each spectrum was measured at 15 min intervals after the addition of the phosphine.

Table 4. Rate Constants *k* for the Reactions of **2** with Phosphites or Phosphines and pK_a and Cone Angles[a]

	k/L mol^{-1} s^{-1}	pK_a	cone angle/deg
$P(OMe)_3$	6.01×10^{-2}	2.6	107
$P(OEt)_3$	3.38×10^{-3}	3.31	109
$P(OPh)_3$	1.91×10^{-3}	−2.00	128
$P(O^iPr)_3$	1.01×10^{-4}	4.08	130
PMe_3	3.82×10^{-1}	8.65	118
PMe_2Ph	2.30×10^{-1}	6.5	122
$PMePh_2$	1.69×10^{-3}	4.57	136
PPh_3	1.40×10^{-5}	2.73	145
PCy_3	2.73×10^{-3}	9.70	170

[a] pK_a and cone angle: Rahman, Md. M.; Liu, H. Y.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1989**, *8*, 1.

The reaction of the SO_2 complex **2** with a phosphine or a phosphite involves **2** and two molecules of a reactant (eq 1). In principle, an oxygen atom should be abstracted by a phosphine or a phosphite from the SO_2 ligand first to form a SO ligand, and then the SO ligand reacts consecutively with the second molecule of a phosphine or a phosphite. However, the NMR and UV−vis spectra of the solution of **2** and a phosphine or a phosphite do not show any extra band assignable to a SO intermediate. As the UV−vis spectra of the reaction of **2** with a phosphite, $PMePh_2$, or PPh_3 show clear isosbestic points, a SO intermediate must be very short-lived.[24]

$$[(Ph_3P)_2N][Re_3S_3(SO_2)Cl_6(PMe_2Ph)_3] + 2PR_3 \rightarrow [(Ph_3P)_2N][Re_3S_4Cl_6(PMe_2Ph)_3] + 2OPR_3 \quad (1)$$

The reaction order *n* for a phosphine or a phosphite has been determined from the initial rate of the reactions of $P(OPh)_3$ in two different concentrations to be $n = 0.95$.[25] Although an integer value was not obtained, we have regarded the reaction as first order in reactants. It can be assumed that the second oxygen atom on the SO_2 ligand reacts with a phosphine or phosphite as quickly as the first oxygen atom to form two molecules of oxide. Therefore, we treat the present reaction as a pseudo-second-order reaction between the SO species ([SO] = 2[**2**]) and a phosphine or phosphite (eq 2). The reaction rate is expressed

$$\text{rate} = k[SO][PR_3] \quad (2)$$

in eq 3, where A_0 is the initial concentration of **2**, B_0 the initial concentration of a phosphine or phosphite, and *x* the

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(25) Atkins, P. W. *Physical Chemistry*, 6th ed.; Oxford University Press: Oxford, 1998; p 772.

concentration of reacted **2**.[26] The quantities kt (eq 4) are

$$\frac{dx}{dt} = k[2A_0 - 2x][B_0 - 2x] \tag{3}$$

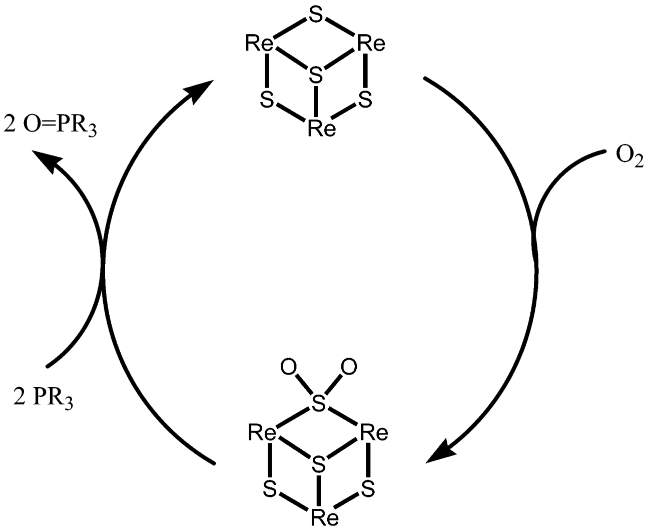
plotted against time t, and the rate constants k are obtained from the linear part of the initial period of the reactions. The spectral change and kinetic data are given in the Supporting Information, and the rate constants are shown in Table 4.

$$kt = \frac{1}{2(B_0 - 2A_0)} \ln \frac{A_0(B_0 - 2x)}{B_0(A_0 - x)} \tag{4}$$

Trimethylphosphine, dimethylphenylphosphine, and tricyclohexylphosphine reacted rapidly and in the presence of more than 2 equiv of phosphine; isosbestic points were not observed. Therefore, the rate was calculated using only initial rates. The above procedure should give at least relative rates of the oxygen atom abstraction by phosphines or phosphites from complex **2**. The relative rates are $PMe_3 > PMe_2Ph > P(OMe)_3 > P(OEt)_3 > P(OPh)_3 > PCy_3 > PMePh_2 > P(O^iPr)_3 > PPh_3$. The results show that phosphines or phosphites with smaller cone angles and higher nucleophilicity[27] (basicity) react faster, and suggest that the approach of phosphines or phosphites to the oxygen atoms on sulfur dioxide is controlled by steric congestion in the ligand environment and abstraction of oxygen atoms by the nucleophilicity of phosphines or phosphites. Tricyclohexylphosphine is the most basic reagent among them, and it has a large cone angle. Therefore, the position of PCy_3 indicates a compromise between basicity and steric influence.

The present reaction is an OAT reaction via a bridging SO_2 ligand in a trinuclear sulfide cluster complex of rhenium. The SO_2 complex **2** forms readily by the action of dioxygen on complex **1**, and complex **2** reacts with tertiary phosphines or phosphites to give phosphine oxides or phosphoric esters and regenerates **1**. As complex **2** catalyzes phosphine oxygenation in an O_2 atmosphere, the catalytic cycle illustrated in Scheme 1 seems plausible. Most of phosphine oxidation by rhenium complexes proceeds via rhenium oxo intermediates that originate from an oxygen source such as pyridine oxide, dimethyl sulfoxide, or dioxygen.[6] Formation of bridging SO_2 from metal thiolates has been known,[28] and a recent report on the reaction of PPh_3 with an iron sulfinate complex is relevant to our reaction in this Article.[29] The majority of homogeneous catalysis occurs on a metal center in a mononuclear or dinuclear complex. Therefore, the present reaction offers a unique catalysis mediated by a ligand in a metal cluster compound. We expect that further study will give us a clue to elucidate the reasons why only one bridging sulfur ligand among three in the trirhenium sulfide clusters is oxygenated and the bridging SO_2 ligand is moderately reactive to phosphines. General applicability of this reaction to other oxygen sources and oxygen atom acceptors and/or other SO_2 complexes is still to be explored.

Scheme 1



Supporting Information Available: Kinetic data. This material is available free of charge via the Internet at http://pubs.acs.org. X-ray crystallographic data reported in this Article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-235943 (**1**) and CCDC-235944 (**2**). Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

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