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Conversion of the (μ_2-Sulfido)dirhenium(III) Complexes $Re_2(\mu\text{-}S)(\mu\text{-}X)X_3(CS)(\mu\text{-}LL)_2$ (X = Cl, Br; LL = dppm, dpam) and Related Species to the Analogous μ_2-Sulfur Dioxide Compounds

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The μ_2-sulfido-bridged dirhenium(III) complexes $Re_2(\mu\text{-}S)(\mu\text{-}X)X_3(CS)(\mu\text{-}LL)_2$ (**1**) (X = Cl or Br when LL = dppm; X = Br when LL = dpam) and $[Re_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_2(CS)(\mu\text{-}dppm)_2(NCR)]PF_6$ (**2**) (R = Me or Et) react with the one-electron oxidant $NOPF_6$ in the presence of O_2 to afford in high yield the analogous diamagnetic μ_2-SO_2 complexes $Re_2(\mu\text{-}SO_2)(\mu\text{-}X)X_3(CS)(\mu\text{-}LL)_2$ (**3**) and $[Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_2(CS)(\mu\text{-}dppm)_2(NCR)]PF_6$ (**4**), respectively. This oxygenation can also be effected through the use of gaseous NO_2 and 3-chloroperbenzoic acid in place of $NOPF_6$. The structural identity of the products has been shown by a single-crystal X-ray structure analysis of $Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_3(CS)(\mu\text{-}dppm)_2$ (**3a**), which has confirmed an edge-shared bioctahedral structure and a short Re–Re distance (2.628 (1) Å). Data for a crystal of composition **3a**$\cdot C_2H_4Cl_2\cdot CH_2Cl_2$ at +20 °C are as follows: triclinic space group $P\bar{1}$, a = 11.2311 (7) Å, b = 14.316 (2) Å, c = 19.854 (2) Å, α = 86.672 (8)°, β = 80.297 (6)°, γ = 81.033 (7)°, V = 3106.4 (8) Å^3, and Z = 2. The structure was refined to R = 0.044 (R_w = 0.070) for 6416 data with $I > 3\sigma(I)$. The mechanism for the oxygenation of **1** and **2** in the presence of $NOPF_6$ involves the direct attack of NO_2 upon the μ_2-sulfido bridge. NO_2 is produced by the reaction of NO (the byproduct of the oxidation of **1** and **2** to $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$) with small amounts of O_2 in the system. Support for NO_2 being the actual oxygen transfer reagent for the conversion of μ-S to μ-SO_2 is the failure of the oxygenation reactions to proceed in the absence of O_2 or absence of $NOPF_6$. These oxygenation reactions are catalytic in $NOPF_6$.

Introduction

In studies aimed at exploiting the multielectron redox capability of compounds that contain the triply-bonded dirhenium(II) core, we have recently reported upon the uses of $Re_2X_4(\mu\text{-}dppm)_2$ (X = Cl, Br; dppm = $Ph_2PCH_2PPh_2$), and closely related compounds, as reagents for the reductive coupling of nitriles[1] and for the 2-electron reduction of CS_2.[2] In the latter system, we found[2] that $Re_2X_4(\mu\text{-}dppm)_2$ and $Re_2Br_4(\mu\text{-}dpam)_2$ (dpam = $Ph_2AsCH_2AsPh_2$) react with CS_2 to afford the dirhenium(III) complexes $Re_2(\mu\text{-}S)(\mu\text{-}X)X_3(CS)(\mu\text{-}LL)_2$. These reactions were noteworthy because they constituted the first instances where a multiply-bonded dimetal complex[3,4] had brought about the 2-electron reduction of CS_2 and where the CS and S^{2-} fragments were incorporated into the resulting dimetal product. In subsequent studies of the redox chemistry of the $Re_2(\mu\text{-}S)(\mu\text{-}X)X_3(CS)(\mu\text{-}LL)_2$ compounds, and the nitrile-containing derivatives $[Re_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_2(CS)(\mu\text{-}dppm)_2(NCR)]PF_6$, we have discovered that the μ-S unit is readily oxygenated to μ-SO_2 with no change in the remainder of the coordination geometry. The results of this work are described in the present report.[5]

Experimental Section

Starting Materials. The compounds $Re_2(\mu\text{-}S)(\mu\text{-}X)X_3(CS)(dppm)_2$ (X = Cl, Br), $Re_2(\mu\text{-}S)(\mu\text{-}Br)Br_3(CS)(dpam)_2$, $[Re_2(\mu\text{-}S)(\mu\text{-}X)X_3(CS)(dppm)_2]PF_6$ (X = Cl, Br), and $[Re_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_2(CS)(dppm)_2(NCR)]PF_6$ (R = CH_3, CH_2CH_3) were prepared according to the literature procedures.[2] All solvents were obtained from commercial sources and were used as received. Except as otherwise noted, syntheses were performed with the use of an atmosphere of dry nitrogen, and solvents were deoxygenated prior to use.

A. Synthesis of $Re_2(\mu\text{-}SO_2)(\mu\text{-}X)X_3(CS)(LL)_2$ Using $NOPF_6$. (i) X = Cl, LL = dppm. A suspension of $Re_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(CS)(dppm)_2$ (0.100 g, 0.074 mmol) and $NOPF_6$ (0.019 g, 0.110 mmol) was stirred in CH_2Cl_2 (10 ml) *which was not deoxygenated.* A color change from green to orange-red was observed. After 1 h, the reaction mixture was filtered and excess diethyl ether was added to the filtrate to initiate the precipitation of a red-brown solid. The product was filtered off, washed with diethyl ether, and vacuum dried; yield 0.086 g (84%). Anal. Calcd for $C_{52}H_{46}Cl_6O_2P_4Re_2S_2$ (i.e. $Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_3(CS)(dppm)_2\cdot CH_2Cl_2$): C, 42.30; H, 3.15. Found: C, 41.99; H, 3.44.

Note that much smaller (catalytic) quantities of $NOPF_6$ can be used in this reaction, and ones like it, with no significant decrease in the product yield (see Discussion).

(ii) X = Br, LL = dppm. A procedure similar to method A(i) was used to prepare this complex in 82% yield. Anal. Calcd for $C_{55}H_{54}Br_4O_3P_4Re_2S_2$ (i.e. $Re_2(\mu\text{-}SO_2)(\mu\text{-}Br)Br_3(CS)(dppm)_2\cdot(C_2H_5)_2O$): C, 40.20; H, 3.31. Found: C, 40.37; H, 3.10. The presence of lattice diethyl ether was confirmed by ^1H NMR spectroscopy.

(iii) X = Br, LL = dpam. Following a procedure similar to that described in method A(i), this complex was isolated in 84% yield. Anal. Calcd for $C_{53}H_{48}As_4Br_4Cl_4O_2Re_2S_2$ (i.e. $Re_2(\mu\text{-}SO_2)(\mu\text{-}Br)Br_3(CS)(dpam)_2\cdot 2CH_2Cl_2$: C, 33.24; H, 2.53. Found: C, 33.06; H, 2.37. An ^1H NMR spectrum (in $CDCl_3$) confirmed the presence of lattice CH_2Cl_2.

B. Synthesis of $Re_2(\mu\text{-}SO_2)(\mu\text{-}X)X_3(CS)(dppm)_2$ Using NO_2. (i) From $Re_2(\mu\text{-}S)(\mu\text{-}X)X_3(CS)(dppm)_2$. Both the chloride and bromide complexes can be prepared by suspending $Re_2(\mu\text{-}S)(\mu\text{-}X)X_3(CS)(dppm)_2$ (ca. 0.10 g) in CH_2Cl_2 (10 mL) and then passing a gentle stream of NO_2 gas through the mixture for ca. 5 s. An immediate change in color from green to dark red takes place. The reaction mixture was stirred for 30 min and filtered. An excess of diethyl ether was added to the filtrate to cause precipitation of the red-brown product. The solid was filtered off, washed with diethyl ether (15 mL), and dried. Both the chloride and bromide products were isolated in ca. 90% yield, and their identity was confirmed on the basis of their electrochemical and spectroscopic properties.

(ii) From $[Re_2(\mu\text{-}S)(\mu\text{-}X)X_3(CS)(dppm)_2]PF_6$. With the use of a reaction procedure and workup similar to method B(i), these paramagnetic salts were reacted with NO_2 to afford the μ-SO_2 complexes $Re_2(\mu\text{-}SO_2)(\mu\text{-}X)X_3(CS)(dppm)_2$; yield ca. 90%. The identity of the products was established on the basis of their electrochemical and spectroscopic properties.

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C. Synthesis of $\mathrm{Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_3(CS)(dppm)_2}$ Using 3-Chloroperbenzoic Acid. A mixture of $\mathrm{Re_3(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(CS)(dppm)_2}$ (0.100 g, 0.074 mmol) and $\mathrm{3\text{-}ClC_6H_4CO_3H}$ (0.040 g, 0.222 mmol) was stirred in $\mathrm{CH_2Cl_2}$ (10 mL) for 1 h. After this time, the red reaction mixture was filtered and excess diethyl ether was added to the filtrate to precipitate a red-brown solid. The solid was filtered off and washed with diethyl ether (15 mL); yield 0.082 g (80%). The identity of this complex was confirmed from its electrochemical and spectroscopic properties.

D. Synthesis of $\mathrm{[(\eta^5\text{-}C_5H_5)_2Co][Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_3(CS)(dppm)_2]}$. A solution of $\mathrm{Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_3(CS)(dppm)_2}$ (0.100 g, 0.072 mmol) and $\mathrm{(\eta^5\text{-}C_5H_5)_2Co}$ (0.014 g, 0.072 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL) was stirred for 1 h. An insoluble lime green product was filtered off, washed with diethyl ether, and vacuum dried; yield 0.087 g (76%). Anal. Calcd for $\mathrm{C_{60.5}H_{55}Cl_5CoO_2P_4Re_2S_2}$ (i.e. $\mathrm{[(C_5H_5)_2Co][Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_3(CS)(dppm)_2]\cdot 0.5CH_2Cl_2}$): C, 45.51; H, 3.42. Found: C, 45.34; H, 3.45.

E. Synthesis of $\mathrm{[Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_2(CS)(dppm)_2(NCR)]PF_6}$. (i) Procedure A. (a) R = $\mathrm{CH_3}$. A solution of $\mathrm{[Re_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_2(CS)(dppm)_2(NCCH_3)]PF_6}$ (0.100 g, 0.067 mmol) and $\mathrm{NOPF_6}$ (0.012 g, 0.067 mmol) in $\mathrm{CH_2Cl_2}$ (10 mL), which had not been deoxygenated, was stirred for 1 h. During this period the color of the solution changed from green to red. The reaction mixture was filtered and diethyl ether was added to the filtrate to initiate precipitation of a red-brown solid. This solid was filtered off, washed with diethyl ether (15 mL), and vacuum dried; yield 0.074 g (72%). Anal. Calcd for $\mathrm{C_{53}H_{47}Cl_3F_6NO_2P_5Re_2S_2}$: C, 41.29; H, 3.07. Found: C, 40.88; H, 3.26.

(b) R = $\mathrm{CH_2CH_3}$. This complex was prepared using a procedure similar to that described in method E(i)(a) with the use of $\mathrm{[Re_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_2(CS)(dppm)_2(NCC_2H_5)]PF_6}$ as the starting material; yield 0.080 g (80%). Anal. Calcd for $\mathrm{C_{54}H_{49}Cl_3F_6NO_2P_5Re_2S_2}$: C, 41.69; H, 3.17. Found: C, 41.80; H, 3.34.

(ii) Procedure B. (a) R = $\mathrm{CH_3}$. A solution of $\mathrm{Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_3(CS)(dppm)_2}$ (0.100 g, 0.072 mmol) and $\mathrm{TlPF_6}$ (0.025 g, 0.072 mmol) in 10 mL of $\mathrm{CH_3CN}$ was stirred under reflux for 1 h. After this time, the reaction mixture was filtered to remove the insoluble TlCl and excess diethyl ether was added to the orange filtrate to yield a red-brown solid. This product was filtered off, washed with diethyl ether, and then dissolved in 5 mL of acetone. Next, $\mathrm{KPF_6}$ (0.184 g, 1.00 mmol) dissolved in 10 mL of ethanol was added to the acetone solution and the mixture stirred for 18 h. The solvent was then reduced in volume to ca. 5 mL, and 30 mL of diethyl ether was added to precipitate a red solid. The mixture was filtered, and the solid was washed with water (3 × 5 mL), ethanol (5 mL), and diethyl ether (3 × 15 mL) and then vacuum dried; yield 0.063 g (57%). Electrochemical and spectroscopic measurements showed that the product was the same as that isolated using the procedure described in method E(i)(a).

(b) R = $\mathrm{CH_2CH_3}$. With the use of a procedure similar to that described in method E(ii)(a) but with $\mathrm{C_2H_5CN}$ in place of $\mathrm{CH_3CN}$, a red-brown solid was isolated in 77% yield. Its electrochemical and spectroscopic properties were identical to those of the complex whose preparation is described in method E(i)(b).

F. Synthesis of $\mathrm{Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_2(CS)(dppm)_2(NCCH_3)}$. The one-electron reduction of $\mathrm{[Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_2(CS)(dppm)_2(NCCH_3)]PF_6}$ was achieved upon stirring a mixture of this complex (0.080 g, 0.052 mmol) and 1 equiv of $\mathrm{(\eta^5\text{-}C_5H_5)_2Co}$ (0.010 g, 0.053 mmol) in 10 mL of acetone at room temperature for 12 h. The insoluble green product was filtered off and washed with 15 mL of acetone to remove any trace amounts of unreacted cobaltocene as well as the $\mathrm{[(\eta^5\text{-}C_5H_5)_2Co]PF_6}$ reaction byproduct. The remaining solid was finally washed with 15 mL of diethyl ether and vacuum dried; yield 0.062 g (85%). The identity of this product was based upon its IR and ESR spectra and cyclic voltammetric properties.

Preparation of Single Crystals for Structure Determination. Crystals of composition $\mathrm{Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_3(CS)(dppm)_2\cdot C_2H_4Cl_2\cdot CH_2Cl_2}$ were grown by the slow diffusion of diisopropyl ether into a solution of this complex in a 90:10 mixture (by volume) of 1,2-dichloroethane and dichloromethane. Suitable dark red crystals were obtained after a period of 2 weeks.

X-ray Crystallography. The structure of $\mathrm{Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_3(CS)(dppm)_2\cdot C_2H_4Cl_2\cdot CH_2Cl_2}$ was determined at +20 °C by application of standard procedures. The basic crystallographic parameters for this complex are listed in Table I. The cell constants are based on 25 reflections with $21 < \theta < 23°$. Three standard reflections were measured after 5000 s of beam time during data collection; there were no symmetric variations in intensity. Calculations were performed on a microVAX II computer using the Enraf-Nonius structure determination package. The crystal was found to belong to the triclinic space group $P\bar{1}$ (No. 2). Lorentz and polarization corrections were applied to the data. An empirical absorption correction[6] was applied, but no correction for extinction was made.

Table I. Crystallographic Data for $\mathrm{Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_3(CS)(\mu\text{-}dppm)_2\cdot C_2H_4Cl_2\cdot CH_2Cl_2}$

chem formula	$\mathrm{Re_2Cl_8S_2P_4O_2C_{54}H_{50}}$	V, Å^3	3106.4 (8)
fw	1575.05	Z	2
space group	$P\bar{1}$ (No. 2)	T, °C	20
a, Å	11.2311 (7)	λ(Mo Kα), Å	0.710 73
b, Å	14.316 (2)	ρ_{calcd}, g cm^{-3}	1.684
c, Å	19.854 (2)	μ(Mo Kα), cm^{-1}	44.98
α, deg	86.672 (8)	transm coeff	1.00–0.31
β, deg	80.297 (6)	R^a	0.044
γ, deg	81.033 (7)	$R_w{}^b$	0.070

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Table II. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) for the Non-Hydrogen Atoms and Non-Phenyl Group Atoms of $\mathrm{Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_3(CS)(\mu\text{-}dppm)_2\cdot C_2H_4Cl_2\cdot CH_2Cl_2}$[a]

atom	x	y	z	B
Re(1)	0.21950 (4)	0.60917 (3)	0.25899 (2)	2.46 (1)
Re(2)	0.10158 (4)	0.76954 (4)	0.21740 (2)	2.52 (1)
Cl(B)	0.0010 (3)	0.6546 (2)	0.2949 (2)	3.08 (7)
Cl(11)	0.4252 (3)	0.5307 (3)	0.2382 (2)	4.06 (8)
Cl(12)	0.1947 (3)	0.4689 (2)	0.3304 (2)	3.73 (7)
Cl(21)	−0.0904 (3)	0.8697 (3)	0.2158 (2)	4.09 (8)
S(2)	0.2399 (4)	0.9391 (3)	0.1193 (2)	6.1 (1)
S(B)	0.3158 (3)	0.7114 (2)	0.1874 (2)	3.08 (7)
P(11)	0.1735 (3)	0.5165 (2)	0.1665 (2)	2.99 (7)
P(12)	0.2759 (3)	0.6805 (2)	0.3582 (2)	2.98 (7)
P(21)	0.0504 (3)	0.7044 (3)	0.1146 (2)	2.94 (7)
P(22)	0.1120 (3)	0.8565 (2)	0.3202 (2)	3.06 (7)
O(1B)	0.3987 (7)	0.7647 (6)	0.2126 (4)	3.5 (2)
O(2B)	0.3583 (7)	0.6890 (6)	0.1156 (4)	3.4 (2)
C(2)	0.177 (1)	0.8669 (8)	0.1604 (6)	2.6 (2)*
C(1B)	0.152 (1)	0.5941 (9)	0.0927 (5)	2.8 (3)
C(2B)	0.254 (1)	0.8096 (9)	0.3499 (7)	3.4 (3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$. The starred B value is for an atom that was refined isotropically.

The structure was solved by the use of the Patterson heavy-atom method, which revealed the positions of the Re atoms. The remaining non-hydrogen atoms were identified in succeeding difference Fourier syntheses. The atoms of the molecules of lattice $\mathrm{CH_2Cl_2}$ and $\mathrm{C_2H_4Cl_2}$ (gauche isomer) are located about general positions. Hydrogen atoms of the dppm ligands were included at fixed positions which were calculated by assuming idealized geometry and a C–H bond distance of 0.95 Å. We assumed that the value of B(H), i.e., the isotropic equivalent thermal parameter for the hydrogen atoms, was equal to $1.3[B_{eqv}(\mathrm{C})]$ at the time of the inclusion of this parameter in the refinement procedure. While these hydrogen atoms were used in the calculation of F_c, their positions were not refined. The structure was refined in full-matrix least squares where the function minimized was $\sum w(|F_o| - |F_c|)^2$, where w is the weighting factor defined as $w = 1/\sigma^2(F_o)$. The non-hydrogen atoms of the dirhenium complex were refined anisotropically; corrections for anomalous scattering were applied to these atoms.[7]

Positional parameters and their errors for all atoms, except the phenyl group atoms and those of the lattice $\mathrm{CH_2Cl_2}$ and $\mathrm{C_2H_4Cl_2}$ molecules, are listed in Table II. Important intramolecular bond distances and angles are given in Table III. Full details of the crystal data, data collection parameters, and all structural parameters are available as supplementary material.

Physical Measurements. A Perkin-Elmer 1800 FTIR spectrometer was used to record the IR spectra of the compounds as mineral oil (Nujol) mulls. Electrochemical measurements were carried out on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium

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(7) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1. (b) For the scattering factors used in the structure solution, see: Cromer, D. T.; Waber, J. T. *Ibid.*, Table 2.2B.

Table III. Important Bond Distances (Å) and Bond Angles (deg) for $Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_3(CS)(\mu\text{-}dppm)_2\cdot C_2H_4Cl_2\cdot CH_2Cl_2$[a]

Distances			
Re(1)–Re(2)	2.6281 (5)	Re(2)–Cl(21)	2.400 (2)
Re(1)–Cl(B)	2.433 (2)	Re(2)–S(B)	2.406 (2)
Re(1)–Cl(11)	2.386 (2)	Re(2)–P(21)	2.480 (2)
Re(1)–Cl(12)	2.415 (2)	Re(2)–P(22)	2.481 (2)
Re(1)–S(B)	2.251 (2)	Re(2)–C(2)	1.947 (8)
Re(1)–P(11)	2.493 (2)	S(2)–C(2)	1.476 (9)
Re(1)–P(12)	2.486 (2)	S(B)–O(1B)	1.457 (6)
Re(2)–Cl(B)	2.460 (2)	S(B)–O(2B)	1.463 (6)
Angles			
Re(2)–Re(1)–Cl(B)	58.00 (5)	Re(1)–Re(2)–P(22)	94.77 (6)
Re(2)–Re(1)–Cl(11)	135.48 (6)	Re(1)–Re(2)–C(2)	125.2 (2)
Re(2)–Re(1)–Cl(12)	143.32 (6)	Cl(B)–Re(2)–Cl(21)	90.92 (8)
Re(2)–Re(1)–S(B)	58.47 (6)	Cl(B)–Re(2)–S(B)	109.92 (7)
Re(2)–Re(1)–P(11)	93.99 (6)	Cl(B)–Re(2)–P(21)	92.75 (7)
Re(2)–Re(1)–P(12)	93.69 (6)	Cl(B)–Re(2)–P(22)	87.48 (8)
Cl(B)–Re(1)–Cl(11)	166.45 (8)	Cl(B)–Re(2)–C(2)	176.2 (3)
Cl(B)–Re(1)–Cl(12)	85.33 (8)	Cl(21)–Re(2)–S(B)	158.97 (9)
Cl(B)–Re(1)–S(B)	116.47 (8)	Cl(21)–Re(2)–P(21)	82.99 (8)
Cl(B)–Re(1)–P(11)	88.83 (7)	Cl(21)–Re(2)–P(22)	85.17 (8)
Cl(B)–Re(1)–P(12)	94.13 (7)	Cl(21)–Re(2)–C(2)	86.9 (2)
Cl(11)–Re(1)–Cl(12)	81.20 (8)	S(B)–Re(2)–P(21)	92.93 (8)
Cl(11)–Re(1)–S(B)	77.02 (8)	S(B)–Re(2)–P(22)	98.13 (8)
Cl(11)–Re(1)–P(11)	88.64 (8)	S(B)–Re(2)–C(2)	72.4 (2)
Cl(11)–Re(1)–P(12)	86.81 (8)	P(21)–Re(2)–P(22)	168.16 (8)
Cl(12)–Re(1)–S(B)	158.20 (8)	P(21)–Re(2)–C(2)	90.1 (2)
Cl(12)–Re(1)–P(11)	85.33 (8)	P(22)–Re(2)–C(2)	89.2 (2)
Cl(12)–Re(1)–P(12)	87.72 (8)	Re(1)–Cl(B)–Re(2)	64.98 (5)
S(B)–Re(1)–P(11)	95.01 (8)	Re(1)–S(B)–Re(2)	68.63 (6)
S(B)–Re(1)–P(12)	90.13 (8)	Re(1)–S(B)–O(1B)	119.2 (3)
P(11)–Re(1)–P(12)	172.21 (8)	Re(1)–S(B)–O(2B)	120.2 (3)
Re(1)–Re(2)–Cl(B)	57.02 (5)	Re(2)–S(B)–O(1B)	115.9 (3)
Re(1)–Re(2)–Cl(21)	147.86 (7)	Re(2)–S(B)–O(2B)	115.9 (3)
Re(1)–Re(2)–S(B)	52.90 (5)	O(1B)–S(B)–O(2B)	110.9 (4)
Re(1)–Re(2)–P(21)	95.27 (6)	Re(2)–C(2)–S(2)	176.5 (6)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the silver/silver chloride (Ag/AgCl) electrode at room temperature and are uncorrected for junction potentials. Under our experimental conditions $E_{1/2} = +0.47$ V vs Ag/AgCl for the ferrocenium/ferrocene couple. Voltammetric experiments were performed with a Bioanalytical Systems Inc. Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035 B x-y recorder. All NMR spectra were recorded on CD_2Cl_2 solutions of the complexes. The $^{31}P\{^1H\}$ NMR spectra were obtained with use of a Varian XL-200 spectrometer operated at 80.98 MHz with an internal deuterium lock and 85% H_3PO_4 as an external standard. ^1H NMR spectra were obtained on a Varian Gemini-200 spectrometer. Resonances were referenced internally to the residual protons in the incompletely deuteriated solvent (δ +5.35). X-Band ESR spectra were recorded at ca. −160 °C with the use of a Varian E-109 spectrometer. Conductivity measurements were performed on ca. 10^{-3} M acetonitrile solutions by using an Industrial Instruments Inc. Model RC-16B2 conductivity bridge.

Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

Results

The complexes of types **1** and **2** show an accessible, reversible, one-electron oxidation with $E_{1/2}$ values of ca. +0.45 and ca. +0.80

$Re_2(\mu\text{-}S)(\mu\text{-}X)X_3(CS)(\mu\text{-}LL)_2$	$[Re_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_2(CS)(\mu\text{-}dppm)_2(NCR)]PF_6$
1a; X = Cl, LL = dppm	**2a**; R = Me
b; X = Br, LL = dppm	b; R = Et
c; X = Br, LL = dpam	

V vs Ag/AgCl, respectively, in the cyclic voltammograms of their solutions in 0.1 M TBAH–CH_2Cl_2.[2] In the case of **1**, this oxidation can be accessed with $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ or $NOPF_6$ to give the paramagnetic species $[\mathbf{1}]PF_6$.[2] In the present study, we have found that if the reaction medium is not rigorously deoxygenated when $NOPF_6$ is used as the oxidant, the dark blue-green color of the oxidized species $[\mathbf{1}]^+$ is rapidly discharged and the orange-red μ-sulfur dioxide complexes **3** are produced in very high yield.

$Re_2(\mu\text{-}SO_2)(\mu\text{-}X)X_3(CS)(\mu\text{-}LL)_2$	$[Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_2(CS)(\mu\text{-}dppm)_2(NCR)]PF_6$
3a; X = Cl, LL = dppm	**4a**; R = Me
b; X = Br, LL = dppm	b; R = Et
c; X = Br, LL = dpam	

The conversion of **1** to **3** can also be accomplished through the use of NO_2 and 3-chloroperbenzoic acid as the oxygen-transfer agents. Although the oxidized species $[\mathbf{1}]^+$ do not react further with NO^+, they do convert to **3** in high yield when exposed to NO_2. While the oxidation of the nitrile-containing complexes **2** to $[\mathbf{2}]^+$ was not previously attempted,[2] we find in the present study that the reaction of **2** with 1 equiv of $NOPF_6$ in CH_2Cl_2, which had not been deoxygenated, produces **4**. The formation of **4** can also be achieved by the reaction of **3** with $TlPF_6$ in a CH_2Cl_2/RCN mixed solvent according to eq 1.

$$Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_3(CS)(dppm)_2 + TlPF_6 + RCN \rightarrow [Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_2(CS)(dppm)_2(NCR)]PF_6 \quad (1)$$

The spectroscopic and electrochemical properties of complexes **3** and **4** are summarized in Table IV. Also, while conductivity measurements on acetonitrile solutions of **3** showed them to be nonconducting, solutions of **4** in this same solvent had Λ_m values of ca. 165 Ω^{-1} cm^2 mol^{-1}, in accord with 1:1 electrolyte behavior. The retention of the CS ligand in **3** and **4** is shown by the presence of a single intense ν(CS) mode in the IR spectra of these complexes (Table IV). The ν(CS) bands of **4** are shifted by ca. 20 cm^{-1} to higher frequencies compared to their neutral precursors **3**, in accord with an increase in the positive charge on the dimetal core and, consequently, a decrease in the metal-to-CS(π^*) back-bonding. The oxidation of the μ_2-S unit to μ_2-SO_2 is demonstrated through the appearance of IR-active bands at ca. 1150 and ca. 1055 cm^{-1}, which are characteristic of the $\nu(SO_2)$ modes of a bridging μ_2-SO_2 ligand.[8–11] In all instances the $^{31}P\{^1H\}$ NMR spectra of the dppm complexes appear as AA′XX′ patterns (Table IV) in accord with unsymmetrical edge-sharing bioctahedral structures. The methylene protons of the dppm ligands appear in the ^1H NMR spectra as AB patterns with superimposed P–H coupling whereas for the dpam complex the $-CH_2-$ resonance consists of a pair of doublets.

The cyclic voltammograms (CV's) of solutions of **3a–c** in 0.1 M TBAH–CH_2Cl_2 are very similar and show three reversible processes (an oxidation and two reductions) at $E_{1/2}$(ox) ca. +1.1, $E_{1/2}$(red) ca. −0.2, and $E_{1/2}$(red) ca. −1.1 V vs Ag/AgCl. The accessibility and reversibility of the process at ca. −0.2 V was demonstrated by the reduction of $Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_3(CS)(dppm)_2$ to the paramagnetic salt $[(\eta^5\text{-}C_5H_5)_2Co][Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_3(CS)(dppm)_2]$ (**5**) through the use of $(\eta^5\text{-}C_5H_5)_2Co$ as reductant (eq 2). This reduction to **5** is accompanied by a shift in the ν(CS) mode of ca. −15 cm^{-1}. The CV of the salt is similar to that of the neutral precursor except for an additional process at $E_{1/2}$(red) = −0.9 V that is attributed to the $[(\eta^5\text{-}C_5H_5)_2Co]^+$

$$Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_3(CS)(dppm)_2 + (\eta^5\text{-}C_5H_5)_2Co \xrightarrow{CH_2Cl_2} [(\eta^5\text{-}C_5H_5)_2Co][Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_3(CS)(dppm)_2] \quad (2)$$

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Table IV. Selected Electrochemical and Spectral Data for μ_2-Sulfur Dioxide Complexes of Dirhenium

	CV half-wave potentials, V[a]			IR, cm^{-1} [d]		^{1}H NMR, δ[e]		^{31}P{^{1}H} NMR, δ[h]
complex	$E_{1/2}$(ox)	$E_{1/2}$(red)(1)	$E_{1/2}$(red)(2)	ν(CS)	ν(SO)	–CH$_2$–[f]	RCN[g]	
$Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_3(CS)(dppm)_2$ (**3a**)	+1.12	–0.20	–1.08	1308	1148, 1056	+3.05 m, +5.05 m		–6.9, –51.8
$Re_2(\mu\text{-}SO_2)(\mu\text{-}Br)Br_3(CS)(dppm)_2$ (**3b**)	+1.11	–0.13	–1.12	1308	1148, 1056	+2.99 m, +5.67 m		–13.3, –73.0
$Re_2(\mu\text{-}SO_2)(\mu\text{-}Br)Br_3(CS)(dpam)_2$ (**3c**)	+1.07	–0.18	–1.10	1306	1156, 1054	+2.69 d, +4.80 d		
$[Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_2(CS)(dppm)_2(NCMe)]PF_6$ (**4a**)	+1.75[b]	+0.23	–0.68	1328	1158, 1060	+3.97 m, +5.87 m	+2.22 s	–6.0, –26.5
$[Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_2(CS)(dppm)_2(NCEt)]PF_6$ (**4b**)	+1.72[b]	+0.22	–0.72	1328	1158, 1058	+3.95 m, +5.86 m	+0.69 t, +2.65 q	–6.1, –27.3
$[(\eta^5\text{-}C_5H_5)_2Co][Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_3(CS)(dppm)_2]$ (**5**)	+1.14	–0.21[c]	–1.10	1294	1124, 1014			
$Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_2(CS)(dppm)_2(NCMe)$ (**6**)	+1.70[b]	+0.20[c]	–0.73	1296	1144, 1028			

[a] Measured on 0.1 M TBAH–CH_2Cl_2 solutions and referenced to the Ag/AgCl electrode with a scan rate (v) of 200 mV/s at a Pt-bead electrode. Under our experimental conditions $E_{1/2} = +0.47$ V vs Ag/AgCl for the ferrocenium/ferrocene couple. In all cases $i_{p,a} \approx i_{p,c}$ and $E_{p,a} - E_{p,c}$ values are in the range 130–90 mV. [b] This couple is very close to the solvent limit, and the value quoted is estimated to be ±0.05 V. [c] $E_{1/2}$(ox) value. [d] Recorded as Nujol mulls. Complexes that contain the $[PF_6]^-$ anion show a characteristic absorption due to ν(P–F) near 845 cm^{-1}. [e] Spectra recorded in CD_2Cl_2. Abbreviations are as follows: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. [f] The –CH$_2$– resonances of the dppm and dpam ligands. [g] Resonances due to the alkyl groups of the nitrile ligands. [h] Spectra recorded in CD_2Cl_2. These spectra have the appearance of AA′XX′ patterns; the chemical shifts quoted are those of the centers of the two multiplets.

cation. A solution of $[(\eta^5\text{-}C_5H_5)_2Co][Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_3(CS)(dppm)_2]$ in DMSO has an X-band ESR spectrum which exhibits a complex signal centered at $g \approx 2.4$ showing poorly resolved hyperfine structure.

In the case of the nitrile-containing complexes **4**, the CV's show an oxidation and two reversible reductions which are shifted by ca. +0.5 V relative to the corresponding processes in the CV of **3a** (see Table IV). While the electrolysis of solutions of **4a** and **4b** in 0.2 M TBAH–CH_2Cl_2 at –0.10 V generates the green neutral species $Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_2(CS)(dppm)_2(NCR)$, electrolysis at –0.85 V (i.e. beyond the second reduction) results in decomposition of the solutions (as monitored by cyclic voltammetry). The chemical reduction of **4a** to $Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_2(CS)(dppm)_2(NCMe)$ (**6**) by $(\eta^5\text{-}C_5H_5)_2Co$ in acetone occurs in high yield. The IR spectrum and cyclic voltammetric properties of **6** are given in Table IV. The X-band ESR spectrum of a CH_2Cl_2 solution of this complex at –160 °C exhibits a fairly isotropic signal at $g = 2.19$ showing well resolved but complicated hyperfine structure (P and Re).

To confirm the structural identity of the complexes **3**–**5**, the single-crystal X-ray structure of a representative example was determined. An ORTEP representation of **3a** is shown in Figure 1. The important details of the crystallographic and structural parameters are given in Tables I–III.

Discussion

The conversions of the dirhenium(III) μ_2-S complexes $Re_2(\mu\text{-}S)(\mu\text{-}X)X_3(CS)(\mu\text{-}LL)_2$ (**1**; X = Cl, Br, LL = dppm, dpam) and $[Re_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_2(CS)(\mu\text{-}dppm)_2(NCR)]PF_6$ (**2**; R = Me, Et) to the analogous μ_2-SO_2 derivatives **3** and **4** proceed with retention of the basic edge-shared bioctahedral structure of the parent sulfido species. The latter derivatives constitute the first *series* of metal–metal-bonded dirhenium complexes that contain a bridging SO_2 ligand, although around the time of the publication of our preliminary report[5] the novel bis-μ_2-SO_2 complex anion $[Re_2(\mu\text{-}SO_2)_2(CN)_8]^{6-}$ was also prepared and structurally characterized.[12]

The X-ray crystal structure determination of $Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_3(CS)(\mu\text{-}dppm)_2$ (**3a**) (Figure 1) reveals the close structural similarity of this complex to $[Re_2(\mu\text{-}S)(\mu\text{-}Br)Br_2(CS)(\mu\text{-}dpam)_2(NCEt)]PF_6$.[2] The μ_2-SO_2 ligand has S–O distances (average 1.460 Å) and an O–S–O angle (110.9 (4)°) that closely resemble those reported for the complex $K_6[Re_2(\mu\text{-}SO_2)_2(CN)_8]\cdot 2H_2O$[12] and several complexes that contain a single μ_2-SO_2 bridge.[8,9,13] Although the structurally characterized μ-sulfido complex $[Re_2(\mu\text{-}S)(\mu\text{-}Br)Br_2(CS)(\mu\text{-}dpam)_2(NCEt)]PF_6$ shows[2] an apparent disparity in the Re–S distances (2.240 (8) and 2.263 (8) Å), these are not different within 3σ. However, the μ_2-SO_2 complex **3a** has Re–S distances that are quite different (2.251 (2) and 2.406 (2) Å), no doubt a reflection on the disparity in the ligand sets about the two Re atoms; the two atoms differ in having a π-acceptor CS ligand in place of a σ-donor Cl$^-$ ligand. This asymmetry in the bonding of the SO_2 ligand resembles that encountered previously in the structures of the carbonyl complexes $[Re_2(\mu\text{-}CO)(\mu\text{-}Cl)Cl_2(\mu\text{-}dppm)_2(PR_3)]PF_6$ (R = Me, Et) in which the μ-CO ligand is asymmetrically bound to the two Re atoms.[14]

The Re–Re distance of 2.628 (1) Å in **3a** is very similar to that in $K_6[Re_2(\mu\text{-}SO_2)_2(CN)_8]\cdot 2H_2O$ (2.653 (1) Å),[12] a complex which like **3a** can be considered as a derivative of dirhenium(III) if the μ-SO_2 ligand is treated as being dianionic. A distance of this magnitude in an edge-shared bioctahedral dirhenium(III) species is consistent with a Re=Re bond as represented by a $\sigma^2\pi^2\delta^{*2}\delta^2$ ground-state configuration.[15,16] Interestingly, the Re–Re distance of 2.628 (1) Å in **3a** is ca. 0.3 Å shorter than the comparable distance in $[Re_2(\mu\text{-}S)(\mu\text{-}Br)Br_2(CS)(\mu\text{-}dpam)_2(NCEt)]PF_6$. For the latter complex we have argued[2] that the ground-state configuration is $\sigma^2\pi^2\delta^{*2}\pi^{*2}$ (i.e. a Re–Re bond order of less than one) and that the destabilization of δ relative to π* has its origin in the interaction of the former with the filled "nonbonding" orbitals on the bridging sulfido ligand. If this is the case, then the loss of the nonbonding sulfur orbitals upon oxidation of μ-S to μ-SO_2 (as in the case of **3a**) could lead to a relative stabilization of the metal-based δ orbital so that it drops below π*. The shortening of ca. 0.3 Å that we observe is consistent with this explanation, although it is not in and of itself proof.

As we have mentioned in a previous article,[2] the oxidation of complexes of type **1** to the paramagnetic cations [**1**]$^+$ through the use of $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ or $NOPF_6$ proceeds cleanly in the absence of O_2 with no evidence for any subsequent reactions. We have found during the course of the present study that freshly prepared samples of preformed [**1**]PF_6 do not react with $NOPF_6$ either in the presence or absence of small amounts of O_2. Moreover, the conversion of the μ_2-sulfido complexes **1** and **2** to their μ_2-SO_2 analogues **3** and **4** upon reaction with $NOPF_6$ occurs only when O_2 is present. Additionally, we find that the oxygenations proceed cleanly and essentially quantitatively when the stoichiometric ratios **1**:$NOPF_6$ and **2**:$NOPF_6$ are anywhere between ca. 50:1 and ca. 1:1, although the latter ratio was used in the preparative scale reactions described in the Experimental

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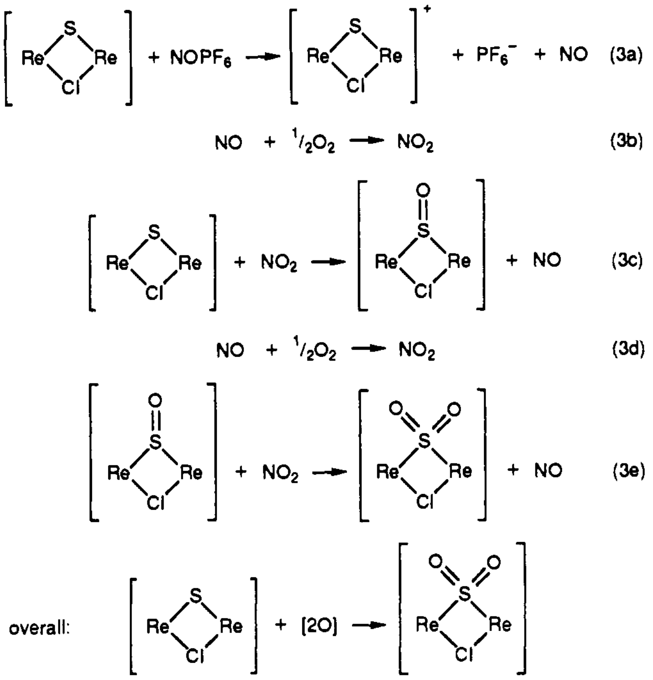
Section. The following sequence of reactions would constitute a plausible series of steps for the conversions of **1** and **2** into **3** and **4**, respectively, and would be consistent with the reactions occurring in the presence of catalytic amounts of $NOPF_6$.



Note that after the production of a small amount of NO in step 3a it is unnecessary for the oxidation of the dirhenium(III,III) core to occur in any subsequent turnovers. The conversions of **1a** and **1b** to **3a** and **3b** by direct reaction with NO_2 (in the absence of $NOPF_6$) is further support for this pathway. Interestingly, we find that when NO_2 is reacted with the oxidized derivatives [**1a**]PF_6 and [**1b**]PF_6 instead of **1a** and **1b**, the μ-SO_2 complexes **3a** and **3b** are still obtained. This accords with the electrochemical properties of **3a** and **3b** (Table IV), which show that the oxidized species [**3a**]$^+$ and [**3b**]$^+$ would be potent one-electron oxidants ($E_{1/2}$(red) ca. +1.1 V) and therefore easily reduced to **3a** and **3b** in the reaction medium.

When **1a** is reacted with 2.5 equiv of 3-chloroperbenzoic acid, a well-known oxygen-transfer reagent,[8,17] it is converted to **3a** in high yield. With the use of only 1 equiv of this reagent, **3a** is still obtained, along with unreacted starting material. Since we were unable to isolate or detect a μ-SO intermediate, as we proposed is formed in step 3c, it must react very rapidly to form the final μ-SO_2 product if it is indeed involved in the mechanism. However, its implication as an intermediate is reasonable in view of the relative ease of forming μ-SO complexes in other systems.[17,18]

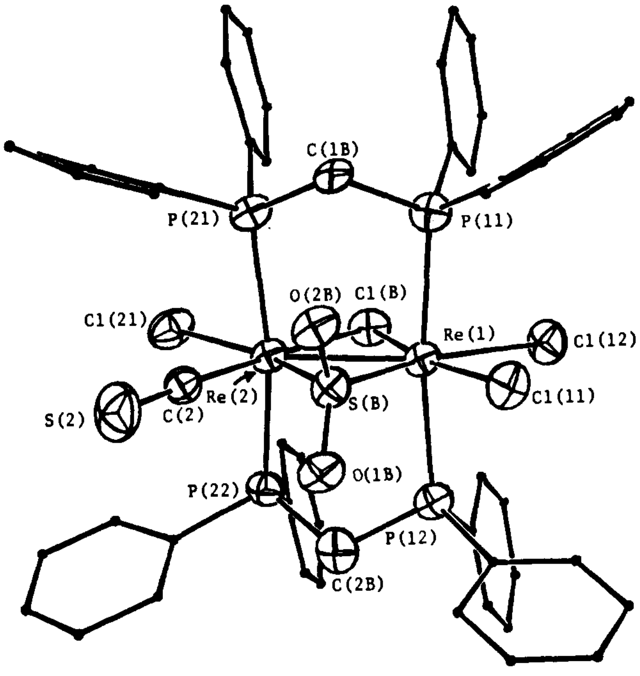


Figure 1. ORTEP representation of the structure of the molecule $Re_2(\mu$-$SO_2)(\mu$-$Cl)Cl_3(CS)(\mu$-dppm$)_2$. The thermal ellipsoids are drawn at the 50% probability level except for those of the phenyl carbon atoms, which are circles of arbitrary radius.

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Supplementary Material Available: Tables giving full details of the crystal data and data collection parameters (Table S1), positional parameters for the non-hydrogen atoms (Table S2) and the hydrogen atoms (Table S3), thermal parameters (Table S4), and complete listings of bond distances (Table S5) and bond angles (Table S6) (18 pages). Ordering information is given on any current masthead page.

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