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Article

Rhenium(V) Complexes with Thiolato and Dithiolato Ligands: Synthesis, Structures, and Monomerization Reactions

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The new compound $\{(PhS)_2ReO(\mu\text{-}SPh)\}_2$, **1**, was synthesized from Re_2O_7 and PhSH and then used as the synthon for a number of hitherto unknown oxorhenium(V) compounds. Reactions between dithiols and **1** (2:1 ratio) afford $\{PhSReO(dt)\}_2$, where the dithiols, dtH_2, are 1,2-ethanedithiol ($edtH_2$), 1,3-propanedithiol ($pdtH_2$), 1,3-butanedithiol ($pdtMeH_2$), 1,2-benzenedithiol ($bdtH_2$), 2-(mercaptomethyl)thiophenol ($mtpH_2$), and 2-mercaptoethyl sulfide ($mesH_2$). Similar reactions carried out with a 3:1 ratio of dtH_2 to **1** afford $[(ReO)_2(dt)_3]$, dt = edt, pdt. When NEt_3 was introduced prior to the 3:1 reaction between $edtH_2$ and **1**, a compound containing an anionic complex was isolated, $[PPh_4][ReO(edt)_2]$. The new compounds were characterized analytically, spectroscopically, and crystallographically. The Re–O groups in two of the compounds, **1** and $\{ReO(\mu\text{-}SPh)(bdt)\}_2$, exist in rare anti orientations; the others adopt the more familiar syn geometry, as discussed. Selected monomerization reactions of $\{PhSReO(dt)\}_2$ were also carried out: $\{PhSReO(dt)\}_2 + 2L = 2[PhSReO(dt)L]$. The rate for L = 4-phenylpyridine is given by $v = \{k_a[L] + k_b[L]^2\} \times [\{PhSReO(dt)\}_2]$, as it is for the reactions of $\{MeReO(dt)\}_2$; for all of these compounds, the reaction proceeds nearly entirely by the third-order pathway. Values of $k_b/L^2\ mol^{-2}\ s^{-1}$ at 25.0 °C are 5.8×10^2 (mtp), 2.97×10^3 (pdt), 4.62×10^5 (edt), and 3.87×10^5 (bdt). The rate law for the reactions of $\{PhSReO(dt)\}_2$ with $L = PAr_3$ is $v = k_a[L]/\{1 + \kappa[L]\} \times [\{PhSReO(dt)\}_2]$. For PPh_3, values at 25.0 °C of $k_a/L\ mol^{-1}\ s^{-1}$ ($\kappa/L\ mol^{-1}$) for $\{PhSReO(dt)\}_2$ are 9.64×10^{-2} (1.87) for mtp, 3.43×10^{-2} (0.492) for pdt, 1.91 (1.42) for edt, 1.84×10^{-2} (0.82) for bdt, and 1.14×10^3 (10.6) for **1**. Mechanisms are proposed that are consistent with the data obtained and with earlier work.

Introduction

Different groups of oxorhenium(V) thiolate complexes have attracted considerable interest for three reasons. First, they find extensive application because ^{186}Re and ^{188}Re emit β particles of therapeutically useful energies.[1–4] Second, the rhenium complexes are structural models of their less easily handled technetium analogues that find use in nuclear medicine, particularly as heart imaging agents.[1] Third, many such rhenium compounds catalyze oxygen atom transfer (OAT) reactions, as recently reviewed.[5,6]

We have previously reported dithiolate (dt) compounds prepared from $MeReO_3$, which, thus, contain a Me–Re bond.[7,8] Monomeric compounds are typified by [MeReO(dt)L] and dimers by $\{MeReO(dt)\}_2$. Ligand L is a general Lewis base, PAr_3, pyridine, tetramethylthiourea, R_2S, and so forth, and the dt ligands include 1,2-ethanedithiolate (edt), 1,3-propanedithiolate (pdt), and mtp, the dianion of 2-(mercaptomethyl)thiophenol. Compounds lacking a Me–Re bond include $[(ReO)_2(mtp)_3]$[9] and others that have been described by Zubieta and et al.[10–16] and Abu-Omar et al.[17–19] Both

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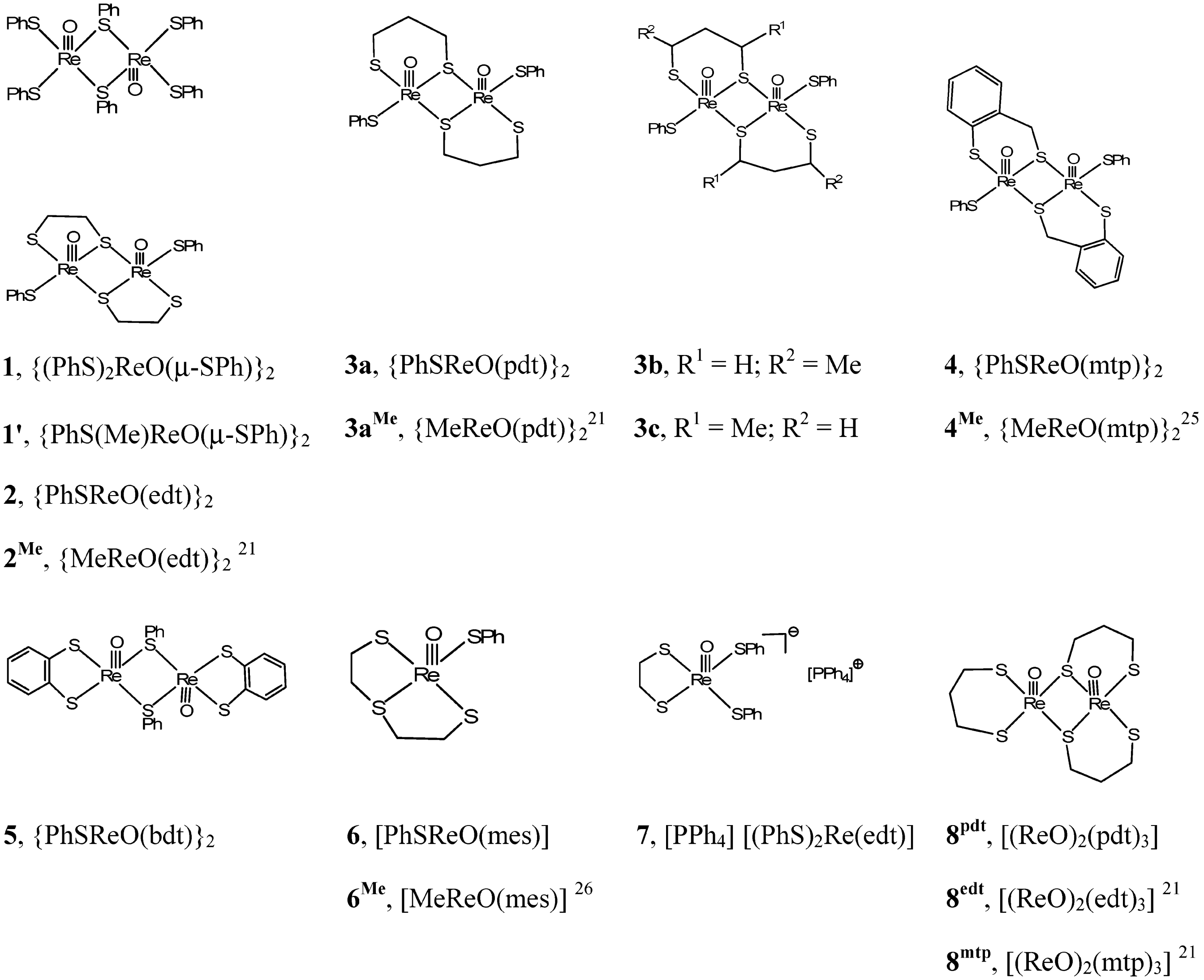
Chart 1. Structural Formulas of New Benzenethiolato and Other Oxorhenium(V) Complexes and Selected Previously Known Analogues



1, $\{(PhS)_2ReO(\mu\text{-}SPh)\}_2$

1′, $\{PhS(Me)ReO(\mu\text{-}SPh)\}_2$

2, $\{PhSReO(edt)\}_2$

2^{Me}, $\{MeReO(edt)\}_2$ [21]

3a, $\{PhSReO(pdt)\}_2$

3a^{Me}, $\{MeReO(pdt)\}_2$[21]

3b, $R^1 = H$; $R^2 = Me$

3c, $R^1 = Me$; $R^2 = H$

4, $\{PhSReO(mtp)\}_2$

4^{Me}, $\{MeReO(mtp)\}_2$[25]

5, $\{PhSReO(bdt)\}_2$

6, [PhSReO(mes)]

6^{Me}, [MeReO(mes)] [26]

7, $[PPh_4]$ $[(PhS)_2Re(edt)]$

8^{pdt}, $[(ReO)_2(pdt)_3]$

8^{edt}, $[(ReO)_2(edt)_3]$ [21]

8^{mtp}, $[(ReO)_2(mtp)_3]$ [21]

monomers and, especially, dimers catalyze OAT reactions,[6,9,20−22] YO + X → Y + XO, for which combinations of YO (e.g., C_5H_5NO, *tert*-BuOOH, R_2SO) have been used, their reaction partners X being, for example, PAr_3, R_2S, and R_2SO.

This research has the following objectives. First, new oxorhenium(V) dithiolates were sought with a PhS−Re group rather than Me−Re. Toward that end, the new compound $\{(PhS)_2ReO(\mu\text{-}SPh)\}_2$, **1**, was synthesized. Chart 1 displays structural formulas that emphasize the fact that every compound features rhenium(V) in a five-coordinate, square-pyramidal (precise or approximate) geometry with an apical oxo group. In most, the two Re−O groups are disposed in a syn configuration,[5] whereas in two of the new compounds, **1** and **5**, they are anti. Second, reactions between **1** and various dithiols were used to prepare several new compounds, **2**−**7**. Third, we sought to improve the synthesis of $[(ReO)_2(dt)_3]$,[9] **8**. The new complexes were thoroughly characterized by elemental analysis, spectroscopy, and crystallography; their ligand frameworks and chelating ring size differ from those of their Me−Re counterparts,[21,23] which becomes a factor that might reasonably be expected to affect the kinetics and thermodynamic parameters. Finally, the kinetics of selected monomerization reactions of the dimers with triarylphosphines and 4-phenylpyridine (4-PhPy) was studied.

Results, Interpretation, and Discussion

Preparation of 1; Reactions with Dithiols. The reaction between dirhenium heptoxide and excess benzenethiol in THF−Et_2O yields **1** as a pure product isolated in 79% yield.

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The reduction of Re(VII) to Re(V) is balanced by the oxidation of some of the thiol to diphenyl disulfide, according to the stoichiometry in eq 1.

$$Re_2O_7 + 10PhSH \rightarrow \{(PhS)_2ReO(\mu\text{-}SPh)\}_2\,(\mathbf{1}) + 4PhSSPh + 5H_2O \quad (1)$$

With a 2:1 ratio of 2-mercaptoethyl sulfide (mes) to **1**, the monomeric compound [PhSReO(mes)], **6**, was formed. The products of the reactions of **1** with dithiols depend on the ratios of the reagents. The use of a dithiol:**1** ratio of ≥3:1 affords $[(ReO)_2(dt)_3]$, **8**, eq 2.

$$\{ReO(SPh)_3\}_2 + 3dtH_2 \rightarrow [(ReO)_2(dt)_3] + 6PhSH \quad (2)$$

Reaction 2 is reproducible and amenable to easy workup; it proceeds in high yield. Limiting the dithiol:**1** ratio to 2:1 afforded four new dimeric compounds, $\{PhSReO(dt)\}_2$, **2**−**5**, according to eq 3 for dt = edt (**2**), pdt (**3a**), pdtMe (a mixture of **3b** and **3c**), mtp (**4**), and bdt (= 1,2-benzenedithiolate) (**5**).

$$\{ReO(SPh)_3\}_2 + 2dtH_2 \rightarrow \{PhSReO(dt)\}_2 + 4PhSH \quad (3)$$

At intermediate ratios of the reactants, mixtures are formed. For example, $edtH_2$ and **1** in a 1:1 ratio give a mixture of **2** and unreacted **1**; likewise, $pdtH_2$ and **1** in a 1:1 ratio gave a mixture of **3a** and **1**. The addition of more than 1 equiv of dtH_2 ($edtH_2$, $pdtH_2$, or $mtpH_2$) to the dimers **2**, **3a**, and **4** leads to the formation of $\mathbf{8^{edt}}$, $\mathbf{8^{pdt}}$, and $\mathbf{8^{mtp}}$, respectively.

Still another variant was discovered. When NEt_3 was added prior to the 2:1 reaction between $edtH_2$ and **1**, a new compound containing the anion $[(PhS)_2ReO(edt)]^-$ was obtained; it was isolated as the $[PPh_4]$ salt, **7**. With a 3:1 ratio of the reagents in the presence of NEt_3, **7** was obtained along with the known compound $[PPh_4][ReO(edt)_2]$.[27]

The reactions are summarized in Scheme 1. As suggested by the sequences shown, it appears that **1** reacts with dithiols in steps that involve one or more intermediates. The suggestions in Scheme 1 were made to preserve five-coordinate forms; even then, the scheme is simplified in that each reaction of a bidentate dithiol can be assumed to proceed in (at least) two steps. No further experiments were feasible, however, so further amplification of the details is unwarranted.

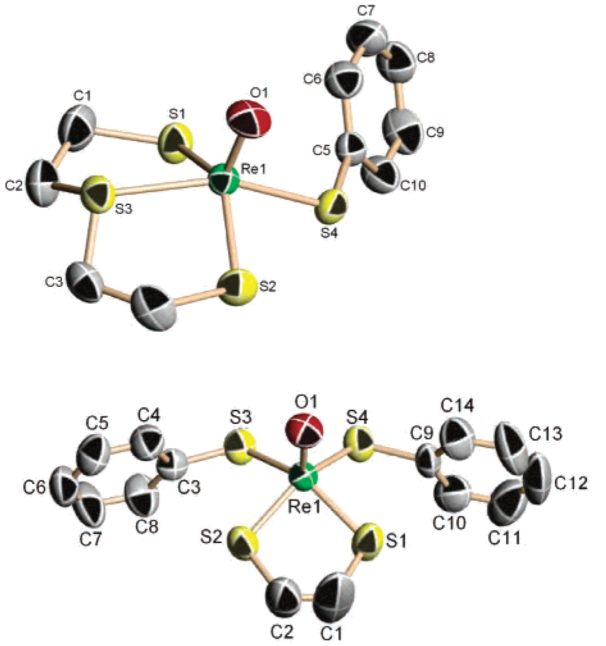
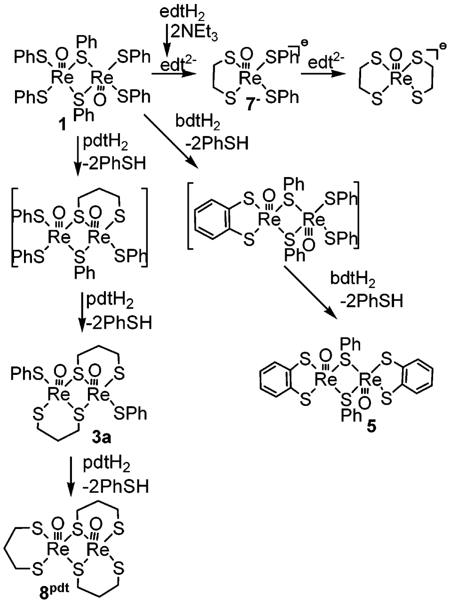


Figure 1. ORTEP diagrams with thermal ellipsoids drawn to 50% probability for [PhSReO(mes)], **6**, and $[PPh_4][ReO(edt)(PhS)_2]$, **7**.

Scheme 1. Reactions of **1** with Dithiols, Illustrated for $pdtH_2$, $edtH_2$, and $bdtH_2$



¹H NMR Spectra. NMR spectra were obtained in CD_2Cl_2 and C_6D_6, as depicted in Figures S1−S8 of the Supporting Information. The spectral patterns and chemical shifts of the proton resonances are significantly influenced by the deuterated solvents, which is typical behavior. The proton spectra are complicated by the diastereotopic protons of the chelated backbone.[28−30] The five- or six-membered metalloheterocyclic rings can interconvert between envelope and half-chair, or between chair and boat, conformers. Compounds **1** and **2** show broad, poorly resolved resonances, whereas the others appear as sharp multiplets at room temperature. As the temperature is lowered, the NMR spectra in CD_2Cl_2 display pattern changes, a result of slow ring inversion. The methylene protons of **4**, however, exhibit two *temperature-invariant* doublets at 5.04 and 4.68 ppm as a result of the stereochemical rigidity of the *o*-benzenedithiolato ligand.

Structural Considerations: Monomeric Compounds. The ORTEP diagrams of **6** and **7** are shown in Figure 1, and selected bond distances and angles are listed in Tables 1 and 2. Monomeric oxorhenium(V) complexes, in general,

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Table 1. Selected Bond Lengths (pm) and Angles (deg) of **6**

Re(1)−O(1)	167.2(6)	O(1)−Re(1)−S(1)	115.9(2)
Re(1)−S(1)	227.8(2)	O(1)−Re(1)−S(2)	115.3(3)
Re(1)−S(2)	228.4(2)	O(1)−Re(1)−S(3)	100.6(2)
Re(1)−S(3)	236.2(2)	S(3)−Re(1)−S(4)	154.44(8)[b]
Re(1)−S(4)	231.3(2)	O(1)−Re(1)−S(4)	104.7(2)
		S(1)−Re(1)−S(2)	128.77(9)[a]

[a] α. [b] β; see text.

Table 2. Selected Bond Lengths (pm) and Angles (deg) of **7**

Re(1)−O(1)	169.0(4)	O(1)−Re(1)−S(3)	108.20(18)
Re(1)−S(1)	230.0(2)	O(1)−Re(1)−S(4)	107.45(18)
Re(1)−S(2)	229.50(19)	S(1)−Re(1)−S(3)	141.21(9)[a]
Re(1)−S(3)	235.20(18)	S(2)−Re(1)−S(4)	144.38(8)[b]
Re(1)−S(4)	234.76(19)	S(1)−Re(1)−S(4)	86.67(8)
S(1)−Re(1)−S(2)	84.72(8)	S(2)−Re(1)−S(3)	87.85(7)
O(1)−Re(1)−S(1)	110.31(19)	S(3)−Re(1)−S(4)	77.59(7)
O(1)−Re(1)−S(2)	108.00(18)		

[a] α. [b] β; see text.

have approximate square-pyramidal structures. Inevitably, however, some degree of distortion toward trigonal-bipyramidal geometry can be noted. Following literature precedent,[31] we use the parameter τ to differentiate the limiting forms. One defines these angles in the following manner: let β be the largest angle $L^1{-}Re{-}L^2$, and let α be the second largest. The definition of τ is $(\beta - \alpha)/60$; thus, $\tau = 0.00$ for a square pyramid ($\alpha = \beta = 180°$) and $\tau = 1.00$ for a trigonal bipyramid ($\alpha = 120°$, $\beta = 180°$). Of course, in all of the actual structures, the Re atom will be displaced toward the oxo group above the mean ligand plane; therefore, even with C_{4v} symmetry, α and β will be close to one another but both will be less than 180°.

Compound **6** has the least regular structure, with $\tau = 0.43$; the rhenium atom in **6** lies in an intermediate coordination environment. The Re−S3 and Re−S4 bond lengths are unequal, 236.2(2) and 231.3(2) pm, respectively; on the other hand, the Re−S1 and Re−S2 distances are equal, an average of 228.3 pm. A regular structural progression can be seen when the thioether S atom of the mes ligand is replaced by O ($\tau = 0.17$)[32] or NH ($\tau = 0.61$).[33] Compound **6** and these analogues are the most sterically constrained and, thus, more distorted, owing to the presence of a tridentate ligand.

Crystals of **7** comprise a discrete mixed-ligand anion, a PPh_4 cation, and three toluene solvate molecules. The geometry about Re(V) is square-pyramidal with an apical oxo group ($\tau = 0.05$). The average Re−S length for edt is 229.8(2) pm, whereas that for the two benzenethiolate ligands is 235.0(2) pm. The Re−O distance of 169.0(4) pm is notably shorter than the distance found in the anionic complex $[Ph_4P][ReO(edt)_2]$, (174.2 pm).[27]

Table 3. Selected Bond Lengths (pm) and Angles (deg) of **1**

Re(1)−O(1)	166.1(5)	O(1)−Re(1)−S(3)	104.29(17)
Re(1)−S(5)	228.59(18)	S(5)−Re(1)−S(6)	85.95(7)
Re(1)−S(6)	230.27(18)	Re(1)−S(3)−Re(2)	97.38(5)
Re(1)−S(4)	239.52(16)	O(2)−Re(2)−S(1)	112.85(17)
Re(1)−S(3)	241.73(16)	O(2)−Re(2)−S(2)	106.95(15)
Re(2)−O(2)	166.4(5)	O(2)−Re(2)−S(3)	104.83(16)
Re(2)−S(2)	227.74(17)	O(2)−Re(2)−S(4)	109.25(17)
Re(2)−S(1)	228.94(18)	S(1)−Re(2)−S(2)	85.29(6)
Re(2)−S(4)	240.07(16)	S(1)−Re(2)−S(3)	92.24(6)
Re(2)−S(3)	242.12(16)	S(2)−Re(2)−S(4)	86.01(6)
O(1)−Re(1)−S(4)	109.94(17)	S(3)−Re(2)−S(4)	73.49(5)
O(1)−Re(1)−S(5)	107.33(17)	Re(1)−S(4)−Re(2)	98.54(6)
O(1)−Re(1)−S(6)	107.76(17)	S(4)−Re(1)−S(5)	140.64(6)[a]
S(3)−Re(1)−S(4)	73.66(5)	S(3)−Re(1)−S(6)	147.95(6)[b]
S(3)−Re(1)−S(5)	85.42(6)	S(1)−Re(2)−S(4)	137.74(7)[c]
S(4)−Re(1)−S(6)	94.38(6)	S(2)−Re(2)−S(3)	146.43(6)[d]

[a] α_1. [b] β_1. [c] α_2. [d] β_2; see text.

Table 4. Selected Bond Lengths (pm) and Angles (deg) of **2**

Re(1)−O(1)	168.6(5)	O(1)−Re(1)−S(3)[a]	103.95(18)
Re(1)−S(1)	227.90(17)	S(1)−Re(1)−S(2)	89.41(6)
Re(1)−S(2)	227.29(15)	S(1)−Re(1)−S(3)[a]	87.24(6)
Re(1)−S(3)	235.14(15)	S(2)−Re(1)−S(3)	84.59(6)
Re(1)−S(3)[a]	242.58(14)	S(3)−Re(1)−S(3)[a]	75.14(6)
O(1)−Re(1)−S(1)	111.7(2)	Re(1)−S(3)−Re(1)[a]	92.713(5)
O(1)−Re(1)−S(2)	107.57(18)	S(1)−Re(1)−S(3)	135.11(6)[b]
O(1)−Re(1)−S(3)	112.5(2)	S(2)−Re(1)−S(3)[a]	147.21(6)[c]

[a] Symmetry operation: $-x + 1, y, -z + \frac{1}{2}$. [b] α. [c] β; see text.

Table 5. Selected Bond Lengths (pm) and Angles (deg) of **4**

Re(1)−O(1)	168.5(6)	S(4)−Re(1)−S(1)	73.46(7)
Re(1)−S(1)	241.9(2)	S(1)−Re(1)−S(2)	87.42(8)
Re(1)−S(2)	228.8(2)	Re(1)−S(1)−Re(2)	98.73(8)
Re(1)−S(3)	230.9(2)	O(2)−Re(2)−S(5)	108.5(2)
Re(1)−S(4)	237.5(2)	O(2)−Re(2)−S(6)	104.4(3)
Re(2)−O(2)	168.1(6)	O(2)−Re(2)−S(1)	114.6(2)
Re(2)−S(5)	228.3(2)	O(2)−Re(2)−S(4)	105.5(3)
Re(2)−S(6)	231.0(3)	S(1)−Re(2)−S(4)	73.27(8)
Re(2)−S(1)	237.9(2)	S(1)−Re(2)−S(6)	89.72(9)
Re(2)−S(4)	242.5(2)	S(4)−Re(2)−S(5)	87.19(9)
O(1)−Re(1)−S(1)	103.6(2)	S(6)−Re(2)−S(5)	88.16(9)
O(1)−Re(1)−S(2)	108.8(2)	Re(1)−S(4)−Re(2)	98.67(8)
O(1)−Re(1)−S(3)	105.7(2)	S(2)−Re(1)−S(4)	135.96(9)[a]
O(1)−Re(1)−S(4)	114.1(2)	S(1)−Re(1)−S(3)	150.33(9)[b]
S(3)−Re(1)−S(4)	90.09(8)	S(1)−Re(2)−S(5)	135.96(9)[c]
S(3)−Re(1)−S(2)	87.82(8)	S(4)−Re(2)−S(6)	149.62(9)[d]

[a] α_1. [b] β_1. [c] α_2. [d] β_2; see text.

Structural Considerations: Dimeric Compounds. The bond distances and angles of compounds **1** ($\tau = 0.13, 0.14$), **2** ($\tau = 0.20$), **4** ($\tau = 0.24, 0.23$), and **5** ($\tau = 0.00, 0.05$) are presented in Tables 3−6; ORTEP diagrams are shown in Figure 2. The structural data and ORTEP diagrams for $\mathbf{8^{pdt}}$ are presented in the Supporting Information because they closely resemble the established compounds $\mathbf{8^{edt}}$ and $\mathbf{8^{mtp}}$.[6] The terminal Re−S distances of all of the dimers are shorter than those of the bridging ones by 1−12 pm. The differences are comparable to those found in most transition-metal complexes containing both bridging and terminal thiolato ligands.[34] The diamond-like $[Re_2S_2]$ cores in **1** and $\mathbf{8^{pdt}}$ are nearly symmetric; the four bridging Re−S distances are not significantly different, having an average length of 240.9(2) pm in **1** and 238.6(2) pm in $\mathbf{8^{pdt}}$. The cores of **2**, **4**, and **5** are asymmetric with the different bridging Re−S bond

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Table 6. Selected Bond Lengths (pm) and Angles (deg) of **5**

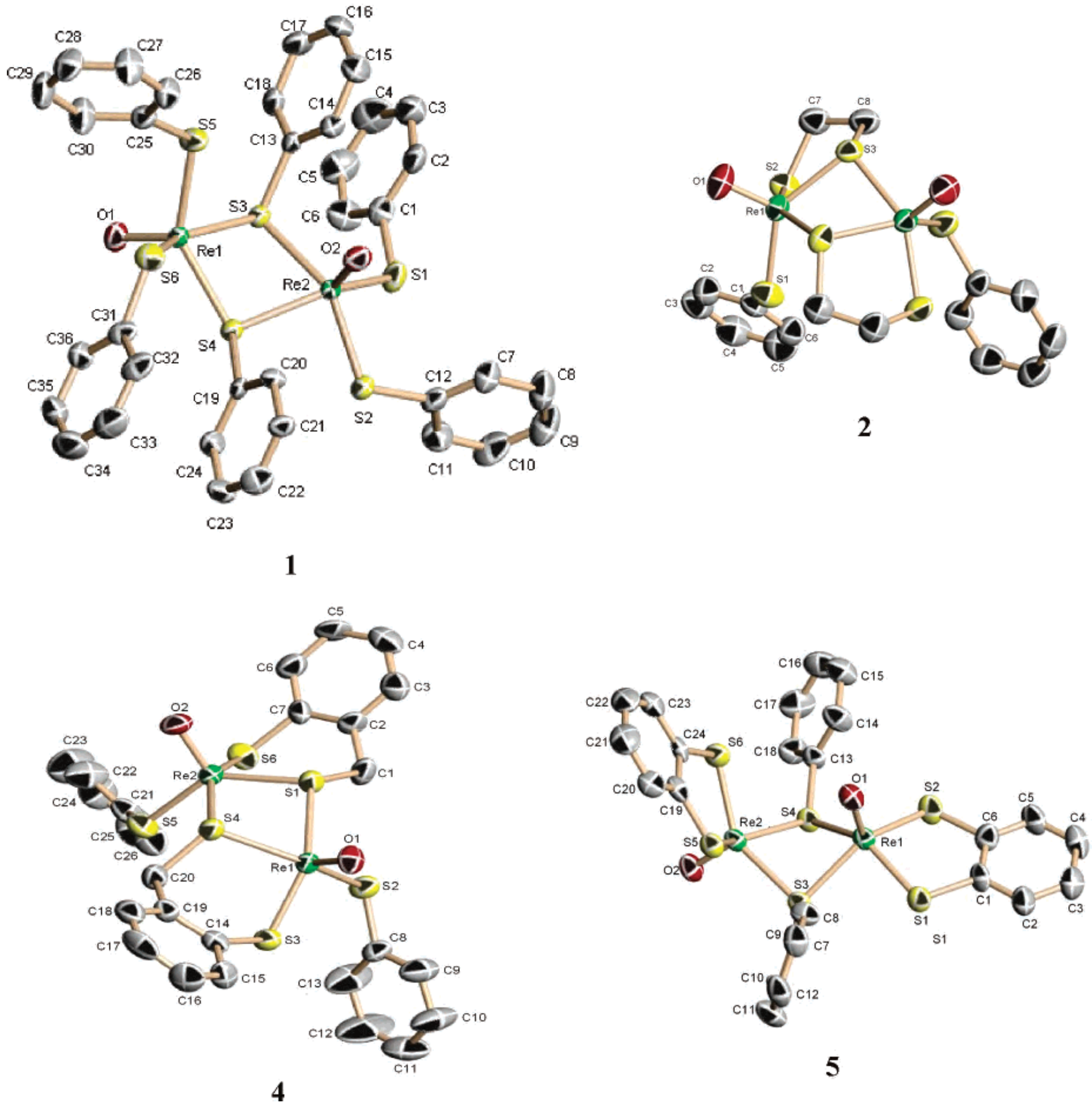
Re(1)−O(1)	167.0(6)	S(4)−Re(1)−S(2)	89.00(8)
Re(1)−S(1)	226.7(2)	S(1)−Re(1)−S(2)	85.61(9)
Re(2)−O(2)	167.2(6)	Re(1)−S(3)−Re(2)	90.14(7)
Re(2)−S(5)	226.0(2)	O(2)−Re(2)−S(5)	110.1(2)
Re(1)−S(2)	226.7(2)	O(2)−Re(2)−S(6)	108.5(2)
Re(1)−S(3)	239.2(2)	O(2)−Re(2)−S(3)	107.7(2)
Re(1)−S(4)	238.0(2)	O(2)−Re(2)−S(4)	108.8(2)
Re(2)−S(6)	228.1(2)	S(3)−Re(2)−S(4)	73.12(7)
Re(2)−S(3)	240.7(2)	S(3)−Re(2)−S(5)	87.45(8)
Re(2)−S(4)	239.4(2)	S(4)−Re(2)−S(6)	89.49(8)
O(1)−Re(1)−S(1)	109.7(2)	S(6)−Re(2)−S(5)	85.97(8)
O(1)−Re(1)−S(2)	109.7(2)	Re(1)−S(4)−Re(2)	90.73(7)
O(1)−Re(1)−S(3)	108.7(2)	S(1)−Re(1)−S(4)	141.10(8)[a]
O(1)−Re(1)−S(4)	108.4(2)	S(2)−Re(1)−S(3)	141.18(9)[b]
S(3)−Re(1)−S(4)	73.63(7)	S(4)−Re(2)−S(5)	140.21(8)[c]
S(3)−Re(1)−S(1)	86.93(8)	S(3)−Re(2)−S(4)	143.25(9)[d]

[a] α_1. [b] β_1. [c] α_2. [d] β_2; see text.

lengths, 235.14(15) versus 242.58(14), 237.7(2) versus 242.2(3), and 226.9(6) versus 239.3(7) pm, respectively.

The Four-Membered Re_2S_2 Rings. The two most noticeable characteristics of the dimeric structures are the arrangements of the two rhenium−oxo bonds and the bridging groups conjoining both rhenium centers. The two Re−O bonds in **1** and **5** are oriented anti to one another; in the other dimers, they are syn. The two Re atoms of **1** and **5** are held together by two bridging thiophenylato ligands, $(\mu\text{-SPh})_2$; two Re centers of $\mathbf{8^{pdt}}$ are connected by two sulfur atoms from the same Re center; in **2** and **4**, the two Re centers are bridged by two sulfur atoms from each Re center. The literature reports two compounds that are the syn and anti configurations of $\{(Bu^t)_2ReO(\mu\text{-}S)\}$,[35] formally Re(VI) but with a Re−Re bond, as well as Mo(V) compounds with $[M_2Y_2S_2]^{2+}$ cores (Y = O or S).[36,37]

Structures **I** and **III** differ conformationally (see Chart 2). The first has a bent M_2S_2 moiety with a dihedral angle between the two MS_2 planes of <180°; the third is



1

2

4

5

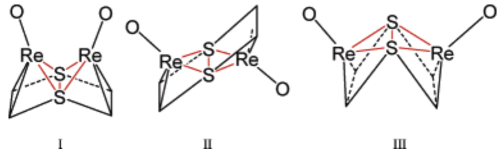
Figure 2. ORTEP diagrams with thermal ellipsoids drawn to 50% probability for $\{(PhS)_2ReO(\mu\text{-SPh})\}_2$, **1**; $\{PhSReO(edt)\}_2$, **2**; $\{PhSReO(mtp)\}_2$, **4**; and$\{PhSReO(bdt)\}_2$, **5**.

Table 7. Summary of Relevant Structural Data[a] Pertaining to the $[Re_2S_2]$ Cores of Oxorhenium(V) Dimers

compound	Re···Re [b]	Re−O	$Re-S_b$[c]	$S_b\cdots S_b$[c]	$Re-S_b-Re$	S_b-Re-S_b	τ[d]	dihedral angle,[e]	ref
$\{(PhS)_2ReO(\mu\text{-}SPh)\}_2$ (**1**)	363.4	166.3(5)	240.86(16)	288.5	97.96(6)	73.58(5)	0.13, 0.14	140.8	*f*
$\{Me(ReO)(SPh)_2\}_2$ (**1′**)	336.9	169.7(5)	239.45(7)	286.5	89.4(1)	73.5(3)	0.08, 0.17	122.8	24
$[(ReO)_2(edt)_3]$ ($\mathbf{8^{edt}}$)	366.0	167.6(4)	238.7(21)	294.4	100.1(3)	76.2(8)	0.03, 0.00	153.9	21
$[(ReO)_2(pdt)_3]$ ($\mathbf{8^{pdt}}$)	364.7	166.5(6)	238.6(2)	287.1	99.7(8)	73.95(7)	0.04, 0.06	146.2	*f*
$[(ReO)_2(mtp)_3]$ ($\mathbf{8^{mtp}}$)	372.7	168.0(3)	238.2(16)	288.9	103.0(8)	74.7(3)	0.04, 0.06	159.4	21
$\{PhS(ReO)(edt)\}_2$ (**2**)	345.7	168.6(5)	238.86(15)	291.3	92.71(5)	75.14(6)	0.20	131.8	*f*
$\{PhS(ReO)(mtp)\}_2$ (**4**)	364.1	168.3(2)	240.0(23)	286.7	98.70(3)	73.37(10)	0.24, 0.23	142.2	*f*
$\{PhS(ReO)(bdt)\}_2$ (**5**)	339.7	167.1(1)	239.3(7)	286.0	90.4(3)	73.37(3)	0.00, 0.05	124.5	*f*
$\{Me(ReO)(edt)\}_2$ ($\mathbf{2^{Me}}$)	363.1	167.9(2)	236.7(15)	292.0	100.17(7)	76.17(3)	0.00, 0.03	154	21
$\{Me(ReO)(pdt)\}_2$ ($\mathbf{3^{Me}}$)	368.0	167.4(2)	236.9(6)	284.5	101.94(4)	73.80(4)	0.03, 0.05	152.6	21
$\{Me(ReO)(mtp)\}_2$ ($\mathbf{4^{mtp}}$)	370.7	167.5(4)	237.3(9)	289.7	102.7(2)	75.23(5)	0.05, 0.19	160.8	25

[a] Distances are in pm; angles are in degrees. [b] Nonbonded distance. [c] S_b is a bridging sulfur atom. [d] A measure[31] of square-pyramidal ($\tau = 0.00$) versus trigonal-bipyramidal ($\tau = 1.00$) structures, see text. [e] *Acute* angle between the two $Re(S_b)_2$ planes. [f] This work.

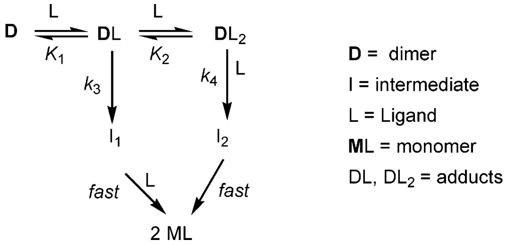
Chart 2. Three Conformations of the Re_2S_2 Rings



represented by dihedral angles that are also <180°, but only because of the convention that a dihedral angle between two planes is defined as an *acute* angle. Clearly, the two are different conformations. In the present cases, despite the syn arrangements of the ReO groups, compounds **2**, **4**, and $\mathbf{8^{pdt}}$ adopt the unusual conformation **III** in which the dihedral angles between the ReS_2 planes are, respectively, 131.8°, 142.2°, and 146.2°. Structure **II** represents the anti configuration, which has a planar M_2S_2 moiety, with a dihedral angle very close to 180°.

Table 7 summarizes the important distances and angles for the dimeric oxorhenium(V) complexes with $[Re_2O_2S_2]$ cores, both those new to this work and some previously reported. The $Re-O_t$ bond lengths lie within the range of 168(3) pm observed in most structurally characterized Re^VO species.[38−40] In comparison, idealized $Re^V{\equiv}O$ and $Re^V{=}O$ distances have been estimated to be approximately 160 and 176 pm, respectively.[38−43] The $S_b\cdots S_b$ bond distances are virtually invariant; the nonbonded Re···Re distances show somewhat wider variation, 336.9−372.7 pm, much longer than the Re−Re bond length of 253.19(7) pm in $\{Re(OMe)_5\}_2$,[44] indicating the absence of metal−metal bonds in the present cases. The S_b-Re-S_b angles lie within a narrow range, averaging 75(1)°. The $Re-S_b-Re$ angles show an obvious correlation with the Re···Re nonbonded distances: the wider the angle, the longer the Re···Re distance.

Scheme 2. Generalized Mechanism for the Monomerization of Oxorhenium(V) Dimers by Reactions with Ligands



Several factors are reflected in the configurations of the Mo═O units. Theoretical studies of the $[Mo_2Y_2S_2]^{2+}$ cores (Y = O or S) showed a direct Mo−Mo bonding interaction, resulting in a more stable syn isomer (Y = S),[45] and a direct π-bonding interaction between two Mo═O units, giving a more stable syn isomer (Y = O).[46] Other factors affecting the arrangement of syn and anti modes include the steric interactions among the ligands[36,47] and inter- and intramolecular H-bonding between the terminal oxo groups and the N−H groups of the ligand.[48] At present, it is not clear why the rhenium dimers adopt syn arrangements with the unusual conformation **III**. Perhaps it originates from the different electronic configurations, d^1 for Re^{VI} and Mo^V as compared to d^2 for Re^V.

Monomerization Reactions. Monomerization of dimeric rhenium compounds containing the Me−Re group with several ligands, especially phosphines and pyridines, have been studied extensively before.[21,23] The general reaction is **D** + 2L = 2**M**L (**D** = dimer, **M**L = monomer). Scheme 2 presents the general reaction scheme derived from previous work.

In its most general form, the rate of product (**M**L) formation in the forward direction is described by eq 4. In actual studies, however, limiting forms of eq 4 are always realized.

$$v_f = \left\{\frac{k_3K_1[L] + k_4K_1K_2[L]^2}{1 + K_1[L] + K_1K_2[L]^2}\right\}[\mathbf{D}] \qquad (4)$$

Studies with the new dimeric compounds $\{PhSReO(dt)\}_2$ were carried out for the representative cases L = PAr_3 and

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Table 8. Summary of Kinetic Constants[a,b] for the Monomerization of the PhS−Re and Me−Re Dimers with Triphenylphosphine

dt (compond #)	k_a	κ	k_3	k_b
		Part A: $\{PhSReO(dt)\}_2$		
$(PhS)_2$ (**1**)	1136(17)	10.55(42)	107.7(28)	
edt (**2**)	1.91(7)	1.42(76)	1.35(68)	
pdt (**3a**)	0.0343(4)	0.492(47)a	0.0697(59)	
mtp (**4**)	0.0964(22)	1.87(15)	0.0516(31)	
bdt (**5**)	8.50(59)	705(62)	0.121(3)	
		Part B: $\{MeReO(dt)\}_2$		
edt ($\mathbf{2^{Me}}$)	0.83(1)			23.7(4)
pdt ($\mathbf{3a^{Me}}$)	0.013(1)			0.18(4)
mtp ($\mathbf{4^{Me}}$)	0.0157(5)			0.051(6)

[a] Units: k_a, L mol^{-1} s^{-1}; κ, L mol^{-1}; k_3, s^{-1}; k_b, L^2 mol^{-2} s^{-1}. As usual, the parameters are given to a greater number of significant figures than actually warranted so that they will reproduce the experimental values of k_ψ. [b] Although the data are of questionable meaning because **3b,c** is a mixture, the values $k_a = 0.0184(18)$, $k = 0.82(44)$, and $k_3 = 0.023(10)$ were obtained.

Table 9. Kinetic Data for Monomerization of **4** with Triarylphosphines at 25 °C in Benzene

$P(C_6H_4\text{-}p\text{-}X)_3$	3σ	k_a/L mol^{-1} s^{-1}	k/L mol^{-1}	$k_3/10^{-2}$ s^{-1}
CH_3O	−0.81	2.05(6)	21(1)	0.96(2)
CH_3	−0.51	0.563(36)	14(2)	4.1(2)
H	0	0.0964(22)	1.9(2)	5.1(3)
F	0.18	0.0473(17)	1.1(1)	4.3(4)
Cl	0.69	0.0188(10)	*a*	*a*

[a] Could not be satisfactorily resolved; see text.

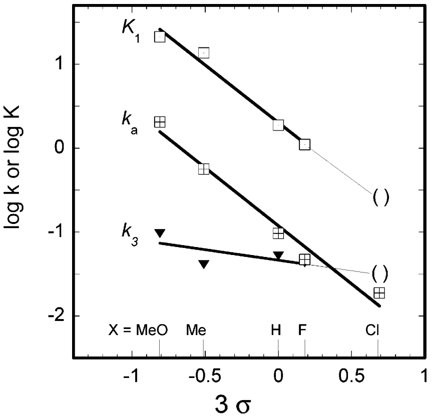

Figure 3. Correlation of the three kinetic parameters from Table 8 against the Hammett substituent constants σ for the reactions of $\{PhSReO(mtp)\}_2$, **4**, with $P(C_6H_5\text{-}p\text{-}X)_3$. The values of k_a (eq 5) for X = Cl could not be resolved into the components K_1 and k_3 (see text).

Table 10. Summary of Rate Constants[a] for the Monomerization of the PhS−Re and Me−Re Dimers with 4-Phenylpyridine at 25 °C in Benzene

dt (compound #)	k_a/L mol^{-1} s^{-1}	k_b/L^2 mol^{-2} s^{-1}
	Part A:$\{PhS(ReO)(dt)\}_2$[a]	
PhS (**1**)[b]		
mtp (**4**)	0.3(3)	$5.79(43) \times 10^2$
edt (**2**)	*c*	$4.62(15) \times 10^5$
bdt (**5**)	*b, c*	$3.87(55) \times 10^5$
pdt (**3a**)	2(1)	$2.97(23) \times 10^3$
	Part B: $\{MeReO(dt)\}_2$	
mtp ($\mathbf{4^{Me}}$)	≤ 1[c]	70.0(6)[d]
edt ($\mathbf{2^{Me}}$)	22(20)	$2.04(8) \times 10^4$
pdt ($\mathbf{3^{Me}}$)	0.17(3)	35(4)

[a] Although the data are of questionable meaning because **3b,c** is a mixture, the values $k_a = 2.4(4)$ and $k_b = 1.95(7) \times 10^3$ were obtained. [b] Too rapid for convenient measurement. [c] Insignificant. [d] Correct in ref 23; incorrectly cited as 7.0 in ref 21.

4-phenylpyridine (PhPy). Data for the reactions between PPh_3 and **1**, **2**, **3a**, **4**, and **5** (or **D** in general) will be presented first. The reactions were carried out with $[PPh_3]_0 \gg [\mathbf{D}]_0$; the reactions proceeded to completion and followed first-order kinetics. The pseudo-first-order rate constants obey eq 5. Comparison of eq 4 and 5 gives $k_a = k_3K_1$ and $\kappa = K_1$.

$$k_\psi = \frac{k_a[L]}{1 + \kappa[L]} = \frac{k_3[L]}{K_1^{-1} + [L]} \tag{5}$$

Fitting of the data can be done to either form, but both were used to obtain reliable estimates of the standard deviations. Values of the kinetic parameters are listed in Table 8, which also includes data for the Me−Re analogues,[21,23] for which the kinetic data were expressed by a different form, eq 6.

$$k_\psi = k_a[L] + k_b[L]^2 \tag{6}$$

Analysis of the data for $\{PhSReO(dt)\}_2$ according to Scheme 2 and eqs 4 and 5 allows these conclusions: $K_2[L] \ll k_3/k_4$ and $K_1K_2[L]^2 \ll 1 + K_1[L]$. Table 9 presents the data for the reaction of **4** with a family of triarylphosphines, $P(C_6H_4\text{-}p\text{-}X)_3$.

The kinetic parameters for the reactions of **4** with $P(C_6H_4\text{-}p\text{-}X)_3$, Table 9, are plotted as log k_a versus the Hammett σ value, Figure 3. The reaction constants ρ are -1.38 ± 0.13 (k_a), -1.37 ± 0.15 (K_1), and -0.25 ± 0.20 (k_3). The formation constant for **D**L (K_1, Scheme 2) is strongly influenced by the substituent; thus, the composite constant, k_a ($= K_1k_3$), is as well. On the other hand, the X substituent exerts a minimal influence on the unimolecular rate constant k_3. This is an entirely new finding resulting from the study of the $\{PhSReO(dt)\}_2$ reactions, which was not available for data pertaining to $\{MeReO(dt)\}_2$, where k_3 could not be deconvoluted into its components. The rate constants for the reactions of $\{PhSReO(dt)\}_2$ with 4-PhPy follow eq 6. The kinetic parameters are given in Table 10 in comparison with their Me−Re counterparts where they exist.

Monomerization Mechanism. Because eqs 5 and 6 have different kinetic forms, an appreciation of the mechanistic differences between $\{PhSReO(dt)\}_2$ and $\{MeReO(dt)\}_2$ in their reactions with PPh_3 proceeds as follows. The ratio of the k_a values, this being the parameter that the experiments

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define for both families, can be expressed in terms of two factors with the use of the notation in Scheme 2:

$$\frac{k_a{}^{PhS}}{k_a{}^{Me}} = \left(\frac{k_3{}^{PhS}}{k_3{}^{Me}}\right)\left(\frac{K_1{}^{PhS}}{K_1{}^{Me}}\right) \tag{7}$$

The values of the k_a ratios are 6.1 (mtp), 2.3 (edt), and 2.6 (pdt). Now, $K_1{}^{PhS}/K_1{}^{Me} \gg 1$, as determined from the stated inequalities manifested from the kinetic data. Thus, the *relative* inherent reactivities, which are represented by the k_3 values, can be expressed as

$$\frac{k_3{}^{Me}}{k_3{}^{PhS}} = \frac{(K_1{}^{PhS}/K_1{}^{Me})}{(k_a{}^{PhS}/k_a{}^{Me})} \tag{8}$$

The numerator of eq 8 is $\gg 1$, and the denominator falls in the range 2.3−6.1. Clearly then, $k_3{}^{Me} \gg k_3{}^{PhS}$ for any of these three dithiolates. This leaves two issues that require justification. First, why is $K_1{}^{PhS} \gg K_1{}^{Me}$? This, we suggest, reflects CH_3^- being, in general, a much stronger σ donor than PhS^-, as evidenced in many ways, such as the relative pK_a values, $CH_4 \ll PhSH$. Further, PhS^- can be displaced as PhSH by dtH_2 (driven, in part, by the chelate effect), whereas CH_4 cannot. Thus, the formation constant of **D**L will be much larger for the PhS−Re family. Second, why is $k_3{}^{Me} \gg k_3{}^{PhS}$? This, too, can be attributed to the relative σ-donor strengths of CH_3^- and PhS^-, which will weaken μ-S−Re bonds more for Me−Re than for PhS−Re, this being the prerequisite for the onset of monomerization following the coordination of L at the vacant sixth coordination position.

The values of k_a are larger for **1** as compared to others; otherwise, k_a and κ vary in the order **5** > **2** ≫ **4** > **3a**. These observations can be explained in terms of hard and soft acid−base theory[49] and geometric constraints.[50,51] Ligands with C-donor frameworks, as compared to those with aliphatic or aromatic S-donor frameworks, are more effective charge donors to an electropositive metal center. Geometric constraints imposed by chelating ligands can enhance the basicity of the transition-metal center; both result in the decrease of the metal-center electrophile. Thus, the reactivity decreases in those complexes with the Me group or aliphatic backbone. Similar effects have been observed in a number of examples.[52−56]

One can examine the influence of changes in the size of the chelate ring on reactivity toward monomer formation. This change can affect interactions between the donor atoms of the chelate ligand and the rhenium atom by varying the bite angle and the conformation of the chelate ring. This has been shown for Mo(V)/Mo(IV) couples, where potentials decrease with an increasing size of the chelate ring.[57] Another factor in reactivity is the ring strain in chelate systems, such as **2**,[58−60] which contains alternating five-membered and four-membered chelate rings and may suffer more strain than present in **3a**, which contains alternating six-membered and four-membered chelate rings. One can draw analogies between these cases and the strain energies (SE) of bicyclo-[3,2,0]heptane (SE = ~33 kcal mol^{-1}) versus those of bicyclo[4,2,0]octane (SE = ~25.6 kcal mol^{-1}).[61]

Experimental Section

General Methods. All chemicals were obtained from commercial sources and used as received unless otherwise noted. 2-(Mercaptomethyl)thiophenol was prepared according to literature methods.[62,63] Solvents were purified and dried following conventional procedures and were freshly distilled prior to use. ^{1}H NMR spectra were recorded on a Bruker DRX-400 MHz spectrometer. The spectrophotometric measurements were carried out with a Shimadzu model 3101 spectrophotometer and an OLIS RSM-1000 stopped-flow apparatus with a rapid scanning monochromator. Elemental analyses were performed by the Chemical Analysis facility at Iowa State University with a Perkin-Elmer CHN/S analyzer, Model 2400 series II. The analytical and spectroscopic data for compounds **1**−**8**$^{\mathbf{pdt}}$ are summarized in Table 11.

{(PhS)$_2$ReO(μ-SPh)}$_2$, 1. To a solution of thiophenol (3.28 mL, 31.9 mmol) was added a solution of rhenium(VII) oxide (1.55 g, 3.19 mmol) in THF (15 mL) dropwise by a cannula over 1 h with vigorous stirring. A dark red precipitate formed, and the resulting mixture was stirred for 2 h. The solid, isolated by filtration and washed with ether, was obtained in 79% yield.

{PhS(ReO)(edt)}$_2$, 2. 1,2-Ethanedithiol (46 μL, 0.56 mmol) was added by syringe to a suspension of **1** (299 mg, 0.28 mmol) in toluene (35 mL), and the mixture was stirred overnight under a N_2 atmosphere and then filtered. After the red-brown filtrate had been concentrated to ca. 3 mL, 40 mL of dry ether was added. The resulting red-brown solid was filtered, washed with ether, and vacuum-dried. The product was obtained in 75% yield. The same procedure was used to prepare {PhSReO(pdt)}$_2$, **3a** (62% yield) and **3b**−**c** (45%) [the mixture was not separable, but is comprised of 87% **3b** and 13% **3c** on the basis of proton integrations]; {PhSReO(mtp)}$_2$, **4** (74%); {ReO(μ-SPh)(bdt)}$_2$, **5** (59%); and {PhSReO(mes)}$_2$, **6** (91%).

[Ph$_4$P] [(PhS)$_2$ReO(edt)], 7. A solution of 1,2-ethanedithiol (24 μL, 0.283 mmol) and triethylamine (0.25 mL, 1.8 mmol) in CH_2Cl_2 (25 mL) was added dropwise by cannula to a solution of **1** (100 mg, 0.094 mmol) in CH_2Cl_2 (15 mL). The resultant mixture was stirred for 2 h, after which, tetraphenylphosphonium bromide (0.1 g, 0.24 mmol) was added. Concentration gave a red solution, which was purified by chromatography on silica (10 × 3 cm). Elution with dichloromethane provided two orange compounds, fraction I being **7** (44%) and fraction II [Ph$_4$P] being [(ReO)(edt)$_2$].[27]

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Table 11. Analytical and Spectroscopic Data for Compounds **1**−**8**

#	empirical formula	elem anal. found (calcd) C, H, S	^{1}H NMR δ (CD_2Cl_2, except as noted)	UV−vis, C_6H_6 λ_{max}/nm (log ϵ)
1	$C_{36}H_{30}O_2Re_2S_6$	40.53 (40.82) 3.17 (2.85) 16.51 (18.16)	7.20 (m, 2H), 7.09 (m, 3H) [$CDCl_3$]	434 (sh, 3.93) 385 (sh, 3.78)
2	$C_{16}H_{18}O_2Re_2S_6$·0.2Et_2O	24.62 (24.55) 2.28 (2.45) 21.71 (23.41)	7.46 (m, 2H, *o*-H), 7.38 (m, *m*-H, 2H), 7.28 (m, 1H, *p*-H), 4.57 (d, 1H, $SCH\mathit{H}CH_2$), 3.39 (m, 2H, $SCH_2CH\mathit{H}$), 3.17 (m, 1H, $SCH\mathit{H}CH_2$)	396 (3.88) 355 (4.04)
3a	$C_{18}H_{22}O_2Re_2S_6$	26.05 (25.89) 2.72 (2.66) 22.76 (23.04)	7.50−7.47 (m, 2H), 7.44−7.35 (m, 6H), 7.33−7.26 (m, 2H), 4.42−4.16 (m, 2H), 4.02−3.92 (m, 1H), 3.54−3.18 (m, 6H), 3.07−3.00 (m, 1H), 2.89−2.62 (m, 2H)	462 (sh, 3.26) 405 (sh, 3.72) 354 (4.00)
3b,c	$C_{20}H_{26}O_2Re_2S_6$·0.5$C_4H_{10}O$	28.85 (29.35) 3.48 (3.47) 21.52 (21.37)	**3b**: 7.46−7.41 (m, 4H), 7.38−7.34 (m, 4H), 7.29−7.25 (m, 2H), 4.33−4.24 (m, 2H), 3.55−3.46 (m, 2H), 3.26−3.18 (m, 2H), 3.05−2.91 (m, 2H), 2.75−2.58 (m, 2H), 1.79 (d, 6H). **3c**: 7.46−7.41 (m, 4H), 7.38−7.34 (m, 4H), 7.29−7.25 (m, 2H), 4.51−4.45 (m, 2H), 4.09−4.04 (m, 2H), 3.40−3.34 (m, 2H), 3.05−2.91 (m, 2H), 2.75−2.58 (m, 2H), 1.28 (d, 6H)	465 (sh, 3.70) 410 (sh, 4.04) 364 (4.27)
4	$C_{26}H_{22}O_2Re_2S_6$	34.43 (33.53) 2.56 (2.38) 19.59 (20.66)	7.50 (m, 5H, benzenethiolate), 7.39 (m, 2H), 7.28 (m, 2H), 5.04 (d, 1H, CH_2), 4.68 (d, 1H, CH_2)	406 (3.78)
5	$C_{24}H_{18}O_2Re_2S_6$·0.2C_7H_8	33.41 (33.10) 2.44 (2.14) 21.13 (20.88)	8.08 (dd, 4H), 7.80−7.74 (m, 10H), 7.14 (dd, 4H)	464 (sh, 3.29) 402 (sh, 3.88) 345 (sh, 4.28) 314 (4.33)
6	$C_{36}H_{30}O_2Re_2S_6$·0.1C_7H_8	27.07 (27.18) 3.01 (2.94) 27.90 (27.13)	7.62 (m, 2*H*, o-*H*), 7.38 (m, 2*H*, m-*H*), 7.23 (m, 1*H*, p-*H*), 4.20 (2*H*, $SCH\mathrm{H}CH_2SCH_2CH\mathrm{H}S$), 3.96 (2*H*, $SCH_2CH\mathrm{H}SCH\mathrm{H}CH_2$), 3.09 (2*H*, $SCH\mathrm{H}CH_2SCH_2CH\mathrm{H}S$), 2.02 (2*H*, $SCH_2CH\mathrm{H}SCH\mathrm{H}CH_2$)	501 (br, 2.8) 399 (3.71)
7	$C_{38}H_{34}POReS_4$·0.5CH_2Cl_2[a]	51.59 (51.69) 4.32 (3.94) 14.43 (14.34)	7.90 (m, 4H, *p*-H), 7.74 (m, 8H, *m*-H), 7.60 (m, 8H, *o*-H), 7.57 (m, 4H, *o*-H), 7.20 (m, 4H, *m*-H), 7.09 (m, 2H, *p*-H), 2.80 (m, 4H, SCH_2)	450 (sh, 3.15) 393 (sh, 3.83) 354 (4.00)
8^{edt}	$C_6H_{12}O_2Re_2S_6$	11.12 (10.58) 1.80 (1.78) 26.06 (28.26)	3.23 (m, 1H, $S_bCH\mathit{H}CH_2$), 2.93 (m, 1H, $S_bCH_2CH\mathit{H}$), 2.58 (m, 2H, SCH_2), 2.42−2.33 (m, 2H, $S_bCH\mathit{H}CH\mathit{H}S$) [$C_6D_6$]	394 (sh, 3.54) 344 (4.00)
8^{pdt}	$C_9H_{18}O_2Re_2S_6$	15.52 (14.95) 2.52 (2.51) 25.77 (26.63)	4.01−3.96 (m, 1H), 3.42−3.34 (m, 2H), 3.32−3.19(m, 3H), 3.10−2.83(m, 2H), 2.85−2.46(m, 1H) [C_6D_6]	352 (4.00)

[a] ESI-MS (negative) *m*/*z*: 513.

Table 12. Summary of Crystal Data for Compounds **1**, **2**, **4**, **5**, **6**, **7**, and **8**^{pdt}

	1	**2**	**4**	**5**	**6**	**7**	**8**^{pdt}
formula	$C_{36}H_{30}O_2Re_2S_6$	$C_{16}H_{18}O_2Re_2S_6$	$C_{26}H_{22}O_2Re_2S_6$	$C_{24}H_{18}O_2Re_2S_6$	$C_{10}H_{13}OReS_4$	$C_{59}H_{58}OPReS_4$	$C_9H_{18}O_2Re_2S_6$
fw, g	1059.36	807.06	931.20	903.14	463.64	1128.46	722.99
cryst syst	triclinic	monoclinic	monoclinic	triclinic	monoclinic	orthorhombic	orthorhombic
space group	$P\bar{1}$	$C2/c$	$C2/c$	$P\bar{1}$	$P2_1/c$	$P2_12_12_1$	$P2_12_12_1$
a, Å	11.464(2)	19.240(2)	28.735(8)	9.4847(19)	9.161(2)	12.891(2)	9.1533(17)
b, Å	11.820(2)	14.422(2)	8.509(2)	9.689(2)	14.542(4)	14.463(3)	12.383(2)
c, Å	13.959(3)	8.0202(11)	23.838(6)	15.028(3)	10.279(3)	29.123(5)	15.641(3)
α, deg	78.763(4)	90	90	88.154(4)	90	90	90
β, deg	74.363(3)	101.408(4)	99.344(8)	89.503(4)	92.611(5)	90	90
γ, deg	86.875(4)	90	90	72.307(3)	90	90	90
V, Å^3	1786.6(6)	2181.6(5)	5751(3)	1315.0(5)	1368.0(6)	5429.7(17)	1772.8(6)
Z	2	4	8	2	4	4	4
D_{calcd}, mg/m^3	1.969	2.457	2.151	2.281	2.251	1.380	2.709
abs coeff, mm^{-1}	7.152	11.671	8.871	9.695	9.469	2.459	14.344
GOF	1.050	1.048	1.006	0.991	1.060	1.128	1.024
R_1,[a]	0.0368	0.034	0.0455	0.0411	0.0421	0.0491	0.0355
wR_2[b] [$I > 2\sigma(I)$]	0.0701	0.0970	0.1022	0.0961	0.0982	0.1073	0.0795

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

[(ReO)$_2$(dt)$_3$], 8^{edt} and 8^{pdt}. 1,2-Ethanedithiol (0.17 mL, 2.02 mmol) was added by syringe to a suspension of **1** (0.7 g, 0.66 mmol) in toluene (50 mL). The resulting mixture was stirred overnight under a N_2 atmosphere and then filtered. After the red-brown filtrate had been concentrated to ca 3 mL, 40 mL of dry ether was added. The resulting red-brown solid, $\mathbf{8}^{\mathbf{edt}}$, was filtered, washed with ether, and vacuum-dried. The same procedure with 1,3-propanedithiol was used for $\mathbf{8}^{\mathbf{pdt}}$. The respective yields were 80% and 82%.

Crystallographic Studies. Single crystals were mounted and centered in the X-ray beam by using a video camera. Crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo Kα ($\lambda = 0.710\,73$ Å) radiation. The final cell parameters were calculated from strong reflections. Data collection was performed by a full sphere routine, taking frames at 0.3° in ω. The dataset was corrected for Lorentz and polarization effects, and the absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements[64] using SADABS software.[65] Crystallographic data for the complexes are listed in Table 12. The heavy atoms were found by the direct or Patterson method; the remaining atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined in a full-matrix anisotropic approximation; all hydrogen atoms were placed in the structure factor calculation at idealized positions and refined as riding atoms with isotropic displacement parameters.

During the refinement of the structure of **1**, two highly positive electron density peaks of 19.4 and 11.3 e/Å^3 were found. The resulting molecular structure and thermal parameters were in good accord with the analogous structure reported previously.[24] To assign these peaks and to improve the R and wR factors, each Re atom was split to two atoms with occupancies of 0.9 for Re1 and Re2 and 0.1 for Re1A and Re2A; the rhenium disorder requires the splitting of the two oxygen atoms with the same occupancies.

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Supporting Information Available: Variable temperature ^{1}H NMR spectra of the compounds in CD_2Cl_2 and C_6D_6 (Figures S1−S8). ORTEP diagrams for $[PPh_4][ReO(edt)(PhS)_2]$, **7**, and $[(ReO)_2(pdt)_3]$, $\mathbf{8}^{\mathbf{pdt}}$ (Figures S9 and S10). Tables of crystallographic parameters, atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen coordinates for **1**, **2**, **4**, **5**, **6**, **7**, and $\mathbf{8}^{\mathbf{pdt}}$. Tables and graphs of the kinetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(65) All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (Sheldrick, G. M.; Bruker Analytical X-ray Systems: Madison, WI).