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Syntheses and Structures of Rhenium(IV) and Rhenium(V) Complexes with Ethanedithiolato Ligands

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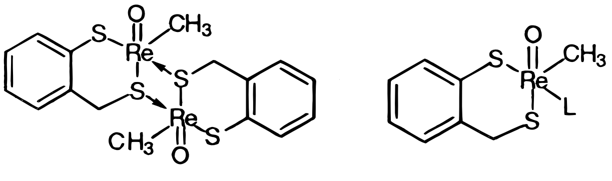
A novel dimeric rhenium(IV) complex, [$Re_2(SCH_2CH_2S)_4$], and a monomeric methyloxorhenium(V) complex, [$CH_3ReO(SCH_2CH_2S)PPh_3$], were synthesized from methyloxorhenium(V) complexes and characterized crystallographically. The structure of [$Re_2(SCH_2CH_2S)_4$], the formation reaction of which showed surprising demethylation conceivably through the homolytic cleaveage of the rhenium−carbon bond, features distorted trigonal prismatic coordination of sulfurs around the metal center and a rhenium−rhenium triple bond. A revised structure, [$Tc_2(SCH_2CH_2S)_4$], is proposed for a related technetium complex, originally identified as [$Tc_2(SCH_2CH_2S)_2(SCH{=}CHS)_2$] (Tisato et al. *Inorg. Chem.* **1993**, *32*, 2042). Additionally, a new compound, $CH_3Re(O)(SPh)_2PPh_3$, was prepared.

Introduction

Methyltrioxorhenium(VII) (abbreviated as MTO) is a versatile and powerful catalyst in a variety of solvents that can be used to catalyze a large number of atom transfer processes.[1−5] Recent efforts to reveal the mechanism of the stereospecific rhenium-catalyzed desulfurization of thiiranes[6] led to the synthesis of a sulfur-bridged methyloxorhenium(V) dimer (**D**) from MTO and the anion of 2-(mercaptomethyl)thiophenol.[7] **D** was shown to monomerize with suitable ligands[8] **L** (pyridines, phosphines, thiourea derivatives, halides), giving rise to a new family of mononuclear five-coordinated rhenium(V) compounds designated **M**−**L**, whose structure together with that of **D**, is shown in Chart 1. Mechanistic studies of the ligand-promoted monomerization reactions of **D** and crystal structures of several **M**−**L** compounds have already been published.[8−11]

Our preliminary studies on the possible catalytic activity of **D** and **M**−**L** complexes indicated that the dithiolate ligand is often oxidized to the corresponding intramolecular cyclic disulfide (persulfide) in oxygen transfer reactions. This happens when the Re(V) compound is oxidized to a metastable Re(VII) species, which forms the disulfide and a Re(V) compound, $CH_3ReO_2L_n$, lacking the dithiolate ligand and known[5,12] to have a fairly short lifetime. This is not advantageous, however, since neither the Re(VII) nor Re(V) species is active in catalysis; thus we have sought a strategy to preserve the five-coordinated methyloxorhenium(V) center for such potential applications. We concluded that replacement of the original dithiolate ligand with one that could not form an intramolecular cyclic disulfide would be desirable.

Chart 1. Oxorhenium Chelates of 2-(Mercaptomethyl)thiophenol



D **M**−**L**

Direct reaction of these dithiols with MTO does not give reduction, however; the product of each is a rhenium(VII) complex after condensation.[13] This also emphasizes the fact that these dithiols are less reducing than 2-(mercaptomethyl)thiophenol because the corresponding intramolecular disulfide would contain a four-membered ring.

Originally, we envisaged that 1,2-ethanedithiol (H_2edt) and 1,2-benzenedithiol (H_2bdt) would react with **D** and **M**−**L** (**L** = PPh_3), replacing one dithiolate chelating ligand with the other, because five-membered chelate rings tend to be favored over six-membered ones. In this paper, we report an unexpected demethylation of the rhenium(V) center as a result of changes in its coordination environment and also describe an alternative method to obtain the edt analogue of **M**−PPh_3, $CH_3ReO(edt)PPh_3$.

Experimental Section

Chemicals and Instrumentation. MTO,[14] *o*-$HSC_6H_4CH_2SH$,[15,16] $(CH_3)_2Re_2(O)_2(SC_6H_5)_4$,[13] and **D**[7] were synthesized according to reported procedures. All other chemicals were purchased from commercial

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10.1021/ic991446n CCC: $19.00

Table 1. Crystal Data and Structure RefinementDetails for **1** and **3**[a,b]

	1	**3**
empirical formula	$C_8H_{16}Re_2S_8$	$C_{21}H_{22}OPReS_2{\cdot}0.5CH_2Cl_2$
fw	741.09	614.14
crystal system	monoclinic	triclinic
space group	$C2/m$	$P\bar{1}$
a, Å	13.8372(11)	9.6319(5)
b, Å	8.2494(7)	10.8611(6)
c, Å	8.9886(6)	11.5774(6)
α, deg	90	71.108(1)
β, deg	125.087(1)	88.737(1)
γ, deg	90	87.125(1)
V, Å^3	839.58(11)	1144.44(11)
Z	2	2
ρ_{calc}, g/cm^3	2.931	1.782
T, K	173(2)	173(2)
μ, mm^{-1}	15.379	5.688
F(000)	684	596
θ range, deg	2.77−28.22	1.9−26.37
index ranges	$-18 \le h \le 18$ $-10 \le k \le 10$ $-1 \le l \le 11$	$-11 \le h \le 12$ $-12 \le k \le 13$ $0 \le l \le 14$
no. of reflns collected	3673	10 087
no. of independent reflns	1049	4639
R_{int}	0.0416	0.0152
Data/restraints/parameters	1049/0/49	4639/2/254
GOF	1.018	1.020
R1	0.0277	0.0202
wR2	0.0603	0.0479
largest diff peak and hole, e Å^{-3}	1.930, −1.732	1.198, −1.177

[a] Radiation: Mo Kα, 0.710 73 Å. [b] Quantity minimized: $R_w(F^2) = \Sigma[w(F_o^2 - F_c^2)]/\Sigma[(wF_o^2)^2]^{1/2}$; $R = \Sigma\Delta/\Sigma(F_o)$, $\Delta = |(F_o - F_c)|$.

sources. ^{1}H NMR spectra were recorded on Varian VXR 300 MHz and Bruker DRX 400 MHz spectrometers. ^{1}H chemical shifts were measured relative to the residual ^{1}H resonance of the deuterated solvent C_6D_6 ($\delta = 7.16$ ppm) or $CDCl_3$ ($\delta = 7.27$ ppm). UV−vis spectra and kinetic curves were recorded using a Shimadzu UV-PC 3101 spectrophotometer. Spectrophotometric grade chloroform purchased from Fisher was used in kinetic experiments. A saturated solution of gaseous methane (Air Products and Chemicals, Inc.) was used to obtain independent confirmation of its chemical shift ($\delta = 0.22$ ppm in $CDCl_3$). The formation of methane was also detected by headspace analysis using a Hewlett-Packard 5790A gas chromatograph with a VZ-10 column and a flame ionization detector.

Synthesis of 1. A 0.75 mL $CDCl_3$ solution containing 2 mM **D** and 200 mM 1,2-ethanedithiol was monitored at room temperature by ^{1}H NMR, as the color changed from yellow to dark brownish. Hexane was layered on this solution after 1 week, and crystals formed in a few days. ^{1}H NMR (C_6D_6): 2.99 (s, 1H), 1.73 (s, 1H) ppm. ^{1}H NMR ($CDCl_3$): 3.27 (s, 1H), 2.24 (s, 1H) ppm. The same preparative procedure was successful in benzene as well. Only a small quantity of **1** was prepared, ca. 2 mg in all, insufficient for elemental analysis, but it formed crystals that diffracted excellently. In four attempts, the yields of **1** were 40−65%.

Synthesis of 2. A 65.6 mg (0.25 mmol) sample of triphenylphosphine was added to a stirred solution of 87.0 mg (0.1 mmol) of $(CH_3)_2Re_2(O)_2(SC_6H_5)_4$ in 10 mL toluene at room temperature. After 1 h, the mixture was concentrated to 1 mL, and 10 mL of hexane was added. The sample was then kept in a freezer overnight. The green powder that formed, $CH_3Re(O)(SPh)_2PPh_3$ (**2**), was collected by filtration and washed with hexane. ^{1}H NMR (C_6D_6): 8.06 (m, 6H), 7.47 (d, 4H, $J =$ 7.6 Hz), 7.00 (m, 15H), 3.08 (d, 3H, $J = 1.6$ Hz) ppm. Anal. Found (calcd) for $C_{31}H_{28}ReOPS_2$: C, 53.5 ± 0.2 (53.35); H, 4.01 ± 0.02 (4.04); S, 7.6 ± 0.5 (9.6).

Synthesis of 3. 1,2-Ethanedithiol (14.2 mg, 0.125 mmol, 0.01 mL) was added to a stirred solution of 66.6 mg (0.1 mmol) of **2** in 10 mL of toluene at room temperature. After 2 h, the solution was concentrated to 1 mL, and 10 mL of hexane was added. The sample was then kept in a freezer overnight. Red crystals of $CH_3Re(O)(edt)PPh_3{\cdot}0.5CH_2Cl_2$ (**3**) formed upon recrystallization from methylene chloride that were suitable for X-ray diffraction analysis. ^{1}H NMR (C_6D_6): 7.74 (m, 6H), 6.94 (m, 9H), 3.60 (m, 1H), 3.31 (m, 1H), 2.88 (d, 3H, $J = 7.6$ Hz), 2.73 (m, 1H), 2.40 (m, 1H) ppm. ^{13}C NMR (C_6D_6): 134.57 (d, $J = 42$ Hz), 131.13 (d, $J = 112.8$ Hz), 130.45 (d, $J = 204$ Hz), 128.76 (d, $J = 42.4$ Hz), 46.32 (d, $J = 25.2$ Hz), 43.50 (s) 11.64 (d, $J = 11.6$) ppm. Anal. Found (calcd) for $C_{21.5}H_{23}ReOPS_2Cl$: C, 42.9 ± 0.3 (42.05); H, 3.97 ± 0.07 (3.77); S, 9.6 ± 0.3 (10.4). The yield of **2** was not determined, but from **2** the yield of **3** was 60%.

Table 2. Atomic Coordinates (×10^4) and Isotropic Displacement Parameters (Å^2 × 10^3) for **1**

	x	y	z	U(eq)
Re(1)	995(1)	0	1635(1)	14(1)
S(1)	1544(2)	0	4575(3)	24(1)
S(2)	2987(2)	0	2920(3)	25(1)
S(3)	631(1)	1761(2)	−761(2)	19(1)
C(1)	3140(9)	0	6128(14)	51(3)
C(2)	3775(10)	0	5367(16)	86(6)
C(3)	1378(6)	915(8)	−1728(9)	29(1)

Table 3. Selected Bond Lengths (Å) and Angles (deg) in **1**[a]

Re(1)−S(1)	2.292(2)	S(2)−C(2)	1.808(12)
Re(1)−S(2)	2.295(2)	S(3)−C(3)	1.827(6)
Re(1)−S(3)	2.3989(14)	S(3)−Re(1)#2	2.4002(14)
Re(1)−S(3)#3	2.4002(14)	C(1)−C(2)	1.390(15)
Re(1)−Re(1)#2	2.6300(6)	C(3)−C(3)#1	1.510(14)
S(1)−C(1)	1.811(10)		

S(1)−Re(1)−S(2)	85.03(8)	S(3)−Re(1)−Re(1)#2	56.79(4)
S(1)−Re(1)−S(3)	142.61(3)	S(3)#2−Re(1)−Re(1)#2	56.74(4)
S(2)−Re(1)−S(3)	91.35(6)	C(1)−S(1)−Re(1)	109.7(4)
S(3)#1−Re(1)−S(3)	74.53(7)	C(2)−S(2)−Re(1)	108.8(4)
S(1)−Re(1)−S(3)#2	90.23(6)	C(3)−S(3)−Re(1)	108.1(2)
S(2)−Re(1)−S(3)#2	142.51(4)	C(3)−S(3)−Re(1)#2	107.1(2)
S(3)#1−Re(1)−S(3)#2	70.52(6)	Re(1)−S(3)−Re(1)#2	66.46(4)
S(3)−Re(1)−S(3)#2	113.54(4)	C(2)−C(1)−S(1)	117.2(8)
S(3)#2−Re(1)−S(3)#3	74.48(7)	C(1)−C(2)−S(2)	119.2(8)
S(1)−Re(1)−Re(1)#2	136.76(6)	C(3)#1−C(3)−S(3)	112.4(2)
S(2)−Re(1)−Re(1)#2	138.21(6)		

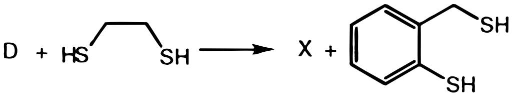
[a] Symmetry transformations used to generate equivalent atoms: (#1) $x, -y, z$; (#2) $-x, -y, -z$; (#3) $-x, y, -z$.

Crystallography of 1 and 3. The crystal evaluations and data collections were performed using a Bruker CCD-1000 diffractometer with Mo Kα (λ = 0.710 73 Å) radiation. The distance from the diffractometer to the crystal was 5.08 cm. All atoms other than hydrogen were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculations at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The software and sources of the scattering factors are contained in the SHELXTL program library.[17] Absorption corrections were carried out with the program SADABS.[18] See Tables 1−5 for listings of crystal data, X-ray experimental details, atomic coordinates, isotropic thermal parameters, and selected bond lengths and angles for **1** and **3**.

Mass Spectrometry. The electrospray method was used for **1**, on a solution prepared in methylene chloride.

Results

The gradual changes in the NMR and UV−vis spectra were followed for several days after addition of H_2edt to a solution of **D** in chloroform. The ^{1}H NMR spectra exhibited evidence for a multistep reaction sequence. The first step was confirmed to be the substitution of the dithiolate ligand in **D** with an edt unit.



(1)

In NMR experiments, simultaneous decline of the signals of **D** and rise of the signals of 2-(mercaptomethyl)thiophenol were

Table 4. Atomic Coordinates ($\times 10^4$) and Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for **3**

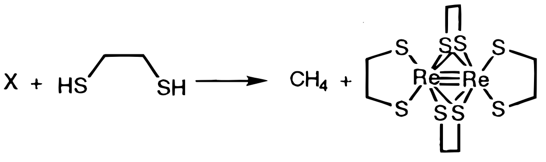
	x	*y*	*z*	*U*(eq)
Re	8541(1)	6749(1)	7687(1)	22(1)
Cl(1)	5493(3)	3739(3)	4904(2)	130(1)
S(1)	8845(1)	5773(1)	6211(1)	33(1)
S(2)	8722(1)	8664(1)	6117(1)	25(1)
P	7150(1)	8087(1)	8651(1)	21(1)
O	9892(2)	6291(2)	8651(2)	34(1)
C(1)	6870(4)	5453(3)	8241(4)	37(1)
C(2)	9878(4)	6919(3)	5048(3)	35(1)
C(3)	9194(4)	8262(3)	4723(3)	35(1)
C(4)	7180(3)	7434(3)	10315(3)	25(1)
C(5)	7749(4)	6201(4)	10917(3)	36(1)
C(6)	7813(4)	5759(4)	12186(3)	45(1)
C(7)	7321(4)	6545(4)	12842(3)	43(1)
C(8)	6743(4)	7767(4)	12252(3)	39(1)
C(9)	6675(3)	8220(3)	10991(3)	31(1)
C(10)	7745(3)	9722(3)	8367(3)	25(1)
C(11)	9138(3)	9838(3)	8567(3)	31(1)
C(12)	9639(4)	11053(4)	8431(3)	39(1)
C(13)	8761(5)	12148(4)	8086(4)	45(1)
C(14)	7389(5)	12036(4)	7881(5)	56(1)
C(15)	6874(4)	10824(4)	8019(4)	44(1)
C(16)	5335(3)	8273(3)	8202(3)	25(1)
C(17)	4289(4)	7765(4)	9042(3)	40(1)
C(18)	2922(4)	7859(5)	8654(4)	51(1)
C(19)	2590(4)	8454(4)	7453(4)	45(1)
C(20)	3618(4)	8955(4)	6612(4)	44(1)
C(21)	4991(4)	8854(4)	6986(3)	37(1)
C(21)	4991(4)	8854(4)	6986(3)	37(1)
C(22)	4492(10)	5211(5)	4184(6)	97(4)

Table 5. Selected Bond Lengths (Å) and Angles (deg) in **3**

Re−O	1.681(2)	Re−P	2.4369(8)
Re−C(1)	2.140(3)	S(1)−C(2)	1.826(4)
Re−S(2)	2.2870(8)	S(2)−C(3)	1.846(3)
Re−S(1)	2.2915(8)	C(2)−C(3)	1.504(5)
O−Re−C(1)	112.24(14)	S(1)−Re−P	150.83(3)
O−Re−S(2)	116.37(9)	C(2)−S(1)−Re	103.33(11)
C(1)−Re−S(2)	131.26(11)	C(3)−S(2)−Re	107.85(11)
O−Re−S(1)	108.52(8)	C(16)−P−Re	112.81(10)
C(1)−Re−S(1)	82.81(10)	C(10)−P−Re	115.10(10)
S(2)−Re−S(1)	85.32(3)	C(4)−P−Re	112.83(10)
O−Re−P	100.54(8)	C(3)−C(2)−S(1)	109.6(2)
C(1)−Re−P	84.07(10)	C(2)−C(3)−S(2)	110.5(2)
S(2)−Re−P	83.96(3)		

observed. The second-order rate constant was determined from UV−vis spectroscopic measurements and the fact that 366 nm was found to be an isosbestic point for the subsequent process. The rate constant *k* is $(1.65 \pm 0.02) \times 10^{-4}$ L mol^{-1} s^{-1} at 25.0 °C in chloroform. This value is in agreement with the NMR kinetics as well. (The methylene doublet of 2-(mercaptomethyl)-thiophenol, $\delta = 3.83$ ppm in $CDCl_3$, and the methyl singlet of **D**, $\delta = 3.09$ ppm in $CDCl_3$, were followed.) Intermediate **X** has not yet been identified, but the present data are consistent with a monomeric or dimeric (edt)methyloxorhenium(V) complex with an edt chelating ligand.

However, further unexpected reactions took place after the anticipated substitution. The final product was shown to be the quadruply S-bridged rhenium(IV) dimer **1**, which we propose has a triple Re−Re bond, on the basis of its length, the acuteness of the bridging Re−S−Re angle, and the diamagnetism of the compound. The respective Re−Re distances in $Me_2Re_2(O)(\mu\text{-}S)(mtp)_2$ and $Re_2(edt)_4$ are 278 and 266 pm; the latter compound has been proposed to have a bond order of 2 but the same ambiguity as advanced here. The Pauling bond order equation, using the suggested bond orders, gives the expected difference as $60[\log(3) - \log(2)] = 11$ pm, which is not inconsistent with the data. These arguments are not definitive proofs, however, and the "correct" assignment of bond order must remain open.



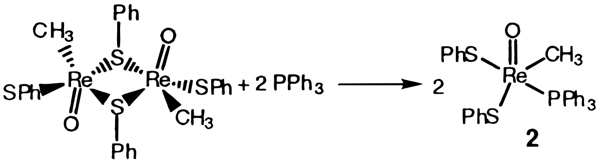
1

(2)

X-ray crystallographic analysis revealed the structure of **1** shown in Figure 1. Formation of methane was confirmed by its NMR signal and also gas chromatographic headspace analysis. The source of hydrogen for the formation of methane was shown to be the excess H_2edt and 2-(mercaptomethyl)thiophenol, a product of step 1. Various S−S-bonded products derived from the oxidation of the dithiols were detected in the NMR spectra. Electrospray mass spectrometry was also used to characterize **1**. The most intense peak for $Re_2C_8H_{16}S_8$ was expected at *m/z* 739.81. In full agreement with this expectation, the results showed a maximum at *m/z* 739.8. **1** was found to be diamagnetic and sparingly soluble in various solvents (its solubility in benzene is estimated to be ∼50 μmol L^{-1}). NMR evidence showed that the reaction of **D** with H_2bdt was very similar to the reaction with H_2edt but slower. This may be rationalized on the basis of the increased steric bulk and rigidity of the bdt unit. The product was not isolated in this case, but it is believed to be analogous to **1**.

M−PPh_3 also reacted with a large excess of H_2edt. This reaction gave an isolable intermediate (**3**) that was later identified as the edt analogue of **M**−PPh_3. NMR spectroscopy showed that methane was slowly formed during the reaction, giving **1** as a final product.

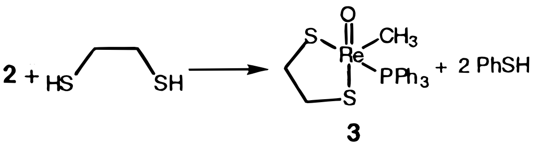
The edt analogue of **M**−PPh_3, [$CH_3ReO(edt)PPh_3$] (**3**), could be synthesized with a different approach using a methyloxorhenium(V) complex with two monodentate thiolate ligands, [$CH_3ReO(SPh)_2PPh_3$] (**2**). This compound was prepared from triphenylphosphine and a sulfur-bridged Re(V) dimer, $(CH_3)_2Re_2(O)_2(SC_6H_5)_4$, as reported earlier:[13]



2

(3)

Treatment of **2** with a slight excess of H_2edt gave **3**:



3

(4)

The crystal structure of **3** is shown in Figure 2. The isolated product **3** reacted slowly with a large excess of H_2edt, giving **1** and methane, as confirmed by the NMR spectra.

Discussion

The dinuclear complex $Re_2(\mu\text{-}edt)_2(edt)_2$, **1**, was obtained as exceptionally well-formed crystals that diffracted excellently, yielding data that refined to high precision. The molecule of **1**

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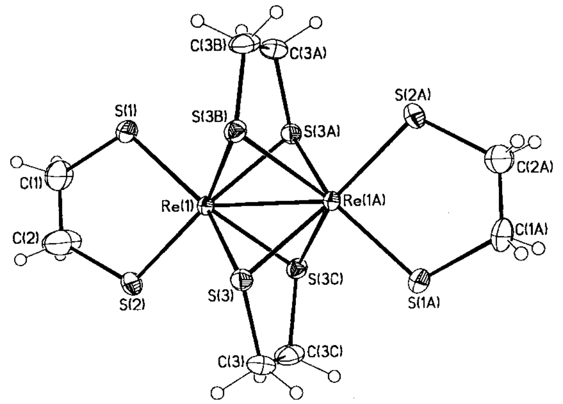

Figure 1. Perspective view of compound **1** with thermal ellipsoids at the 50% probability level.

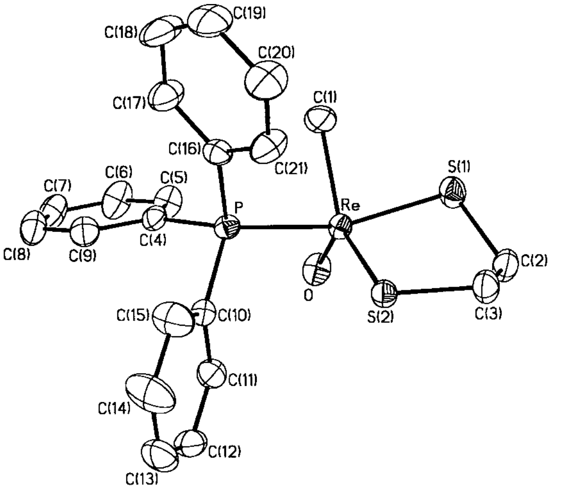

Figure 2. Perspective view of compound **3** with thermal ellipsoids at the 50% probability level.

comprises a crystallographic mirror plane and a 2-fold axis. Therefore, only atoms Re(1), S(1), S(2), S(3), C(1), C(2), and C(3) are symmetry independent. All other atoms are generated by symmetry operations. The mirror plane contains atoms Re(1), S(1), S(2), C(1), and C(2). The 2-fold axis is perpendicular to this plane and passes through the middle of the Re−Re bond. The coordination environment about the rhenium center is slightly disordered trigonal prismatic if the Re−Re bond is ignored. With the Re−Re bond taken into consideration, the geometry becomes capped trigonal prismatic. The Re_2S_8 core of the complex is formed by two trigonal prisms that share a common face defined by atoms S(3), S(3A), S(3B), and S(3C). The Re atom is displaced 131.49(3) pm from this plane. The dihedral angle between triangular faces above and below the rhenium atom (defined by atoms S(1), S(3A), S(3B) and S(2), S(3), S(3C), respectively) is 6.28(8)°, and the chelate twist angle is 0° due to the symmetry considerations.

The preceding angles are in excellent agreement with the corresponding angles found in neutral complexes with similar M_2S_8 cores: $Tc_2(edt)_2(e{=}dt)_2$ (6.0° and 0.0°)[19] (**4**) ($H_2e{=}dt$ = 1,2-ethenedithiol) and $[Tc_2(bdt)_4]\cdot CHCl_3$ (5.0(3)° and 1.2°)[20] (**5**). In contrast, vanadium centers in relevant complexes with the anionic core $[V_2(edt)_4]^{2-}$ (**6**) possess neither trigonal nor octahedral geometry but rather an intermediate distorted coordination environment.[21]

The quadruply μ_2-S-bridged M_2S_8 units in compounds **1**, **4**, **5**, and **6** exhibit D_{2h}, C_i, C_i, and D_2 molecular point symmetries, respectively. The Re−Re bond in **1** (262.99(6) pm) is assigned a formal triple character. The M−M separations in complexes **4**, **5**, and **6** are 261.0(3), 259.1(3), and 261.6(2) pm, correspondingly. In **1**, the Re−S bond lengths involving the bridging ligands, average 239.92(14) pm, are longer than the Re−S separations involving the terminal edt ligand, average 229.4(2) pm, as expected. This 4.6% difference is statistically significant and is also found in **4** (4.2%) and **5** (4.8%). The Re−S distances in **1** fall in the usual range for these types of interactions. The S−Re−S bite angle of the terminal ligand spans 85.06(8)° and is similar to those in complexes **4**−**6**, which were found to be 84.4(2), 83.9(2), and 84.8(1)°, respectively. The bite angle of the bridging ligands in **1** (74.49(4)°) is appreciably smaller and emphasizes the difference between the terminal and bridging ligands. The corresponding values in **4**−**6** are 74.8(1), 75.1(2), and 75.7(1)°, respectively.

It is instructive to compare the intra- and interligand S···S distances in **1**. The intraligand S···S separations are 290.4(3) and 310.0(3) pm, while the interligand S···S lengths range between 277.0(3) and 335.8(2) pm. All these values are substantially shorter than the sum of the van der Waals radii of two sulfur atoms, 360 pm,[22] implicating significant nonbonding S···S interactions. Similar observations were made for **4**, **5**, and other complexes of the type MS_6 with trigonal prismatic coordination spheres. However, such short S···S interactions are not believed to stabilize or destabilize the trigonal prismatic geometries observed in **1**, **4**, and **5**.[20]

We propose that the formula $Tc_2(\mu\text{-}edt)_2(e{=}dt)_2$[19] (**4**) may really be $Tc_2(\mu\text{-}edt)_2(edt)_2$. The NMR data published with **4** appear to be inconsistent with the structural proposal in two ways. Three singlets were found, with an integration ratio of 1:1:1 (3.71, 2.96, and 2.15 ppm in $CDCl_3$), whereas two of the singlets should be triplets for the structure $Tc_2(\mu\text{-}edt)_2(e{=}dt)_2$ because of ${}^3J_{H-H}$ homonuclear coupling between the two nonequivalent adjacent methylene groups of the bridging edt unit. These methylene groups were shown to be nonequivalent in the crystal structure, but it is unclear why they should not be equivalent in solution. The olefinic H is clearly expected above 5.5 ppm[23−27] (see Table 6 in the Supporting Information), whereas the most downfield proton in **4** is at 3.71 ppm. The reported NMR spectrum is more consistent with our structural proposal, assuming that one signal (most probably the one at 2.15 ppm) was erroneously assigned to the molecule. This would leave two singlets with a 1:1 ratio, and the NMR spectrum would be very close to the one we obtained for **1** (3.27 and 2.24 ppm in $CDCl_3$; see Figure 6 in Supporting Information).

Although the determined bond length for the carbon−carbon interatomic distance in the nonbridging edt unit in **4**, 139(2) pm, is clearly closer to the usual length of carbon−carbon double bonds than to that of C−C single bonds, it is consider-

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ably longer than other double bonds in similar environments[24,27−32] (see Table 7 in the Supporting Information). The corresponding value determined for **1** is 138.8(1.6) pm, showing that it is not unreasonable to assume a short carbon−carbon single bond in that position. For earlier Tc(V) complexes, single carbon−carbon bonds as short as 133(2) and 141(4) pm were reported in ethylenediamine ligands.[33]

An elemental analysis was also reported for **4**.[19] The composition required by $Tc_2C_8H_{12}S_8$ (the original proposal) is 17.09%, C, 45.62%, S, and 2.15%, H. The values required by $Tc_2C_8H_{16}S_8$ (revised) are 16.97%, C, 45.29%, S, and 2.85%, H. Experimental analysis gave 17.40%, C, 44.82%, S, 2.25% H. These differences are not considered to be decisive, especially because the purity of the isolated material is a serious concern when the hydrogen content is so low. An elemental analysis of **1** was not performed because it was prepared in too small a quantity. However, electrospray mass spectrometry and ^1H NMR spectroscopy were fully consistent with the structure.

4 was synthesized from $TcCl_6^{2-}$ and H_2edt.[19] The authors were unable to explain the origin of the double bond. They mentioned the possibility of a dehydrogenation reaction, $H_2\text{edt} \rightarrow H_2\text{e=dt} + H_2$. However, their NMR and HPLC measurements showed no evidence for the formation of H_2e=dt. They reported no attempts to detect molecular hydrogen. We note that the dehydrogenation reaction itself would be thermodynamically forbidden at the temperatures used. Anionic $[M_2(\text{edt})_4]^{2-}$ complexes are also known: with M = V(III),[34] they feature a structure similar to that of **1** and **4**; with M = Fe(III) and Mn(III),[21,35] they adopt less symmetric structures, with only two bridging sulfur atoms and no metal−metal bonding. The preparations of all these derivatives involved the use of excess H_2edt, and none showed any signs of dehydrogenation of H_2edt.

The carbon−carbon bond length as revealed by X-ray crystallography appears to have been the only information in support of the e=dt composition, despite the NMR data; the structural assignment appears to lack justification in the symmetry.

Besides the Tc, V, Fe, and Mn analogues already mentioned, rhenium complexes are also known that have features similar to **1**. The anionic bis(edt)sulfidorhenium(V) monomer, $[\text{SRe(edt)}_2]^-$, is the closest monomeric example.[36] Trigonal prismatic coordination geometry was established for the neutral complex tris(*cis*-1,2-diphenylethene-1,2-dithiolato)rhenium(VI), $[\text{Re}(S_2C_2(C_6H_5)_2)_3]$.[30]

Methane is formed as a product of hydrolytic decomposition of MTO.[37−39] It should be noted that the preparation of **D**[7] involves considerable excess of the chelating dithiol ligand but no signs of demethylation were seen in that reaction. Because substitution of the dithiol ligand precedes the formation of methane, it is very likely that the change in the coordination environment of Re induces cleavage of the organometallic bond rather than of the H_2edt, which was used in 25-fold excess. It seems likely that a condensation reaction occurs, giving a bis(edt)methylrhenium(V) complex that loses the methyl group and subsequently dimerizes. A radical pathway may be envisaged because the homolytic cleavage of the rhenium−carbon bond leaves rhenium(IV) immediately with no further redox steps necessary. Involvement of photochemical processes is unlikely, as the reaction was detected in the dark as well. An earlier theoretical study on rhenium−carbon bond homolysis in alkyl- and arylrhenium trioxides supports the viability of this process.[40] The idea of a homolytic bond cleavage and radical process is further supported by the fact that a mixture of different oxidation products was detected from the dithiols. The methyl radicals produced by the bond cleavage are very likely to react with thiols that are present in high concentrations and are known to be scavengers for carbon-centered radicals.

The coordination environment of the Re atom in compound **3** is that of a severely distorted square pyramid. The basal plane is formed by P, C(1), and two S atoms. The atoms are planar within 16 pm, with the Re atom located 75.4(1) pm above this plane. The apical position is occupied by the oxygen atom, with the Re=O vector forming a 4.8(1)° angle with the basal plane. The Re−P distance, 243.70(7) pm, is in excellent agreement with the "average" Re−P single bond distance, 243(5) pm, obtained by averaging the distances of 1853 single Re−P bonds reported in the Cambridge Structural database.[41] The Re−S, Re−O, and Re−C distances agree well with corresponding parameters in **1** and in similar complexes.

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Supporting Information Available: Figures 3−6, showing UV−vis spectra, kinetic curves, and plots of observed rate constants for the reaction between D and 1,2-ethanedithiol and an ^1H NMR spectrum of **1** in C_6D_6, and Tables 6−15, listing comparative NMR and crystallographic data from the literature and structure refinement details, bond lengths, bond angles, thermal parameters, and hydrogen coordinates for **1** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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