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Induced Internal Electron Transfer Chemistry in Rhenium Sulfide Systems

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This paper demonstrates the proclivity with which high-valent rhenium sulfur complexes undergo internal electron transfer. Specifically, reaction of $[Et_4N][ReS_4]$ with 1.5 molar equiv of tetraalkylthiuram disulfide in acetonitrile gives the dinuclear Re(IV) complexes, $Re_2(\mu{-}S)_2(S_2CNR_2)_4$, **1**, in very high yield. This dimer reacts with an additional equivalent of tetraalkylthiuram disulfide in the presence of excess Lewis acids, *or* with 0.5 molar equiv of tetraalkylthiuram disulfide and 1 molar equiv of $[Cp_2Fe][PF_6]$, to give the dinuclear Re(III) species $[Re_2(\mu{-}S{-}S_2CNR_2)_2(S_2CNR_2)_3]^+$, **2**, in high yield. The reaction of $[ReS_4]^-$ with 3 molar equiv of tetraalkylthiuram disulfide in a mixture of dichloromethane and acetonitrile gives the mononuclear Re(V) species $[Re(S_2CN(R)_2)_4][Cl]$, **3**, in high yield. Each of these reactions involves induced internal electron transfer in which the formal oxidation state of the metal center is reduced by the addition of an oxidant (i.e., tetraalkylthiuram disulfide). The bound sulfide is the reductant both for the metal and the external oxidant. The reformation of **1** from **2**, in which the metal is *oxidized*, can be effected using *reductants* such as H_2. Electrochemical properties and chemical reactivities of the complexes are presented. The $Re_2(\mu{-}S)_2(S_2CNR_2)_4$ dimer undergoes a reversible one-electron oxidation to produce $Re_2(\mu{-}S)_2(S_2CNR_2)_4^+$, $\mathbf{1}^+$. This species can be generated chemically and, in the presence of excess sulfur, forms a novel Re(IV) sulfur-bridged dicationic dimer-of-dimers, $[(Re_2(\mu{-}S)(S_2CNR_2)_4)_2S_4]^{2+}$, **4**. The reaction of $\mathbf{1}^+$ with tetraalkylthiuram disulfide give **2,** which can be reconverted to **1** electrochemically via an EEC reaction. Single crystal X-ray diffraction studies of **1-*i*-Bu** ($P2_1/c$ (No. 14), $a = 11.084(2)$ Å, $b = 13.815(3)$ Å, $c = 19.945(4)$ Å, $\beta = 92.23(2)°$, $V = 3052(2)$ Å^3), **[2-Me][O$_3$SCF$_3$]** ($P\bar{1}$ (No. 2), $a = 14.238(4)$ Å, $b = 11.476(4)$ Å, $c = 14.977(5)$ Å, $\alpha = 112.28(2)°$ $\beta = 117.70(2)°$ $\gamma = 89.14(2)°$, $V = 1966(1)$ Å^3), **[3-Me][Cl]** ($C2/c$ (No. 15), $a = 13.174(4)$ Å, $b = 18.736(6) =$ Å, $c = 9.826(3)$ Å, $\beta = 96.46(2)°$, $V = 2410(1)$ Å^3), and **[4-*i*-Bu][PF$_6$]$_2$** ($P2_1$ (No. 4), $a = 15.754(3)$ Å, $b = 22.505(5)$ Å, $c = 20.278(6)$ Å, $\beta = 115.12(2)°$, $V = 6510(3)$ Å^3) are described where the symbols after the number designate the alkyl group, R, of the particular complex.

Introduction

Transition metal sulfides exist as minerals in nature,[1] play integral roles in the catalytic activity of enzymes,[2] and are used extensively in heterogeneous catalysis.[3] In catalytic processes, both biological and abiological, the redox properties of the transition metal sulfides are intimately related to their activity.

In biology, the rich chemistry of metal sulfides is exploited in numerous redox proteins and enzymes such as hydrogenase[2] and nitrogenase.[2,4,5] In industry, transition metal sulfide solids such as MoS_2, WS_2, and ReS_2 are useful in hydroprocessing catalysis,[3,6,7] while precursors to MoS_2 are active in lubrication.[8−10] Studies on MoS_2, reveal the structural dependence of HDS reactivity and affirm that edge planes of layered transition metal sulfide structures contain the catalytically active sites.[3,11−13] The structural properties and reactivity of soluble, molecular transition metal sulfide species mimic aspects of the behavior of the edges of such solids.[3,7,14]

In transition metal sulfide systems, both the metal and sulfur may undergo redox reactions which are an important part of their reactivity. A particularly interesting and, as we show, quite general mode of redox reactivity of transition metal sulfides involves induced internal electron transfer. In one manifestation of this reaction, addition of an external *oxidant* leads to *reduction* of the metal center. For example, when an oxidant, such as elemental sulfur or tetraalkylthiuram disulfide is added to a metal sulfide complex, the bound sulfide (S^{2-}) ligands can transfer electrons to the metal center.[15−21] The counter intuitive consequence of such reactions is that metal centers are *reduced*

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(1) (a) Vaughan, D. J.; Craig, J. R. *Mineral Chemistry of Metal Sulfides*; Cambridge University Press: Cambridge, England, 1978; p 493. (b) Korzhinsky, M. A.; Tkachenko, S. I.; Shmulovich, K. I.; Taran, Y. A.; Steinberg, G. S. *Nature* **1994**, *369*, 51.

(2) Stiefel, E. I.; George, G. N. In *Bioinorganic Chemistry;* Bertini, I., Gray, H. B., Lippard, S. J., Valentine, J. S., Eds.; University Science Books: Mill Valley, CA, 1994; Chapter 7, p 365.

(3) Chianelli, R. R.; Daage, M.; Ledoux, M. *Adv. Catal.* **1994**, *40*, 177.

(4) Stiefel, E. I.; Thomann, H.; Jin, H.; Bare, R. E.; Morgan, T. V.; Burgmayer, S. J. N.; Coyle, C. L. *Metal Clusters in Proteins;* ACS Symposium Series 372; American Chemical Society: Washington, DC, 1987; p 372.

(5) Lindahl, P. A.; Kovacs, J. A. *J. Cluster Sci.* **1990**, *1*, 29.

(6) Weisser, O.; Landa, S. *Sulfide Catalysts, Their Properties and Applications*; Pergamon Press: New York, 1973.

(7) Prins, R.; DeBeer, V. H. J.; Somorjai, G. A. *Catal. Rev.-Sci. Eng.* **1989**, *31*, 1.

(8) Coyle, C. L.; Halbert, T. R.; Stiefel, E. I. US 4,978,464 18 Dec, 1990.

(9) Sarin, R.; Gupta, A. K.; Sareshbabu, A. V.; Martin, V.; Misra, A. K.; Bhatnagar, A. K. *Lubr. Sci.* **1993**, *5*, 213.

(10) Coyle, C. L.; Greaney, M. A.; Stiefel, E. I.; Francis, J. N.; Beltzer, M. US 4,995,996 26 Feb 1991.

(11) Salmeron, M.; Somorjai, G. A.; Wold, A.; Chianelli, R. R.; Liang, K. S. *Chem. Phys. Lett.* **1983**, *90*, 105.

(12) Tanaka, K.; Okuhara, T. In *Third International Conference on the Chemistry and Use of Molybdenum*; Climax Molybdenum: Leadville, CO, 1979; p 170.

(13) Chianelli, R. R. *Catal. Rev.-Sci. Eng.* **1984**, *26*, 361.

(14) Chianelli, R. R.; Daage, M.; Halbert, T. R.; Ho, T. C.; Stiefel, E. I. *Prepr. Am. Chem. Soc., Div. Pet. Chem.* **1990**, *35*, 227.

(15) Coyle, C. L.; Harmer, M. A.; George, G. N.; Daage, M.; Stiefel, E. I. *Inorg. Chem.* **1990**, *29*, 14.

(16) Pan, W. H.; Chandler, T.; Enemark, J. H.; Stiefel, E. I. *Inorg. Chem.* **1984**, *23*, 4265.

(17) *Nomenclature of Inorganic Chemistry, Recommendations 1990;* Blackwell Scientific Publication: London, 1990; p 154.

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upon the addition of *oxidant*. The reaction also occurs in the opposite sense as metal centers can be oxidized upon addition of reductants, such as H_2 or hydride. Related induced internal electron transfer processes may be relevant to both biological systems and industrial processes.

The tetrachalcogenometalate anions of V, Mo, and W formally possess fully oxidized metal centers (d^0) and fully reduced chalcogenides (i.e., S^{2-}, Se^{2-}). The tetrathiometallates have been shown to undergo induced internal electron transfer upon reaction with external oxidants.[15,16] Observed types of sulfur redox transformations include oxidation of sulfido (S^{2-}) to disulfido[17] (S_2^{2-}) or sulfur, with concomitant metal reduction by one or two electrons.[18-21] These induced internal electron transfer reactions provide a powerful synthetic approach to new lower-valent transition metal sulfur (and selenium[22]) compounds.

Although the tetrathioperrhenate anion, ReS_4^-, was isolated more than two decades ago[23] the induced internal electron transfer chemistry of rhenium sulfides has been less thoroughly explored than that of the group VI sulfides.[24,25] Recently, we described an unprecedented $3e^-$ reduction of the Re(VII) center of ReS_4^- induced by the external oxidant tetraalkylthiuram disulfide, to produce the Re(IV) dimer, $Re_2(\mu\text{-}S)_2(S_2CNR_2)_4$, **1**.[26a,b] The Re(IV) centers of this dimer undergo further reduction in an internal electron transfer reaction induced by additional tetraalkylthiuram disulfide and a Lewis acid, leading to the Re(III) dinuclear complex, $[Re_2(\mu\text{-}S{-}S_2CNR_2)_2(S_2CNR_2)_3]^+$, **2**. Complex **2** was shown to regenerate **1** in the presence of appropriate reducing agents, an example of oxidation of a metal center caused by an external reductant. The interconversion of these compounds has provided a rich system within which to study the chemical and electrochemical details of induced internal electron transfer. Here we describe such studies in addition to the synthesis and characterization of a new rhenium sulfide tetranuclear complex, $[(Re_2(\mu\text{-}S)(S_2CNR_2)_4)_2(\mu\text{-}S_4)][PF_6]_2$, **[4-*i*-Bu][PF$_6$]$_2$**, and one previously known compound, $[Re(S_2CNR_2)_4][Cl]$, **[3-Me][Cl]**,[27] which we now show to be accessible in high yield via an induced internal electron transfer reaction.

Experimental Section

Materials and Syntheses. $[NH_4][ReO_4]$ was purchased from Engelhard Corporation and used as received. $[Et_4N][ReS_4]$[26a,28] and $[Cp_2Fe][PF_6]$[29] were synthesized according to literature procedures. Isopropyl- and *tert*-butylthiuram disulfide were synthesized by reacting the required secondary amine with CS_2 in basic aqueous solution followed by oxidation of the resulting dialkyldithiocarbamate to the tetraalkylthiuram disulfides using I_2. Tetramethyl- and tetraethylthiuram disulfide and trimethyl- and triethylsilyl triflates were purchased from Aldrich and used as received. "Sure-Seal" solvents from Aldrich were used without further purification. All syntheses were performed under an argon atmosphere using standard Schlenk-line techniques except where otherwise noted. Specific, yet representative, syntheses are given. Similar procedures for other homologues (Et, *i*-Pr, and *i*-Bu) give similar results. Unless otherwise noted in the discussion, all solid products are reasonably air-stable. Some difficulties were encountered in the purification (elimination of excess sulfur) of **1-Me**. Samples synthesized and purified differently gave similar ^1H NMR spectra yet exhibit differences in their electrochemistry, *vida infra*.

$Re_2(\mu\text{-}S)_2(S_2CN(CH_3)_2)_4$, 1-Me. $[Et_4N][ReS_4]$ (4.9 g, 10.0 mmol) and tetramethylthiuram disulfide, TDS, (3.9 g, 16.2 mmol) were combined in 75 mL of acetonitrile and allowed to react for 24 h at room temperature. The resulting green precipitate was filtered and washed three times with acetonitrile giving 5.6 g of desired product contaminated with sulfur. Purification (as judged by cyclic voltammetry, CV) was effected by precipitating the product from a saturated methylene chloride solution with an equal volume of hexane giving a bright green precipitate in 49% yield. The solid compound decomposes slowly in air, and more rapidly in solution, though solutions seem stable in air for up to several days. ^1H NMR (CD_3CN); δ 3.384 and 2.889 (minor 3.390 and 2.906) MS *m/z* (largest peak in isotope cluster of parent M^+) 918.5 Anal. Calcd for $C_{12}H_{24}N_4Re_2S_{10}$: C, 15.71; H, 2.64; N, 6.11; S, 34.95; Re, 40.60; Found: C, 15.38; H, 2.44; N, 5.78; S, 33.15; Re, 39.81

$Re_2(\mu\text{-}S)_2(S_2CN(C_4H_9)_2)_4$, 1-*i*-Bu. $[Et_4N][ReS_4]$ (6 g, 13.5 mmol) and tetraisobutylthiuram disulfide, TDS, (15 g, 36.7 mmol) were combined in 150 mL of acetonitrile and allowed to react overnight at room temperature. The resulting green precipitate was filtered and washed three times with ether, giving 4.2 g, 50% yield, of the desired product, contaminated with sulfur.

Alternative Synthesis of $Re_2(\mu\text{-}S)_2(S_2CN(CH_3)_2)_4$, 1-Me. $[Re(S_2CN(CH_3)_2)_4][Cl]$ (0.40 g, 0.57 mmol) and $[Et_4N][ReS_4]$ (0.25 g, 0.57 mmol) were allowed to react for 29 h in approximately 300 mL of acetonitrile. The volume was reduced by half and the resulting green precipitate was filtered and washed with three 10-mL portions of acetonitrile and then three 10-mL portions of diethyl ether. The washings were added to the filtrate resulting in the formation of additional green precipitate. This precipitate was filtered, washed with two 10-mL portions of acetonitrile and three 10-mL portions of diethyl ether. The combined precipitates gave 0.34 g of the green product, 65% yield. The material was characterized by ^1H NMR and found to be identical to those obtained in the original synthesis.

Alternative Synthesis of $Re_2(\mu\text{-}S)_2(S_2CN(C_2H_5)_2)_4$, 1-Et. $[Et_4N][ReS_4]$ (0.25 g, 0.57 mmol) and sodium diethyldithiocarbamate trihydrate, Na dtc·$3H_2O$, (1.28 g, 5.7 mmol) were combined in 25 mL of CH_3CN and stirred for 8 days at room temperature in an open flask. The resulting green precipitate was filtered giving 0.22 g of crude **1-Et**, in 63% yield. The material exhibited the characteristic triplet (methyl) and doublet of quartets (diasteriotopic protons of methylene) ^1H NMR spectra. ^1H NMR (CD_3CN); δ 1.027 (t) and 1.381 (t), 3.240 (multiplet center, two d of q), 3.766 (d of q) and 3.886 (d of q).

Alternative Synthesis of $Re_2(\mu\text{-}S)_2(S_2CNR_2)_4$, 1. Complex **1**, Re(IV), can be generated from **2**, Re(III), in various *reducing* environments. Specifically, the regeneration of **1** from **2** can be achieved by reduction with 1 molar equiv of $NaBH_4$ in methanol, $Li(Et)_3BH$ in THF, or by heating **2** in morpholine (90 °C), or tetrahydroquinoline (110 °C). Morpholine and tetrahydroquinoline are reductants, i.e., H donors. Complex **2** is converted to **1** in a 1:1 CD_3CN:CH_2Cl_2 solution under H_2 (80 psi, 22 °C, and 3 days or 475 psi, 75 °C, and 75 min). All reactions were carried out using the methyl derivatives of **1** and **2** and characterized via ^1H NMR.

Synthesis of $[Re_2(\mu\text{-}S{-}S_2CN(CH_3)_2)_2(S_2CN(CH_3)_2)_3][O_3SCF_3]$, [2−Me][O$_3SCF_3$]. $Re_2(\mu\text{-}S)_2(S_2CN(CH_3)_2)_4$ (0.5g, 0.55 mmol) and tetramethylthiuram disulfide (0.132 g, 0.55 mmol) were combined in approximately 25 mL dichloromethane and stirred. The addition of excess $Me_3SiO_3SCF_3$ (~0.15 mL, 0.7 mmol) resulted in a color change from green to red with precipitation of **[2-Me][SO$_3$CF$_3$]** in 70% yield.

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(18) Pan, W. H.; Harmer, M. A.; Halbert, T. R.; Stiefel, E. I. *J. Am. Chem. Soc.* **1984**, *106*, 459.

(19) Pan, W. H.; Halbert, T. R.; Hutchings, L. L.; Stiefel, E. I. *J. Chem. Soc., Chem. Commun* . **1985**, 927.

(20) Halbert, T. R.; Hutchings, L. L.; Rhodes, R.; Stiefel, E. I. *J. Am. Chem. Soc.* **1986**, *108*, 6437.

(21) Ansari, M. A.; Chandrasekaran, J.; Sarkar, S. *Inorg. Chem.* **1988**, *27*, 763.

(22) Gea, Y.; Greaney, M. A.; Coyle, C. L.; Stiefel, E. I. *J. Chem. Soc., Chem. Commun* **1992**, 160.

(23) Müller, A.; Diemann, K.; Rao, V. V. K. *Chem. Ber.* **1970**, *103*, 2961.

(24) Do, Y.; Simhon, D.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 4635.

(25) Müller, A.; Krickemeyer, E.; Bogge, H. *Z. Anorg. Allg. Chem.* **1987**, *554*, 61.

(26) (a) Wei, L.; Halbert, T. R.; Murray, H. H. I.; Stiefel, E. I. *J. Am. Chem. Soc.* **1990**, *112*, 6431. (b) Compounds are abbreviated using a number followed by -Me, -Et, -*i*-Pr, -*i*-Bu, etc., denoting the specific alkyl substituent of the dialkyldithio carbomate or -trithiocarbomate. When general aspects of a complex where the specific alkyl group is unimportant are discussed, only the number will be used.

(27) Rowbottom, J. F.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1974**, 684.

(28) Howard, K. E.; Lockemeyer, J. R.; Massa, M. A.; Rauchfuss, T. B.; Wilson, S. R.; Yang, X. *Inorg. Chem.* **1990**, *29*, 4385.

(29) Duggan, D. M.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 955.

Table 1. Summary of Crystallographic Parameters for Complexes **1−4**

	1-*i*-Butyl	**2-Me**	**3-*i*-Butyl**	**4-Me**
formula	$C_{44}H_{88}N_4ORe_2S_4$	$C_{18}H_{33}F_3N_6O_3Re_2S_{11}$	$C_{75}H_{150}F_{12}N_8OPRe_4S_8$	$C_{12}H_{24}ClN_4ReS_8$
crystal system	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1$ (No. 4)	$C2/c$ (No. 15)
a, Å	11.084(2)	14.238(4)	15.754(3)	13.174(4)
b, Å	13.815(3)	11.476(4)	22.505(5)	18.736(6)
c, Å	19.945(4)	14.977(5)	20.278(6)	9.826(3)
α, deg		112.28(2)		
β, deg	92.23(2)	117.70(2)	115.12(2)	96.46(2)
γ, deg		89.14(2)		
V, Å^3	3052(2)	1966(1)	6510(3)	2410(1)
Z	2	2	2	4
dens (calcd), g/cm^3	1.522	2.075	1.490	1.937
μ, mm^{-1}	4.38	6.95	4.17	5.90
transm factor range	0.607−1.000	0.372−1.000	0.279−1.000	0.77−1.00
2θ limit, deg	3.0−50.7	3.0−45.8	3.0−50.7	3.0−55.0
check reflcns: no. and freq	6, 300	6, 300	6, 300	6, 300
no. of intensities measd	5571	5424	12586	2760
no. of unique intens	5571	5424	12586	2760
no. of intens with $I > 3.0\sigma(I)$	3268	2983	7157	1998
no. params refined	301	389	1113	132
R[a]	0.043	0.057	0.049	0.043
R_w[b]	0.051	0.064	0.055	0.050

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

The red precipitate was filtered and washed with ether and dried *in vacuo*. ^{1}H NMR (CD_3CN): δ 3.753 (s, 1), 3.329 (s, 1), 3.231 (s, 1), 3.202 (s, 1), 2.861 (s, 1). Anal. Calcd for $C_{15}H_{30}F_3N_5O_3PRe_2S_{13}$: C, 15.34; H, 2.57; N, 5.96; F, 4.85; Found C, 15.82; H, 2.66; N, 5.95; F, 4.75.

Synthesis of $[Re_2(\mu\text{-}S{-}S_2CN(CH_3)_2)_2(S_2CN(CH_3)_2)_3][PF_6]$, [2-Me][PF$_6$]. $Re_2(\mu\text{-}S)_2(S_2CN(CH_3)_2)_4$ (0.5 g, 0.55 mmol) was added to 25 mL of dichloromethane and stirred for 15 min. To this solution $[(Cp)_2Fe][PF_6]$ (0.182 g, 0.54 mmol) was added giving a black mixture that was stirred for 10 min followed by addition of tetramethylthiuram disulfide (0.066 g, 0.28 mmol). The mixture was stirred overnight at room temperature. The red-brown product (0.53 g, 0.53 mmol) was isolated in 96.5% yield by reducing the volume to approximately 2 mL in vacuo and precipitating with diethyl ether. ^{1}H NMR (CD_3CN): δ 3.753 (1 H), 3.326 (1 H), 3.232 (1 H), 3.205 (1 H), 2.861 (1 H). Anal. Calcd for $C_{15}H_{30}F_6N_5PRe_2S_{15}$: C, 15.24; H, 2.56; N, 5.92; Re, 31.49; P, 2.62; F, 9.64; Found C, 14.63; H, 2.71; N, 5.38; Re, 28.53; P, 2.74; F, 4.95.

Synthesis of $[Re(S_2CN(CH_3)_2)_4][Cl]$, [3-Me][Cl]. $[Et_4N][ReS_4]$ (1.01 g, 2.25 mmol) and tetramethylthiuram disulfide (2.14 g, 8.90 mmol) were allowed to react in 100 mL of a 1:1 acetonitrile−methylene chloride mixture for 4 days. A small amount of green precipitate was filtered from the solution in the air and the green-brown filtrate was reduced in volume to 70 mL. Approximately 150 mL of THF was added to the filtrate. The resulting brown precipitate was filtered and washed with THF and diethyl ether yielding (1.33 g, 84%) a dark brown powder. Recrystallization of 0.75 g of this crude product from methylene chloride layered with THF gave (0.46 g, 62%) brown crystalline needles. ^{1}H NMR (CD_2Cl_2) δ 3.14, s. Anal. Calcd for $ReC_{12}H_{24}N_4S_8Cl$: C, 20.52; H, 3.44; N 7.98; Cl, 5.05; Found C, 20.54; H, 3.37; N, 7.88; Cl, 5.29.

$[(Re_2(\mu\text{-}S)(S_2CN(C_4H_9)_2)_4)_2(\mu\text{-}S_4)][PF_6]_2$, [4-*i*-Bu][PF$_6$]$_2$. In a nitrogen-filled glovebox crude $Re_2(\mu\text{-}S)_2(S_2CN(C_4H_9)_2)_4$ (0.50 g, 0.39 mmol), containing sulfur impurities, in 50 mL of acetonitrile had ferrocenium hexafluorophosphate (0.13 g, 0.39 mmol) added in four increments. An immediate color change from bright green to brown was observed. The mixture was stirred for 4 h. After removing solvent, the crude solid was extracted with five 25-mL portions of pentane to remove ferrocene. The fifth wash appeared colorless. A crude black product (0.52 g, 0.37 mmol) was obtained, 95% yield. X-ray quality crystals of the product cocrystallized with a microcrystalline product from slow evaporation of an acetonitrile solution.

X-ray Structure Determination. General Data. All X-ray data collection and structure solutions were carried out by Dr. Cynthia S. Day, Crystalytics Co., using a computer-controlled four-circle Nicolet autodiffractometer, normal-focus tube, Mo Kα radiation, graphite monochomator, ω scanning technique at 20 ± 1 °C. Data were reduced, corrections for Lorentz and polarization were applied, and absorption corrections were applied using ψ-scan data. Structure solutions employed heavy-atom Patterson or direct methods techniques. All calculations were performed using a Data General Eclipse S-200 employing the Nicolet (Syntex) E-XTL or SHELXTL interactive crystallographic software package modified by Crystalytics Co. Refinement involved location of hydrogens in some cases and anisotropic refinement of non-hydrogen atoms when possible. Anomalous dispersion was used for Re, S, P, F, and Cl. Other details regarding data collection and refinement are given in Table 1 and below.

$Re_2(\mu\text{-}S)_2(S_2CN(C_4H_9)_2)_4{\cdot}OC_4H_8$, 1-*i*-Bu. Green rectangular parallelepiped crystals were obtained by layering hexane over THF solutions at −20 °C. A crystal with dimensions 0.30 × 0.48 × 0.50 mm was glued inside a thin-walled glass capillary under solvent. Cell dimensions were obtained from 15 reflections of $2\theta > 20°$. The THF molecule of crystallization appears to have at least three possible orientations. These are specified as C_{s1}, C_{s2}, C_{s3}, C_{s4}, C_{s5}; C_{s1}, C_{s2}, C_{s3}, $C_{s4'}$, C_{s5}; and C_{s1}, C_{s2}, C_{s3}, C_{s4}, $C_{s5'}$. It was not possible to assign the oxygen atom to a specific ring position. Therefore, C_{s1}, C_{s2}, and C_{s3} were included in all structure factor calculations as carbon atoms with occupancies of 1.067 as were the $C_{s4'}/C_{s5}$ and $C_{s4}/C_{s5'}$ pairs whose individual occupancies were refined and normalized to this value. In the final least-squares cycle a maximum shift for all parameters was 0.15 σ_p and the average was 0.03 σ_p. The top six peaks (1.35−0.67 e$^-$/Å^3) in the final difference Fourier were within 1.12 Å of the Re atom. No other peaks above background level (0.6 e/Å^3) were observed.

$[Re_2(\mu\text{-}S{-}S_2CN(CH_3)_2)_2(S_2CN(CH_3)_2)_3][O_3SCF_3]{\cdot}CH_3CN$, [2-Me][$O_3SCF_3$]. A red-brown rectangular parallelepiped crystal (0.32 × 0.40 × 0.46 mm) was glued inside a thin-walled glass capillary. Cell dimensions were obtained from 15 reflections of $2\theta > 18°$. The ten methyl groups of the cation were refined as rigid rotors with sp^3-hybridized geometry and C−H bond lengths of 0.96 Å. The refined positions for the rigid rotor methyl groups gave N−C−H angles from 97 to 124°. The isotropic thermal parameter of each hydrogen atom was fixed at 1.2 times the equivalent isothermal parameter of the carbon atom to which it is covalently bonded. In the final least-squares cycle a maximum shift for all parameters was 0.35 σ_p and the average was 0.07 σ_p. The top four peaks (2.38−2.07 e/Å^3) in the final difference Fourier were within 1.12 Å of a Re atom. The next seven highest peaks (1.43−1.00 e/Å^3) were near the disordered CF_3SO_3 anion or Re atoms.

$[Re(S_2CN(CH_3)_2)_4][Cl]$, [3-Me][Cl]. Brown rectangular parallelepiped crystals were grown by slow evaporation of a CH_2Cl_2 solution. A crystal with dimensions 0.07 × 0.24 × 0.62 mm was glued inside a thin-walled glass capillary. Cell dimensions were obtained from 15 reflections of $2\theta > 20°$. The intensity data were corrected for absorption effects using psi scans for 5 reflections having 2θ between 5.4 and 18.6°. The four methyl groups (C_{2a}, C_{3a}, C_{2b}, and C_{3b} and their hydrogen atoms) were refined as rigid rotors with sp^3-hybridized geometry and a C−H bond length of 0.96 Å. The initial orientation of each methyl group was determined from difference Fourier, the final orientation of each methyl group was determined by three rotational parameters. The refined positions for the rigid rotor methyl groups gave N−C−H angles that ranged from 92 to 128°. In the final least-squares cycle a maximum shift for all parameters was 0.15 σ_p and the average was 0.03 σ_p. The two largest peaks (1.51−1.37 e/Å^3) in the final difference Fourier were within 1.0 Å of the Re atom. No other peaks above background level (0.65 e/Å^3) were observed.

$[(Re_2(\mu\text{-}S)(S_2CN(C_4H_9)_2)_4)_2(\mu\text{-}S_4)][PF_6]_2\cdot OC_3H_6$, [4-*i*-Bu][PF$_6$]$_2$. A green rectangular parallelepiped crystal (0.48 × 0.48 × 0.68 mm) was glued inside a thin-walled glass capillary under solvent. Cell dimensions were obtained from 15 reflections of $2\theta > 15°$. The intensity data were corrected for absorption effects using psi scans for five reflections having 2θ between 5.9 and 25.5°. The 128 non-hydrogen atoms were located using the SHELXTL Direct Methods programs. Hydrogen atoms were not located. The acetone molecule of crystallization (O_{1s}, O_{2s}, C_{1s}, C_{2s}, C_{3s}, C_{4s}, C_{5s}, C_{6s}) was refined with final occupancies of 0.5. In the final least-squares cycle the maximum shift for all parameters was 0.15 σ_p with an average of 0.05 σ_p. The top fourteen peaks (1.1−0.7 e/Å^3) in the final difference Fourier were within 1.2 Å of the Re atom. No other peaks above background level (0.6 e/Å^3) were observed.

Measurements. ^{1}H NMR spectra were obtained on a Brucker 360 MHz spectrometer. IR spectra were recorded on a Galaxy Series FTIR-5000 from Mattson. Mass spectral results[30] were obtained at Eidgenössische Technische Hochschule, Zürich, by Dr. K. Hegetschweiler using a ZAB-VSEQ spectrometer with a 8 kV acceleration voltage equipped with a VG-Cs-Ion FAB gun. Elemental analyses were performed by Galbraith Inc., E & R Microanalytical Laboratory, Inc., or Atlantic Microlab, Inc.

Electrochemistry. Electrochemical experiments were performed under argon at ambient temperature. Potentials were recorded relative to a saturated calomel reference electrode (SCE). Solutions of 0.1 M [N(*n*-Bu)$_4$][PF$_6$] in acetonitrile or dichloromethane (Burdick and Jackson or Aldrich sure-seal solvent) were used as electrolytes. Cyclic voltammetry and differential pulse polarography were carried out using a BAS 100 electrochemical analyzer and an IBM voltammetric cell containing a glassy carbon working electrode (area 16 mm^2) and a platinum wire auxiliary electrode. No corrections were made for IR drop. Under these conditions, $E_{1/2}$ for ferrocinium/ferrocene in dichloromethane was 0.449 V with anodic to cathodic peak separation showing quasi-reversible or "chemically reversible" behavior, increasing from 101 mV at a scan rate of 50 mV/s to 179 mV at 500 mV/s.

Controlled-potential electrolysis and coulometry experiments were conducted using a PAR Model 173 potentiostat, model 175 universal programmer, and Model 179 digital coulometer. A platinum mesh basket was used as the working electrode. The counter electrode for bulk reductions was platinum gauze in 0.1 M [N(*n*-Bu)$_4$][I] in acetonitrile, and for bulk oxidations, platinum gauze in 0.1 M HCl in acetonitrile or dichloromethane. Counter and reference electrodes were separated from the bulk solution by bridge tubes. Under these conditions, oxidation of ferrocene required 9.97×10^4 (standard deviation = 0.46×10^4) C/mol (six measurements). All other coulometric measurements were normalized to ferrocene. The precision of coulometric measurements is greater than 90% based on repetitive measurements of ferrocene and **1-Me**. Experimental values for the number of electrons transferred are within 20% of integer values.

Extended Hückel Calculation. Extended Hückel calculations were carried out using software by CAChe Scientific and Tektronix Inc. and visualized in three-dimensional stereoscopic projection on a Mac II-fx platform. The extended Hückel[31] calculations were carried out using the Alvarez parameters[32] for S and default values parameters[33,34] for all other atoms.

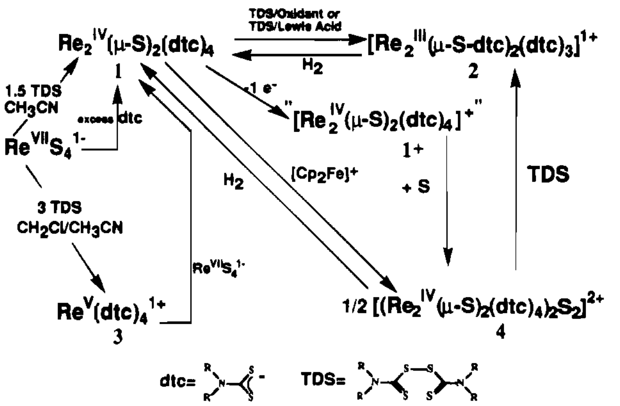

Figure 1. Reaction scheme showing the chemical interconversion of complexes **1**−**4**.

Results

In this section we describe syntheses, chemical interconversions, the structural characterization of **1-*i*-Bu**, **[2-Me]** as the **[PF$_6$]** and **[O$_3$SCF$_3$]** salts, **[3-Me][Cl]**, and **[4-*i*-Bu][PF$_6$]**, and the electrochemistry of the complexes **1-Me** and **2-Me$^+$**.

Synthesis. The overall reaction scheme for the complexes described in this paper is given in Figure 1. Most of the reactions involve induced internal electron transfer in which the metal center or centers are reduced at the expense of a sulfido (S^{2-}) ligand, which is oxidized to give a disulfido linkage or elemental sulfur. For example, ReS_4^- reacts in a 2:3 mole ratio with tetraalkylthiuram disulfide in acetonitrile at room temperature to give the Re(IV) dinuclear complex $Re_2(\mu\text{-}S)_2(S_2CNR_2)_4$, **1**, in nearly quantitative yield. In order to effect reduction of both Re and TDS, coordinated sulfide must be oxidized (not shown).

If ReS_4^- and excess TDS are allowed to react in a mixture of acetonitrile and dichloromethane (~1:1), the mononuclear Re(V) complex, $Re(S_2CNR_2)_4^+$, **3**, is obtained. In both reactions of ReS_4^- the reduced product (dtc) of the external oxidant (TDS) is coordinated to the metal in the resultant complex. Reaction of the mononuclear complexes, **3**, and ReS_4^-, gives the dinuclear complex, **1**, in good yield. Complex **1** reacts with TDS in the presence of a Lewis acid ($Et_3SiOSO_3CF_3$) or an external oxidant (Cp_2Fe^+) to give the cationic dinuclear trithiocarbamate Re(III) complex $Re_2(\mu\text{-}S{-}S_2CNR_2)_2(S_2CNR_2)_3^+$, **2**, in good yield. In an example of induced internal electron transfer in the opposite sense, **2** can be converted back to **1** in the presence of an external reducing agent, such as H_2. The electron flow in these reactions is not immediately obvious as *the metal center is reduced in the presence of an oxidant or oxidized in the presence of a reductant.*

The conversion of **1** to **2** can be carried out in two separate reactions, one-electron oxidation to form either "$Re_2(\mu\text{-}S)_2(S_2CNR_2)_4^+$" or $(Re_2(\mu\text{-}S)_2(S_2CNR_2)_4)_2S_2^{2+}$, **4**, and reaction of either of these products with TDS to form **2**. The dicationic, disulfide-bridged dimer-of-dimers, **4**, is formed when **1** is oxidized by Cp_2Fe^+ in the presence of sulfur. In the absence of sulfur, **1** can be electrochemically oxidized to give "$Re_2(\mu\text{-}S)_2(S_2CNR_2)_4^+$" in solution, a complex that, like **4**, may be a dimer-of-dimers with an S−S linkage between the bridging sulfur atoms; *vide infra*.

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(30) Hegetschweiler, K.; Keller, T.; Amrein, W.; Schneider, W. *Inorg. Chem.* **1991**, *30*, 873.

(31) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

(32) Chen, M. M. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1647.

(33) Ionization potentials come from photoelectron spectroscopy results and the exponents are from nonrelativistic Hartree-Fock atomic calculations.

(34) *CAChe Reference Manual, Version 2.8;* CAChe Scientific: Beaverton, OR, 1991; Appendix F.

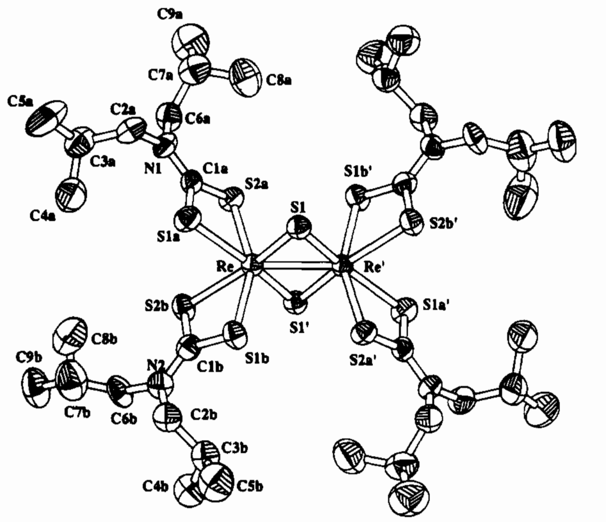

Figure 2. The molecular structure of $Re_2(\mu\text{-}S)_2(S_2CN(C_4H_9)_2)_4$, **1-*i*-Bu,** with crystallographic numbering scheme, thermal ellipsoids shown at 50% probability level. For clarity isobutyl groups are represented by one carbon atom and hydrogen atoms are not shown.

Structural Descriptions. $Re_2(\mu\text{-}S)_2(S_2CN(C_4H_9)_2)_4{\cdot}OC_4H_8$,1-*i*-Bu. This dinuclear complex contains a $Re_2(\mu\text{-}S)_2$ core with each six-coordinate Re center bound to two chelating monoanionic dialkyldithiocarbamate ligands, $S_2CNR_2^-$ = dtc, as shown in Figure 2. The complex has C_{2h} symmetry and lies on a crystallographic inversion center located at the center of the planar $Re_2(\mu\text{-}S)_2$ core. The mirror plane is perpendicular to the Re−Re bond and bisects the bridging sulfur atoms. Each Re center is coordinated to six sulfur atoms in approximate octahedral coordination. The coordination structures of the two metals constitute an edge-shared bioctahedron[35] with the arrangement of the chelating dtc ligands giving the molecule a meso configuration. The Re−Re and Re−(μ-S) distances are 2.546(1) and 2.275(3) Å, respectively. The short Re−Re distance is comparable to that of $Re_2Cl_4(\mu\text{-}SEt)_2(EtS(CH_2)_2SEt)_2$, 2.592 Å, and is consistent with multiple metal−metal bonding.[36] The Re atoms are displaced from the S_6 octahedron in the direction of the bridging edge of the bioctahedron to form the Re−Re bond, a phenomenon also observed in rhombohedral ReS_2.[37] The complex is diamagnetic as observed by its ^1H NMR spectrum, consistent with Re−Re multiple bonding. The formal Re−Re bond order may be two or three, as each Re atom has a d^3 electronic configuration;[36,38] *vide infra.* Sulfur atoms of the dtc ligand *trans* to the bridging sulfide ions are 2.511(3) and 2.519(3) Å from the Re compared to 2.424(3) and 2.430(3) Å for the other chelating sulfur−rhenium distances, respectively. The S−C bond lengths fall within a narrow range (1.70−1.74 Å) as do the dithiocarbamate C−N bond distances (1.34−1.36 Å). All other C−N and C−C bond distances of the dimer are unremarkable. See Table 2 for selected bond distances and angles.

The arrangement of terminal chelating dtc ligands in the X-ray structure of **1** defines a meso diastereoisomer with Λ and Δ configurations, respectively, at the two metal centers. This type of stereoisomerism has been previously recognized for *N*-chelate complexes[39−41] such as $(N\text{-}N)_2M(\mu\text{-}X)_2M(N\text{-}N)_2$,$Ru(N\text{-}N)_2$ WS_4, and $Ru(N\text{-}N)_2(SR)_2$ (e.g., N-N = en, 2,2′-bipyridine; X = OH, S; M = Cr, Ru, R= Et, Ph, C_6H_4Me-*p* or CMe_3).[42,43] ^1H NMR of **1-*i*-Bu** indicates two sets of resonances for *i*-Bu_2NCS_2 with a 1:1 ratio indicative of a pure diastereoisomer, while that of **1-Me** and **1-Et** reveal the presence of two diastereoisomers.

Table 2. Selected Bond Distances (Å) and Angles[a] (deg) for $Re_2(\mu\text{-}S)_2(S_2CN(C_4H_9)_2)_4$, **1-*i*-Bu**

	Bond Distances		
Re−Re′	2.546(1)	Re−S1	2.275(3)
Re−S1′	2.273(3)	Re−S1b	2.424(3)
Re−S1a	2.511(3)	Re−S2b	2.519(3)
Re−S2a	2.430(3)	S2b−C1b	1.70(1)
S1a−C1a	1.70(1)	C1b−N1	1.36(1)
C1a−N1	1.34(1)	N2−C2b	1.45(2)
N1−C2a	1.48(1)	N2−C6b	1.50(2)
N1−C6a	1.48(2)		
	Bond Angles		
Re′−Re−S1	55.9(1)	S1−Re−S1′	111.9(1)
Re′−Re−S1′	56.0(1)	S1−Re−S1a	84.6(1)
Re′−Re−S1a′	139.5(1)	S1−Re−S2a	95.7(1)
Re′−Re−S2a′	102.0(1)	S1−Re−S1b	97.0(1)
Re′−Re−S1b′	103.5(1)	S1−Re−S2b	162.9(1)
Re′−Re−S1b′	136.9(1)	S1′−Re−S1a	161.1(1)
S1a−Re−S1b	88.6(1)	S1′−Re−S2a	97.6(1)
S1a−Re−S2b	83.6(1)	Re−S1−Re	68.1(1)

[a] Atoms labeled with a prime are related to nonprimed atoms by the crystallographic inversion center at 0, 0, 0. Numbers in parentheses are esd's.

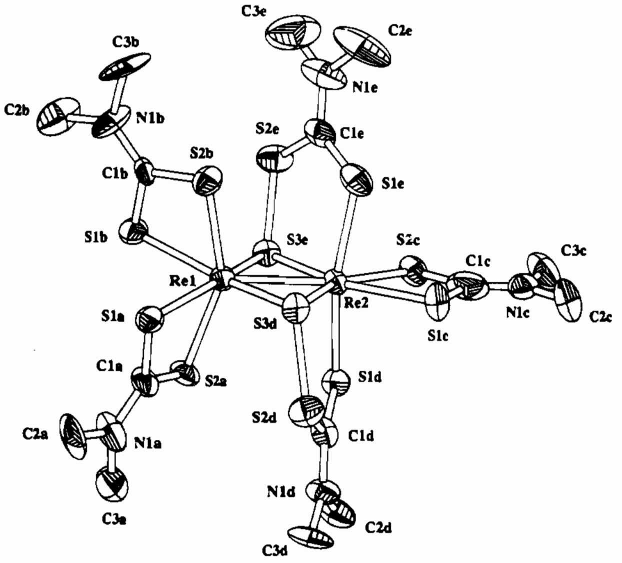

Figure 3. Molecular structure of $[Re_2(\mu\text{-}S{-}S_2CN(CH_3)_2)_2(S_2CN(CH_3)_2)_3][SO_3CF_3]$, **[2-Me][O$_3SCF_3$]**, with crystallographic numbering scheme, thermal ellipsoids shown at 50% probability level. For clarity hydrogen atoms are not shown.

Interestingly, the Re_2S_{10} cores of **1** and **2** may be viewed as two sulfur monolayers of five atoms each sandwiching the two rhenium atoms. This layered arrangement and the multiple bonded nature of $Re^{IV}{}_2(\mu\text{-}S)_2$ presents the same general appearance as a portion of the lattice of layered ReS_2; *vide infra.*

$[Re_2(\mu\text{-}S{-}S_2CN(CH_3)_2)_2(S_2CN(CH_3)_2)_3][O_3SCF_3]{\cdot}CH_3CN$, [2-Me][O$_3SCF_3$]. This cationic dinuclear edge-shared bioctahedral complex has C_2 symmetry and contains a dinuclear Re−Re center with three chelating dialkyldithiocarbamate ligands and two chelating and bridging dialkyltrithiocarbamate

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(35) Canich, J. A. M.; Cotton, F. A. *Inorg. Chem.* **1987**, *26*, 4236.
(36) Heyen, B. J.; Powell, G. L. *Inorg. Chem.* **1990**, *29*, 4574.
(37) (a) Wildervanck, J. C.; Jellinek, F. *J. Less Common Met.* **1971**, *24*, 73. (b) Murray, H. H.; Kelty, S. P.; Chianelli, R. R.; Day, C. S. *Inorg. Chem.* **1994**, *33*, 4418.
(38) Cotton, F. A. *Polyhedron* **1987**, *6*, 667.
(39) Saito, Y. *Top. Stereochem.* **1978**, *10*, 95.
(40) Springborg, J. *Adv. Inorg. Chem.* **1988**, *32*, 55.
(41) Greaney, M. A.; Coyle, C. L.; Harmer, M. A.; Jordan, A.; Stiefel, E. I. *Inorg. Chem.* **1989**, *28*, 912.
(42) Bunzey, G.; Enemark, J. H.; Howie, J. K.; Sawyer, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 4168.
(43) Given, K. W.; Mattson, B. M.; McGuiggan, M. F.; Pignolet, L. H. *J. Am. Chem. Soc.* **1977**, *99*, 4855.

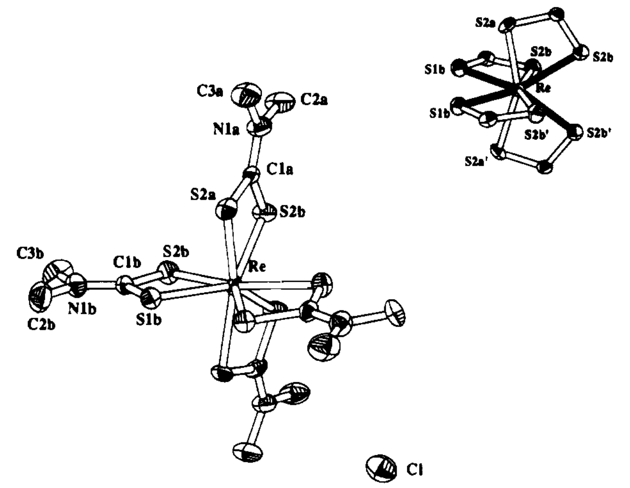

Figure 4. Molecular structure of $[Re(S_2CN(CH_3)_2)_4][Cl]$, **[3-Me][Cl]**, with crystallographic numbering scheme, thermal ellipsoids shown at 50% probability level. Inset (upper right) is view of **[3-Me][Cl]** emphasizing the interpenetrating tetrahedra in the dodecahedral structure. For clarity hydrogen atoms are not shown.

Table 3. Selected Distances (Å) and Angles (deg) for $[Re_2(\mu\text{-}S{-}S_2CN(CH_3)_2)_2(S_2CN(CH_3)_2)_3][O_3SCF_3]\cdot CH_3CN$, **$[2\text{-}Me][O_3SCF_3]$**

	Distances		
Re1–Re2	2.573(2)	S43···S53	3.781(7)
Re1–S11	2.484(9)	Re2–S31	2.471(8)
Re1–S12	2.421(6)	Re2–S32	2.505(9)
Re1–S21	2.485(7)	Re2–S41	2.400(6)
Re1–S22	2.39(5)	Re2–S51	2.39(4)
Re1–S43	2.294(6)	Re2–S43	2.55(9)
Re1–S53	2.319(8)	Re2–S53	2.279(6)
	Bond Angles		
Re2–Re1–S11	136.9(2)	Re1–Re2–S31	142.5(2)
Re2–Re1–S12	104.9(2)	Re1–Re2–S32	146.5(2)
Re2–Re1–S21	137.5(2)	Re1–Re2–S41	95.8(2)
Re2–Re1–S22	103.8(2)	Re1–Re2–S43	56.3(2)
Re2–Re1–S43	54.8(2)	Re1–Re2–S51	95.9(2)
Re2–Re1–S53	55.2(2)	Re1–Re2–S53	56.7(2)
S41–Re2–S43	91.9(2)	S51–Re2–S53	90.8(2)
S41–Re2–S51	168.3(3)	S41–Re2–S53	94.7(2)
S43–Re2–S51	95.5(3)	S43–Re2–S53	113.0(3)
S11–Re1–S12	71.0(3)	S21–Re1–S22	71.0(2)
S31–Re2–S32	71.1(3)	S51–Re2–S53	90.8(2)
S41–Re2–S43	91.9(2)		

ligands, as shown in Figure 3. The disulfide termini of the dialkyltrithiocarbamate ligands bridge the two rhenium centers. The two different rhenium centers are each octahedrally coordinated by sulfur atoms with some axial distortion. One Re center is bound to two chelating dialkyldithiocarbamate ligands and the two bridging sulfur atoms from the disulfide termini of the dialkyltrithiocarbamate ligand. The other Re center is coordinated to one chelating dialkyldithiocarbamate ligand and two sulfur atoms from each of two chelating dialkyltrithiocarbamate ligands; i.e., the "sulfur rich" ligands contain a disulfide linkage and are both chelating and bridging ($\mu\text{-}S{-}S_2CN(CH_3)_2$) to this Re center. The Re–Re distance is 2.573(2) Å, slightly longer than the Re–Re distance of **1-*i*-Bu**. The Re–S bond distances of the chelating dialkyldithiocarbamate ligands that are *trans* to the bridging sulfur atom range from 2.471(8) to 2.505(9) Å (average of 2.486 Å) while those that are not *trans* to the bridging sulfur atom are 2.421(6) and 2.395(7) Å, respectively. The S–S distances are 2.264(7) and 2.194(7) Å. All bond distances associated with dialkyldithiocarbamate fragments are unremarkable. See Table 3 for selected bond distances and angles. Two Os analogs of **2** have been synthesized in low yield and structurally characterized, $[Os_2(\mu\text{-}S{-}S_2CN(C_2H_5)_2)_2(S_2CN(C_2H_5)_2)_3][B(C_6H_5)_4]$ and $[Os_2(\mu\text{-}S{-}S_2CN(CH_3)_2)_2(S_2CN(CH_3)_2)_3][PF_6]\cdot C_7H_8$.[44,45] The Os–Os distance reported as 2.792 Å.

The structure of **2** in the solid state is consistent with the observation of five singlet methyl resonances in the ^1H NMR spectrum in solution. An interesting feature of **2** is its nearly layered structure, wherein sulfur atoms form two sulfur layers with Re atoms in the trigonal antiprismatic sites as in the meso isomer of **1**; *vide infra*.

$[Re(S_2CN(CH_3)_2)_4][Cl]$, [3-Me][Cl]. X-ray analysis of the complex revealed discrete $Re(S_2CN(CH_3)_2)_4^+$ and Cl^- ions. The eight-coordinate rhenium center is chelated by four dialkyldithiocarbamate ligands which supply eight sulfur donor atoms. One pair of S_2CN groups of dialkyldithiocarbamate ligands (dtc ligands containing S1b, S2b, S1b′, and S2b′, inset of Figure 4) is nearly planar and perpendicular to the other pair of chelating ligands (dtc ligands containing S1a, S2a, S1a′ and S2a′, inset of Figure 4). Two sets of dithiocarbamate sulfur atoms (S1a, S1a′ and S1b, S1b′) define collapsed (dark) and elongated tetrahedra (S2a, S2a′ and S2b, S2b′), respectively, (see Figure 4, inset). The angle formed between the planes defined by the sulfur atoms of "equatorial" pairs of dialkyldithiocarbamate ligands (S1a, S1a′, S2a′ and S2a) and (S1b, S1b′, S2b′ and S2b) is 86.7°, slightly distorted from the 90° for ideal D_{2d} symmetry. Similar deviations in this parameter (e.g., 89.4° for $Mo(S_2CNEt_2)_4^+$,[46] 89.4° for $Ta(S_2CNMe_2)_4^+$,[47]) have been reported. The average displacement of sulfur atoms of "equatorial" pairs of dialkyldithiocarbamate ligands from the plane is 0.128 Å, a significant distance compared to 0.03–0.05 Å for $Ta(S_2CNMe_2)_4^+$.[47] Using the nomenclature of Hoard and Silverton,[48] these chelates span the four *m* edges of an idealized D_{2d} dodecahedron giving the *mmm*-D_{2d} stereoisomer[49] that is common for tetrakis(dialkyldithiocarbamate) complexes[46,47,50–52] of early transition elements (e.g., $Ta(S_2CNMe_2)_4^+$,[47] $Nb(S_2CNEt_2)_4^+$,[51] $Mo(S_2CNEt_2)_4^+$,[46] $W(S_2CNEt_2)_4^+$,[52] and $Ti(S_2CNEt_2)_4$).[50] The average $Re{-}S_A$ (S_{1b}, $S_{1b'}$, S_{1a}, $S_{1a'}$) distance (2.492(2) Å) is longer than the average $Re{-}S_B$ (S_{2b}, $S_{2b'}$, S_{2a}, $S_{2a'}$) distance (2.478(3) Å). This reflects the repulsion by atoms at A sites, a common structural feature of this dodecahedral geometry. Other bond distances of the molecule are not unusual and are shown in Table 4. In solution, **[3-Me][Cl]** is nonrigid on the NMR time scale at room temperature. Its ^1H NMR spectrum exhibits a sharp singlet at $\delta = 3.14$, upfield from that of the $Ta(S_2CNME_2)_4^+$ cation[47] ($\delta = 3.40$).

$[(Re_2(\mu\text{-}S)(S_2CN(C_4H_9)_2)_4)_2(\mu\text{-}S_4)][PF_6]_2\cdot OC_3H_6$, $[4\text{-}i\text{-}Bu][PF_6]_2$. This dicationic complex is most simply described as a dimer-of-dimers formed by bridging two $Re_2(\mu\text{-}S)_2(S_2CN(C_4H_9)_2)_4$ complexes through a S–S chain containing one of the bridging sulfides of each dimer unit (Figure 5). The average Re–S bond distance for the bridging sulfido ligands is 2.231 Å compared to 2.319 Å for the Re–S bond to the terminal sulfur atom of the S_4^{2-} bridge. The central S–S bond distance of the S_4^{2-} ligand is 2.000(7) Å. The other two S–S distances are 2.128 and 2.132 Å, respectively. The Re–Re bond distances are 2.615(1) and 2.624(1) Å. See Table 5 for selected bond

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(44) Maheu, L. J.; Pignolet, L. H. *Inorg. Chem.* **1979**, *18*, 3626.

(45) Maheu, L. J.; Pignolet, L. H. *J. Am. Chem. Soc.* **1980**, *102*, 6346.

(46) Garner, C. D.; Howlader, N. C.; Mabbs, F. E.; McPhall, A. T.; Miller, R. W.; Onan, K. D. *J. Chem. Soc., Dalton Trans.* **1978**, 1582.

(47) Lewis, D. F.; Ray, R. C. *Inorg. Chem.* **1976**, *15*, 2219.

(48) Hoard, J. L.; Silverton, J. V. *Inorg.Chem.* **1963**, *2*, 235.

(49) Lippard, S. J.; Russ, B. J. *Inorg. Chem.* **1968**, *7*, 1686–8.

(50) Colapietro, M.; Vaciago, A.; Bradley, D. C.; Hursthouse, M. B.; Rendall, I. F. *J. Chem. Soc., Dalton Trans* **1972**, 1052.

(51) Drew, M. G. B.; Rice, D. A.; Williams, D. M. *J. Chem. Soc., Dalton Trans.* **1985**, 1821.

(52) Wijnhovan, J. G. *Cryst. Struct. Commun.* **1973**, *2*, 637.

Table 4. Selected Bond Distances (Å) and Angles[a] (deg) for $[Re(S_2CN(CH_3)_2)_4][Cl]$, **[3-Me][Cl]**

	Bond Distances		
Re−S1a	2.492(2)	Re−S1b	2.493(2)
Re−S2a	2.488(2)	Re−S1b	2.468(3)
S1a−C1a	1.702(9)	S1b−C1b	1.721(9)
S2a−C1a	1.710(9)	S2b−C1b	1.674(10)
	Bond Angles		
S1a−Re−S2a	67.8(1)	S1b−Re−S2b	68.2(1)
S1a−Re−S1b	136.2(1)	S1b−Re−S1a′	127.7(1)
S1a−Re−S1a′	79.9(1)	S1b−Re−S2a′	79.1(1)
S1a−Re−S1a′	70.7(1)	S1b−Re−S1b′	70.5(1)
S1a−Re−S2a′	137.5(1)	S1b−Re−S2b′	137.7(1)
S2a−Re−S1b	80.2(1)	S2b−Re−S1a′	79.0(1)
S2a−Re−S2b	85.5(1)	S2b−Re−S2a′	100.3(1)
S2a−Re−S2a′	154.5(1)	S2b−Re−S2b′	154.0(1)

[a] Atoms labeled with a prime are related to nonprimed atoms by the crystallographic inversion center at 0, 0, 0 in the unit cell.

distances and angles for **[4-*i*-Bu][PF$_6$]$_2$**. We have found no crystallographically characterized examples of dimers coupled by a single tetrasulfido linkage.[53] However, there is a gold ylide dimer-of-dimers linked by two tetrasulfido bridges and another linked by tetra- and pentasulfido linkages.[54] However, in the gold structures, the terminal sulfur atoms of the dimer-of-dimers bridge are not bridging within each dimer as in the rhenium tetranuclear complex described here.

Electrochemistry. Complexes **1-Me** and **2-Me** were examined electrochemically (cyclic voltammetry and differential pulse polarography) to investigate other accessible redox states. On the basis of these data, coulometric−chemical reactions were conducted to sort out the redox and coordination chemistry in the interconversion of **1-Me** and **2-Me**. The electrochemistry of **1-Me** and **2-Me** is presented first followed by the coulometric-chemical interconversion study.

Electrochemistry of 1-Me. The cyclic voltammogram and differential pulse polarogram between +1.00 and −1.40 V of **1-Me** are shown in Figure 6 (Table 6). Complex **1-Me** exhibits two reversible oxidation waves at 0.17 and 0.76 V, respectively, and one partially reversible reduction wave at −1.15 V. When the scan speed is faster than 50 mV/s, a third oxidation wave appears at a potential between the two oxidation waves (0.17 and 0.76 V, see Figure 6). The magnitude of this wave correlates with a concomitant decrease in magnitude of the wave at 0.76 V.

The addition of sulfur to **1-Me** significantly affects the cyclic voltammetry. Specifically, the reduction wave at −1.15 V becomes more irreversible and several new irreversible waves appear. (Figure 7a) The cyclic voltammogram of sulfur under the same conditions is given in Figure 7b. The voltammogram of **1-Me** with added sulfur is similar in appearance to that of crude **1-Me**. Interestingly, the ^{1}H NMR spectra of **1-Me** with and without added sulfur are virtually indistinguishable.

Electrochemistry of 2-Me. The cyclic votammograms of **2-Me** in acetonitrile between +1.10 and −1.00 V are shown in Figure 8 (Table 6, CH_2Cl_2 solvent). In this region two major redox events are seen, one reversible reduction wave and one partially reversible oxidation wave occurring at −0.59 and 0.74 V, respectively. A minor irreversible oxidation at 0.22 V is also observed. The irreversible oxidation at 0.22 V disappears when the voltammogram is run in the positive direction, indicating that this wave is due to the product of a chemical reaction that follows reduction. The current of the partially reversible wave at −0.59 V is much greater than that observed at 0.74 V. Clearly, both processes cannot be simple one-electron transfers. The greater peak width of the −0.59 V wave compared to the oxidation wave at 0.74 V by differential pulse polarography is consistent with the occurrence of two one-electron reductions at similar potentials.[55]

When the scan range is extended to −1.40 V a new reduction wave is found at −1.09 V. When the scan rate is slowed this wave at −1.09 V becomes more reversible and the reduction wave at −0.59 V becomes less reversible. At a scan speed of 10 mV/s, the latter reduction wave is completely irreversible (Figure 8b). The new wave at −1.09 V occurs at the same potential as the reduction wave for **1-Me**, see Figure 6, indicating that the irreversibility of the −0.59 V wave is due to a chemical reaction (or reactions) that follow reduction. An explanation of this irreversible electrochemical wave consistent with the chemistry of **2-Me** invokes two one-electron reductions followed by loss of one mole of dimethyldithiocarbamate and rearrangement generating **1-Me,** an EEC process. The slower scan rate allows sufficient time for the reduced product to undergo chemical reaction(s), resulting in the formation of **1-Me**.

Electrochemical Interconversion of 1-Me to 2-Me. The schematic diagram for the electrochemical conversion of **1-Me** to **2-Me** is given in Figure 9. To investigate the conversion of **1-Me** to **2-Me**, controlled-potential electrolysis/coulometry of **1-Me** oxidation at 300 mV was carried out (in acetonitrile and dichloromethane, respectively). In the absence of sodium dimethyldithiocarbamate a one-electron oxidized (n = 0.86 e$^-$; standard deviation = 0.04) olive green product (**1-Me$^+$**) resulted. The cyclic voltammetry of **1-Me$^+$**, Table 4, is identical to that of **1-Me**, except that the rest potential of the cation is at a more positive value (+0.26 V) than the neutral parent complex.

In the presence of 1.0−1.2 molar equiv of sodium dimethyldithiocarbamate, controlled-potential electrolysis of **1-Me** at 300 mV leads to the formation of **2-Me** (confirmed by ^{1}H NMR spectroscopic, UV−visible spectroscopic, and cyclic voltammetric analysis) at a rate dependent on the concentration (1.5×10^{-3} to 3.8×10^{-4} M) of **1-Me**. Coulometric oxidation of **1-Me** in the presence of 1.2 equiv of sodium dimethyldithiocarbamate gave n = 1.62 e$^-$, approximately double the number of electrons passed from the electrode when **1-Me** alone is electrolyzed. Thus, in the presence of sodium dimethyldithiocarbamate, two-electron oxidation of **1-Me** results in the formation of **2-Me**.

To further probe the transformation of **1-Me** to **2-Me** the reaction was carried out in three steps, Figure 9. First, the electrochemical oxidation (controlled-potential electrolysis) of **1-Me** was limited to formation of the olive green, one-electron oxidized product **1-Me$^+$** (n = 0.86 e$^-$). Second, 1.3 equiv of sodium dimethyldithiocarbamate was added to **1-Me$^+$**. An immediate color change was observed, from olive green to bright green indicative of **1-Me** formation consistent with the redox activity of sodium dimethyldithiocarbamate, which exhibits irreversible oxidation at 0.07 V. The reaction between the olive green species, **1-Me$^+$**, and sodium dimethyldithiocarbamate is therefore a redox reaction which produces **1-Me** and tetramethylthiuram disulfide. In the final step, **2-Me** was produced by coulometric oxidation at 300 mV of the solution of **1-Me** and thiuram disulfide (n = 0.82 e$^-$ based on the number of equivalents of added dithiocarbamate). In this final step, the one-electron electrochemical oxidation product of **1-Me, 1-Me$^+$**,

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(53) Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Mitchell, E. M.; Mitchell, G. F.; Smith, J. M.; Watson, D. G. *J. Chem. Inf. Comp. Sci.* **1991**, *31*, 187.

(54) Fackler, J. P., Jr; Porter, L. C. *J. Am. Chem. Soc.*, **1986**, *108*, 2750.

(55) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York: 1980.

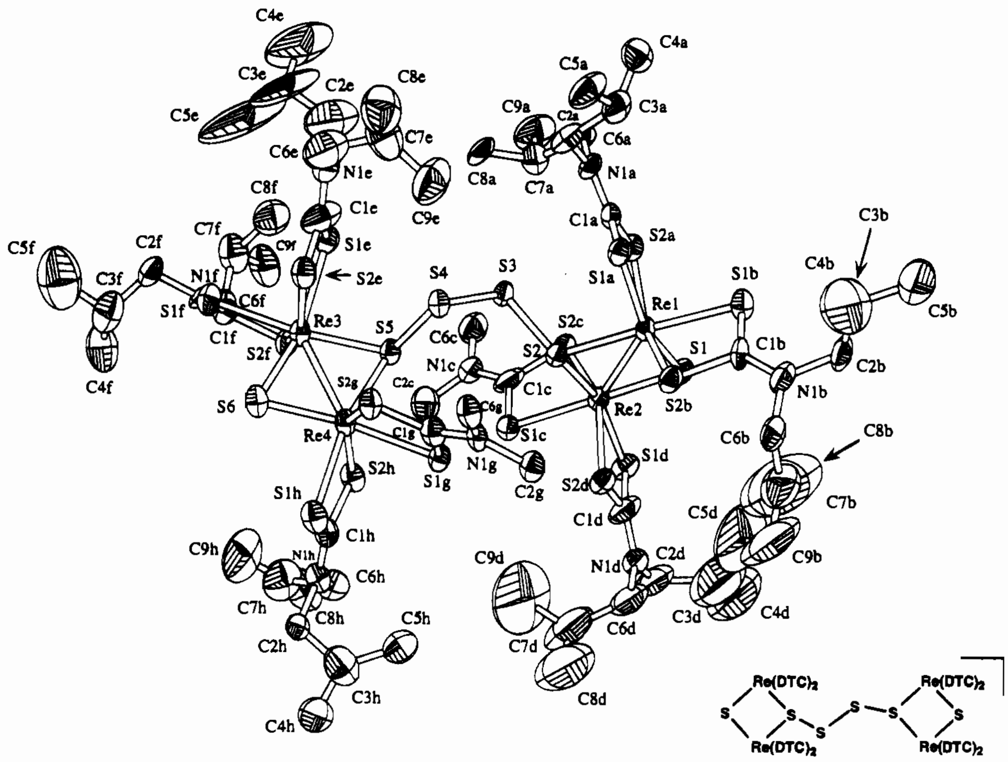

Figure 5. Molecular structure of [(Re$_2$(μ-S)(S$_2$CN(C$_4$H$_9$)$_2$)$_4$)$_2$(μ-S$_4$)][PF$_6$] $_2$•OC$_3$H$_6$, **[4-*i*-Bu][PF6]2**, with crystallographic numbering scheme and thermal ellipsoids shown at 50% probability level. For clarity, hydrogen atoms are not shown.

Table 5. Selected Bond Distances (Å) and Angles (deg) for [(Re$_2$(μ-S)(S$_2$CN(C$_4$H$_9$)$_2$)$_4$)$_2$(μ-S$_4$)][PF$_6$]$_2$•OC$_3$H$_6$, **[4-*i*-Bu][PF$_6$]$_2$**

	Bond Distances		
Re1−Re2	2.615(1)	Re3−Re4	2.624(1)
Re1−S1	2.227(7)	Re3−S6	2.220(7)
Re2−S1	2.242(6)	Re3−S6	2.235(6)
Re1−S2	2.315(5)	Re3−S5	2.313(5)
Re2−S2	2.317(6)	Re4−S5	2.333(6)
Re1−S1a	2.504(7)	Re3−S1e	2.496(7)
Re1−S2a	2.424(6)	Re3−S2e	2.434(8)
Re1−S1b	2.509(6)	Re3−S1f	2.479(6)
Re1−S2b	2.342(6)	Re3−S2f	2.384(6)
Re2−S1c	2.504(6)	Re4−S1g	2.495(5)
Re2−S2c	2.431(5)	Re4−S1g	2.420(6)
Re2−S1d	2.475(8)	Re4−S1g	2.488(8)
Re2−S2d	2.370(6)	Re4−S1g	2.363(8)
S2−S3	2.128(7)	S3−S4	2.000(7)
S4−S5	2.132(9)		
	Bond Angles		
Re1−S2−Re2	68.7(1)	Re3−S5−Re4	68.8(1)
Re1−S1−Re2	71.6(2)	Re3−S6−Re4	72.2(2)
Re1−S2−S3	111.9(3)	Re3−S5−S4	110.7(3)
Re2−S2−S3	113.4(2)	Re4−S5−S4	112.4(3)
S5−S4−S3	100.2(4)	S2−S3−S4	100.9(3)

reacted with tetramethylthiuram disulfide giving **2-Me**. In the absence of electrochemical oxidation of **1-Me** under these same conditions, **1-Me** and tetramethylthiuram disulfide do not give **2-Me**.

The slow *chemical* redox process between **1-Me**$^+$ and tetramethylthiuram disulfide giving **2-Me** can be monitored spectrophotometrically as shown in Figure 10. The initial spectrum of **1-Me**$^+$ shows an absorption maximum at 646 nm and a shoulder at 404 nm. The final spectrum with an absorption maximum at 413 nm and a shoulder at approximately 480 nm is identical to that of **2-Me**. As the spectrum of the olive-green species diminishes with time, an isosbestic point at 533 nm is observed, consistent with clean conversion of reactant to product.

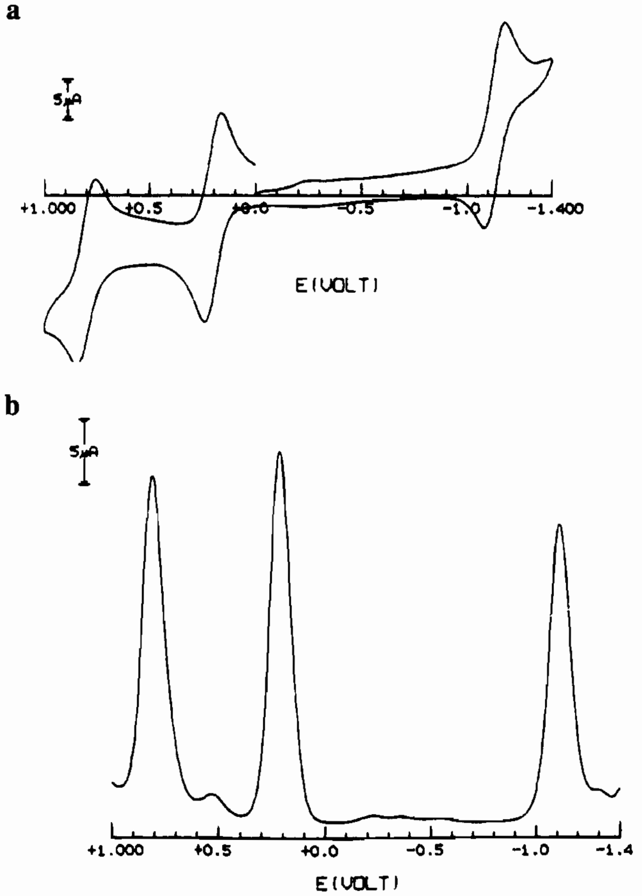

Figure 6. (a) Cyclic voltammetry (+1.0 to −1.4 V) , scan rate 50 mV/s, and (b) differential pulse polarography (+1.0 to −1.4 V), pulse amplitude 50 mV, of **1-Me** in dichloromethane.

Electrochemical Interconversion of 2-Me to 1-Me. Controlled-potential electrolysis of **2-Me** in acetonitrile at −800 mV produced an immediate change in the color of the solution from

Table 6. Cyclic Voltammetric Data[a]

complex	ΔE_p,[b] mV	$E_{1/2}$,[c] V	i_a/i_c
1-Me	72	+0.76	1.11
	66	+0.17	0.95
	79	−1.15	0.73
2-Me	84	+0.74	0.98
	146	−0.59	0.91
1-Me+	92	+0.77	0.97
	77	+0.19	0.97
	91	−1.11	0.79

[a] CH_2Cl_2 solvent, 50 mV/s scan rate. [b] $\Delta E_p = E_{p,a} - E_{p,c}$. [c] $E_{1/2} = (E_{p,a} + E_{p,c})/2$ vs SCE.

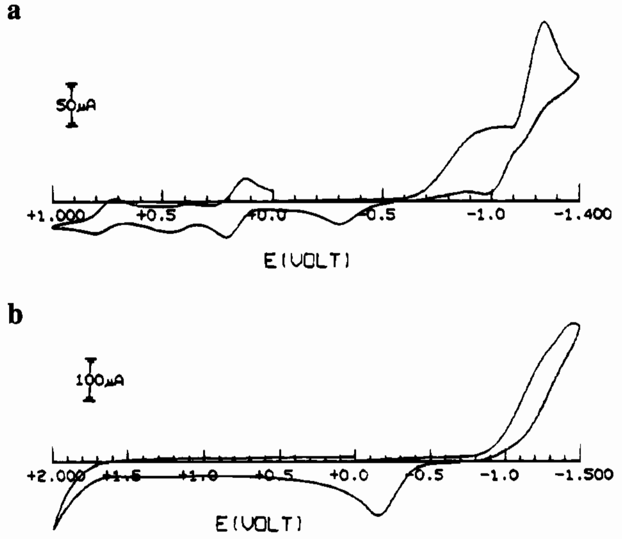

Figure 7. (a) Effect of adding sulfur to **1-Me** on the cyclic voltammogram (+1.0 to −1.4 V). (b) cyclic voltammogram (+2.0 to −1.5 V) of S_8.

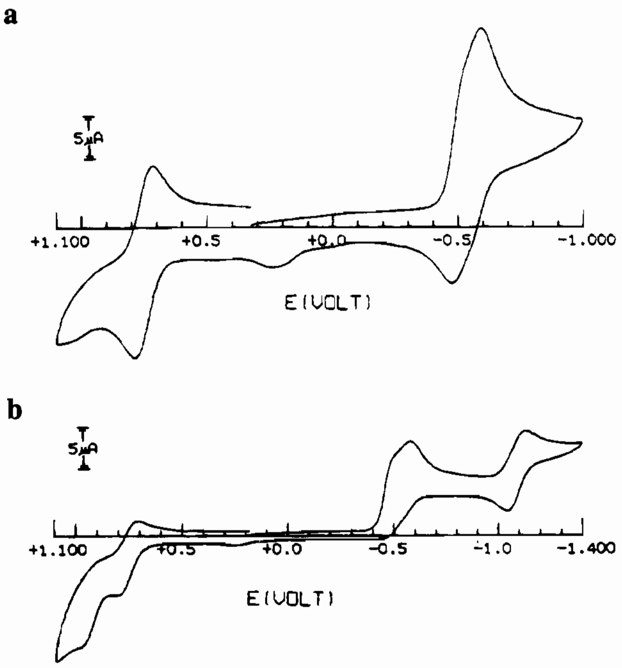

Figure 8. Cyclic voltammetry of **2-Me**$^+$: (a) +1.1 to −1.0 V, 50 mV/s; (b) +1.1 to −1.4 V, 10 mV/s.

red to green and a green solid precipitated. ^{1}H NMR, cyclic voltammetric, and UV−visible spectroscopic analyses of the solid product confirmed the formation of **1-Me**. Coulometric reduction of **2-Me** in acetonitrile at -700 mV gave n = 2.32 e$^-$.

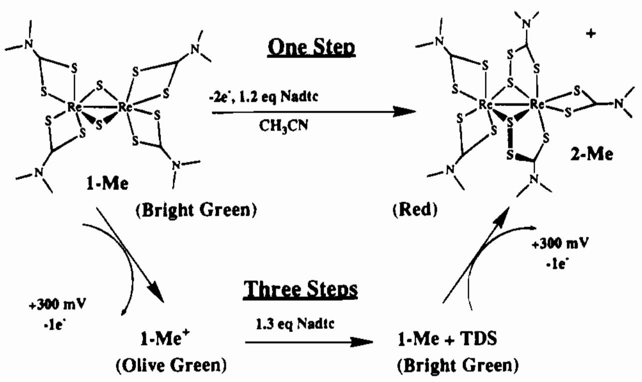

Figure 9. Interconversion scheme of **1-Me** and **2-Me**$^+$.

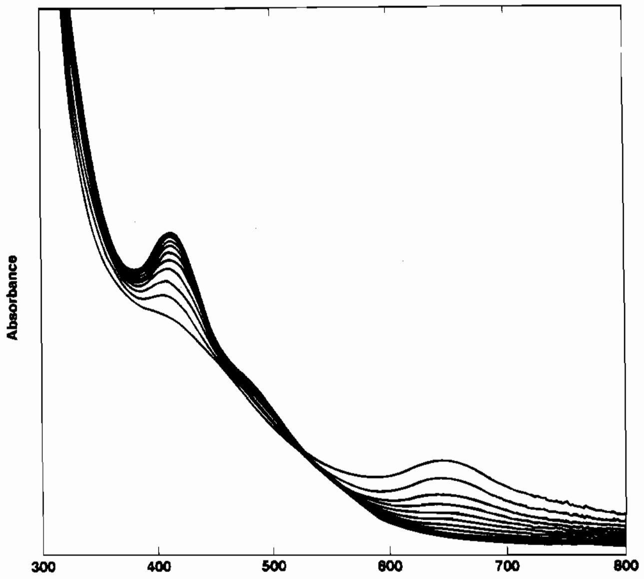

Figure 10. Spectral changes (UV−vis) in the reaction of **1-Me**$^+$ (generated electrochemically) with tetramethylthiuram disulfide (2 × 10^{-4} M) at ambient temperature. Spectra were recorded every 40 min.

Discussion

Electron Balance for the Synthesis of Complexes 1−4. $Re_2(\mu\text{-}S)_2(S_2CNR_2)_4$, 1. Consideration of stoichiometry alone suggests that a 1:1 ratio of ReS_4^- to tetraalkylthiuram disulfide is needed to give the complex with a 1:2 Re:dtc ratio. However, when the mole ratio of TDS to ReS_4^- in acetonitrile is increased from 1:1 to 3:2, the yield of crude product increases from 60% to nearly 100%. The use of excess oxidant, tetraalkylthiuram disulfide, to effect the *reduction* of the metal center (Re^{VII} to Re^{IV}) may be explained by the electron balance of the reaction in eq 1. (In this and other reactions "S" is likely to be some poly-S species which may be combined with some of the dtc produced in the form of mixed polysulfido−$S_2CNR_2^-$ species.)-

$$2ReS_4^- + 3[S_2CNR_2]_2 \rightarrow Re_2(\mu\text{-}S)_2(S_2CNR_2)_4 + 6\text{“S”} + 2S_2CNR_2^- \quad (1)$$

electron balance:

$$2Re^{VII} \rightarrow 2Re^{IV} \text{ six-electron reduction}$$

$$3[S_2CNR_2]_2 \rightarrow 6S_2CNR_2^- \text{ six-electron reduction}$$

$$6S^{2-} \rightarrow 6\text{“S” 12-electron oxidation}$$

Clearly, a 3:2 mole ratio of TDS to $\mathrm{ReS_4^-}$ provides the required number of equivalents to oxidize six coordinated sulfides in two $\mathrm{ReS_4^-}$ to elemental sulfur. Although a balanced equation can be written for the 1:1 reaction, the higher yields obtained in the 3:2 reaction suggest that the oxidation of sulfide is a requisite accompaniment to the reaction of $\mathrm{ReS_4^-}$ with TDS. The reaction of $\mathrm{ReS_4^-}$ and TDS occurs in the absence of air. Interestingly, we have found that in the presence of air the $\mathrm{ReS_4^-}$ and dtc react to form the same green product. No reaction occurs when the same reaction is carried out in argon. Presumably air oxidizes one or both reactants allowing the internal redox to occur.

$$2\mathrm{ReS_4^-} + 4\mathrm{S_2CNR_2^-} \rightarrow \mathrm{Re_2(\mu\text{-}S)_2(S_2CNR_2)_4} + 3\mathrm{S_2^{2-}} \qquad (2)$$

electron balance:

$$2\mathrm{Re^{VII}} \rightarrow 2\mathrm{Re^{IV}} \text{ six-electron reduction}$$

$$6\mathrm{S^{2-}} \rightarrow 3\text{``}\mathrm{S_2^{2-}}\text{''} \text{ six-electron oxidation}$$

In this reaction "$\mathrm{S_2^{2-}}$" is likely to be some poly-S species.

Yet another synthetic route to $\mathrm{Re_2(\mu\text{-}S)_2(S_2CNR_2)_4}$ involves the reaction of $\mathrm{ReS_4^-}$ with $\mathrm{[Re(S_2CNR_2)_4]^+}$ in 1:1 ratio. The electron balance for this reaction is given below in reaction 3.

$$\mathrm{ReS_4^-} + \mathrm{Re(S_2CNR_2)_4^+} \rightarrow \mathrm{Re_2(\mu\text{-}S)_2(S_2CNR_2)_4} + 2\mathrm{S} \qquad (3)$$

electron balance:

$$\mathrm{Re^{VII}} \rightarrow \mathrm{Re^{IV}} \text{ three-electron reduction}$$

$$\mathrm{Re^{V}} \rightarrow \mathrm{Re^{IV}} \text{ one-electron reduction}$$

$$2\mathrm{S^{2-}} \rightarrow 2\text{``S''} \text{ four-electron oxidation}$$

$\mathbf{[Re_2(\mu\text{-}S{-}S_2CN(CH_3)_2)_2(S_2CN(CH_3)_2)_3][O_3SCF_3]}$, 2. There is no rapid reaction between $\mathrm{Re_2(\mu\text{-}S)_2(S_2CNR_2)_4}$ and tetraalkylthiuram disulfide in the absence of either a Lewis acid, such as $\mathrm{R_3SiO_3SCF_3}$, or an additional oxidant, such as $\mathrm{Cp_2Fe^+}$, capable of oxidizing **1**. The optimal synthesis of $\mathrm{[Re_2(\mu\text{-}S{-}S_2CN(CH_3)_2)_2(S_2CN(CH_3)_2)_3][O_3SCF_3]}$ requires a 1:1:1 ratio of the parent dimer **1** to TDS to Lewis acid. Only one dithiocarbamate (formally, half of the reduced TDS reagent) moiety is incorporated into the product, but the conversion of **1** to **2** involves, overall, a two-electron oxidation. Therefore, 2 equiv of oxidant (or 1 equiv of TDS) are necessary. Again, examination of the electron balance, as shown in reaction 4, clarifies this result.

$$\begin{aligned}&\mathrm{Re_2(\mu\text{-}S)_2(S_2CNR_2)_4} + \mathrm{[S_2CNR_2]_2} + \mathrm{R_3SiO_3SCF_3} \rightarrow \\ &\qquad \mathrm{[Re_2(\mu\text{-}S{-}S_2CNR_2)_2(S_2CNR_2)_3][O_3SCF_3]} + \\ &\qquad\qquad \mathrm{[R_3Si^+ + S_2CNR_2^-]} \qquad (4)\end{aligned}$$

electron balance:

$$2\mathrm{Re^{IV}} \rightarrow 2\mathrm{Re^{III}} \text{ two-electron reduction}$$

$$\mathrm{[S_2CNR_2]_2} \rightarrow 2\mathrm{S_2CNR_2^-} \text{ two-electron reduction}$$

$$2\mathrm{S^{2-}} \rightarrow 2\text{``S''} \text{ four-electron oxidation}$$

The stoichiometry of the reaction is consistent with the observation that the reaction gives nearly quantitative yield when a 1:1:1 ratio of **1**:Lewis acid:tetraalkylthiuram disulfide is used. Although not incorporated into the product, the "additional" tetraalkylthiuram disulfide (oxidant) is needed to balance the reaction. The bridging sulfides of the parent complex are formally oxidized and incorporated into the disulfide linkage of the dialkyltrithiocarbamate (μ-S$-$$\mathrm{S_2CNR_2}$) ligand. Formation of "$\mathrm{R_3SiS_2CNR_2}$" as a product would balance the reaction although we have not attempted to isolate or observe this product. Although required for the reaction to proceed, the Lewis acid is not a component of the electron balance.

Another synthetic route to $\mathrm{[Re_2(\mu\text{-}S{-}S_2CN(CH_3)_2)_2(S_2CN(CH_3)_2)_3]^+}$ involves the use of a relatively strong oxidant, $\mathrm{[Cp_2Fe][PF_6]}$, **1**, and 0.5 molar equiv of TDS. Specifically, a 1:1:0.5 ratio of $\mathrm{Re_2(\mu\text{-}S)_2(S_2CNR_2)_4{:}[Cp_2Fe][PF_6]{:}[S_2CNR_2]_2}$ gives the cationic trithiocarbamate dimer in nearly quantitative yield. The overall reaction and electron balance for this synthesis is

$$\begin{aligned}&\mathrm{Re_2(\mu\text{-}S)_2(S_2CNR_2)_4} + {}^1/_2\mathrm{[S_2CNR_2]_2} + \mathrm{[Cp_2Fe][PF_6]} \rightarrow \\ &\qquad \mathrm{[Re_2(\mu\text{-}S{-}S_2CNR_2)_2(S_2CNR_2)_3)][PF_6]} + \mathrm{Cp_2Fe} \qquad (5)\end{aligned}$$

electron balance:

$$2\mathrm{Re^{IV}} \rightarrow 2\mathrm{Re^{III}} \text{ two-electron reduction}$$

$${}^1/_2\mathrm{[S_2CNR_2]_2} \rightarrow \mathrm{S_2CNR_2^-} \text{ one-electron reduction}$$

$$\mathrm{[Cp_2Fe][PF_6]} \rightarrow \mathrm{Cp_2Fe} \text{ one-electron reduction}$$

$$2\mathrm{S^{2-}} \rightarrow 2\text{``S''} \text{ four-electron oxidation}$$

Interconversions of 1 and 2. The transformation of **1** to **2**, involves the reduction of Re(IV) to Re(III) with the concomitant formation of S$-$S bonds. The reaction is induced by trimethylsilyltriflate but *not* by protic acids such as $\mathrm{HBF_4}$·etherate. Lewis acids may display selective reactivity toward various sulfur based ligands. Related acid-induced redox processes have previously been observed e.g., in the acid decomposition of $\mathrm{MoS_4^{2-}}$ to α-$\mathrm{MoS_3}$.[56,57]

The regeneration of **1** from **2** can be achieved by reduction with $\mathrm{NaBH_4}$ in methanol, or by heating in morpholine (90 °C), tetrahydroquinoline (110 °C), or under pressure of $\mathrm{H_2}$ (80 psi, room temperature, 3 days). Morpholine and tetrahydroquinoline are reductants (H donors). Clearly, addition of *reductants* leads to the *oxidation* of Re(III) to Re(IV). The interconversion of **1** and **2** in the presence of a Lewis acid and $\mathrm{H_2}$, respectively, may mimic to some extent patterns in dehydrogenation/hydrogenation reactions of metal sulfide solids.[58,59] The conversion of **1** to **2** represents an example of acid-induced oxidation of sulfide species ($\mathrm{S^{2-}}$), while the back reaction of **2** to **1** involves reductive cleavage of S$-$S bonds. Protonation and hydrogenation of molecular metal sulfides have previously been observed in $\mathrm{Cp_2Mo_2(\mu\text{-}S_2)_2}$ systems, where, for example, S$-$S to $\mathrm{S^{2-}}$ conversions occur and SH groups are formed upon reduction of the bridging sulfides in conjunction with changes in the redox states of the Mo centers.[60] In the present case, substantial structural rearrangements as well as oxidation state changes have occurred in the $\mathrm{Re_2(\mu\text{-}S)_2}$ core.

$\mathbf{[(Re_2(\mu\text{-}S)(S_2CNR_2)_4)_2(\mu\text{-}S_4)][PF_6]_2}$, 4. The generation of this dimer-of-dimers from $\mathrm{Re_2(\mu\text{-}S)_2(S_2CNR_2)_4}$, sulfur, and $\mathrm{[Cp_2Fe][PF_6]}$ does not involve redox of the metal center and hence

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(56) Diemann, E.; Müller, A. *Coord. Chem. Rev.* **1973**, *10*, 79.

(57) Cramer, S. P.; Liang, K. S.; Jacobson, A. J.; Chang, C. H.; Chianelli, R. R. *Inorg. Chem.* **1984**, *27*, 1215.

(58) Francisco, M. A. US 4,950,386, 1990.

(59) Erekson, E. J.; Lee, A. L.; Barone, P. S.; Solomon, I. J. Eur. Pat. Appl. 1990.

(60) Godziela, G.; Tonker, T.; DuBois, M. R. *Organometallics* **1989**, *8*, 2220.

is not an induced internal electron transfer reaction. Only ligand is oxidized in this reaction as one of the bridging sulfide ligands is formally oxidized by $[Cp_2Fe]^+$ giving the dicationic rhenium product and ferrocene as shown in reaction 6.

$$Re_2(\mu\text{-}S)_2(S_2CNR_2)_4 + 2S + [Cp_2Fe][PF_6] \rightarrow {}^1/_2[(Re_2(\mu\text{-}S)(S_2CNR_2)_4)_2(\mu\text{-}S_4)][PF_6]_2 + Cp_2Fe \quad (6)$$

In this reaction "S" represents sulfur present as a contaminant in $Re_2(\mu\text{-}S)_2(S_2CNR_2)_4$, **1**. As in the synthesis of $[Re_2(\mu\text{-}S-S_2CNR_2)_2(S_2CNR_2)_3)]^+$, the bridging sulfide is oxidized to form a sulfur–sulfur linkage.

The reaction of the dicationic dimer-of-dimers with tetraalkylthiuram disulfide in a 1:1 ratio gives the trithiocarbamate cationic dimer in good yield. The electron balance of the induced internal electron transfer reaction is given in reaction 7.

$$[(Re_2(\mu\text{-}S)(S_2CNR_2)_4)_2(\mu\text{-}S_4)][PF_6]_2 + [S_2CNR_2]_2 \rightarrow 2[Re_2(\mu\text{-}S-S_2CNR_2)_2(S_2CNR_2)_3)][PF_6] + 4S \quad (7)$$

electron balance:

$4Re^{IV} \rightarrow 4Re^{III}$ four-electron reduction

$[S_2CNR_2]_2 \rightarrow 2S_2CNR_2^-$ two-electron reduction

$2S^{2-} \rightarrow 2$"S" four-electron oxidation

2"S^-" $\rightarrow 2$"S" two-electron oxidation

The two formal "S^-" moieties in the electron balance are the bridging terminal sulfur atoms of the tetrasulfide ligand that links the two dimers.

$[Re(S_2CNR_2)_4][Cl]$, 3. Numerous tetrakis(dialkyldithiocarbamate) coordinated mononuclear species have been crystallographically characterized. X-ray structures for $M(dtc)_4$ complexes are known for M = Ti,[50] Nb,[51,61] Ta,[47] Mo,[62-64] W,[52] and La.[65,66]

The original synthesis[27] of $[Re(S_2CNR_2)_4][Cl]$ involved the oxidative decarbonylation of low-valent rhenium carbonyls with tetraalkylthiuram disulfides and gave a mixture of rhenium dialkyldithiocarbamate compounds from which the cation was separated in low yield and isolated by methathesis with halide salts. The induced internal electron transfer reaction enables the synthesis of $[Re(S_2CNR_2)_4][Cl]$ starting from ReS_4^- and tetraalkylthiuram disulfides in one step. Interestingly, the chloride counterion is derived from the reaction solvent, CH_2Cl_2. Chemical analysis revealed the stoichiometry of $[Re(S_2CNR_2)_4][Cl]$. The presence of chloride was further confirmed by SEM-EDS (scanning electron microscopy–energy dispersive spectroscopy).

The nominal stoichiometry needed to synthesize $[Re(S_2CNR_2)_4][Cl]$ is a 1:2 ratio of ReS_4^- to tetraalkylthiuram disulfide. The mononuclear cation is synthesized in very high yield using a 1:3 ratio of ReS_4^- to tetraalkylthiuram disulfide, $[S_2CNR_2]_2$, in a 1:1 acetonitrile–dichloromethane solvent mixture. As in previous reactions, the additional TDS is needed to effect electron balance. The overall reaction and electron balance of this synthesis is

$$ReS_4^- + 3[S_2CNR_2]_2 \rightarrow [Re(S_2CNR_2)_4]^+ + 4S + 2S_2CNR_2^- \quad (8)$$

electron balance:

$Re^{VII} \rightarrow Re^{V}$ two-electron reduction

$3[S_2CNR_2]_2 \rightarrow 6S_2CNR_2^-$ six-electron reduction

$4S^{2-} \rightarrow 4S$ eight-electron oxidation

The chloride counterion originates from dichlomethane as a result of its reaction with $S_2CNR_2^-$, giving $CH_2(S_2CNR_2)$ (observed by NMR and mass spectroscopy) and two chloride ions. When tetrathioperrhenate, TDS, and a tetraalkylammonium halide in a 1:3:1 ratio are combined in acetonitrile for 24 h, the parent dimer, $Re_2(\mu\text{-}S)_2(S_2CNR_2)_4$, is obtained, not $[Re(S_2CNR_2)_4]^+$. Clearly, dichloromethane plays a role in the reaction that cannot be simply substituted by supplying a chloride ion.

Relationship between 1 and 3. The two-electron metal reduction process for the conversion of ReS_4^- to $Re(S_2CNR_2)_4^+$ is only observed when a CH_3CN/CH_2Cl_2 solution is used as the reaction solvent. When fewer (2–3) equivalents of tetraalkylthiuram disulfide are used and acetonitrile is the solvent, the reaction gives the neutral green dimer, **1**, $Re_2(\mu\text{-}S)_2(S_2CNR_2)_4$. When excess tetraalkylthiuram disulfide (>10 equiv) and a relatively small CH_2Cl_2: acetonitrile solvent ratio (<2:3) were used, the induced redox reaction gave no trace of **3** but a small amount of $[Re_2(\mu\text{-}S-S_2CN(R)_2)_2(S_2CN(R)_2)_3]^+$ (by ^1H NMR) and an insoluble light-green solid, **7**, tentatively assigned as $[Re_2S_2(S_2CNR_2)_4]_x[S_2CNR_2]_y$. This polymeric solid can be hydrogenated (800 psi H_2) to regenerate the dimer, **1**, and is also formed by the reaction of **1** with $(S_2CNR_2)_2$ in CH_2Cl_2.

Electronic Structural Considerations. Qualitative electronic structure considerations have been used to try to understand the nature of the bonding in the dinuclear rhenium complexes. Two key features are addressed: the Re–Re bond and the electron distribution between ligand based and metal based orbitals. A satisfactory explanation for the observed Re–Re bond distances in complexes **1** (d^3–d^3) and **2** (d^4–d^4) is obtained using a "zero-ith order" approximation for metal–metal-bonded edge-sharing bioctaheral complexes as described by Cotton.[38]

The analysis uses the Re_2S_{10} core of **1** and **2** in idealized D_{2h} symmetry with each rhenium in approximate octahedral geometry, Figure 11a. The six sulfur–metal σ-bonds use the 6s, $6p_x$, $6p_y$, $6p_z$, $5d_{z^2}$, and $5d_{x^2-y^2}$ orbitals. The three 5d atomic orbitals, (d_{xy}, d_{yz}, d_{xz}; "t_{2g} set"), from each metal are used to construct the set of six molecular orbitals, (σ, σ^*, π, π^*, δ and δ^*), which yields three bonding orbitals, shown in Figure 11b, for the rhenium–rhenium bond of the Re_2S_{10} core. Qualitatively it is easy to see how two d_{xy} atomic orbitals will give a σ and σ^* molecular orbital respectively (a_g and b_{2u}). Only slightly less obvious is the combination of two d_{yz} and d_{xz} orbitals, giving the π and δ (and corresponding anti-bonding orbitals) molecular orbitals, respectively. The molecular orbital diagram in Figure

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(61) Dilworth, J. R.; Henderson, R. A.; Hills, A.; Hughes, D. L.; Macdonald, C.; Stephens, A. N.; Walton, D. R. M. *J. Chem. Soc., Dalton Trans.* **1990**, 1077.

(62) Mak, T. C. W.; So, S. P.; Chieh, C.; Jasim, K. S. *J. Mol. Struct.* **1985**, *127*, 375.

(63) van der Aalsvoort, J. G. M.; P . T. Beurskens, P. T. *Cryst. Struct. Commun.* **1974**, *3*, 653.

(64) Jasim, K. S.; Chieh, C.; Mak, T. C. W. *Inorg. Chim. Acta* **1986**, *116*, 37.

(65) Ciampolini, M.; Nardi, N.; Colamarino, P.; Orioli, P. *J. Chem. Soc., Dalton Trans.* **1977**, 379.

(66) Jinshun, H.; Shanhuo, L.; Manfang, W.; Qianer, Z.; Jiaxi, L. *J. Inorg. Chem. (Wuji Huaxue Xuebao)* **1987**, *3*, 1.

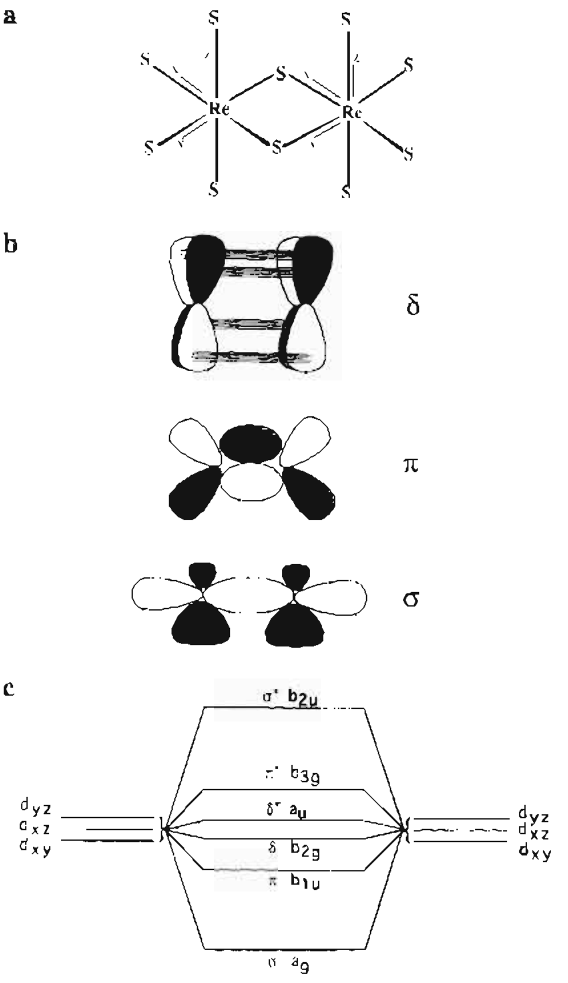

Figure 11. (a) Re_2S_{10} core of **1** and **2** in D_{2h} symmetry. (b) Idealized σ, π, and δ molecular orbitals. (c) Molecular orbital diagram for **1** and **2** in D_{2h} symmetry.

11c is based on a simple group theoretical model[67] with the relative energies of the six molecular orbitals based qualitatively on the differing extent of overlap.

Strictly on the basis of the molecular orbitals described above, a simplified picture for the bonding in **1** and **2** emerges. In **1**, (d^3−d^3), the three pairs of electrons fill the σ, π, and δ orbitals giving a *net or effective* bond order of two (one σ and one π bond with a very weak δ molecular orbital). On the basis of the extent of overlap at Re−Re = 2.55 Å, it can be safely assumed that the δ bond is quite weak and, therefore, for purposes of this discussion, can be ignored. The bonding picture of **2**, (d^4−d^4), is similar. The four pairs of d-electrons fill the σ, π, δ, and δ^* molecular orbitals. Clearly, there is no δ component to the bonding in **2**. Hence, both **1** and **2** are best described as metal−metal double-bonded complexes, consistent with their similar Re−Re bond distances.

This simple yet useful molecular orbital picture can be employed to describe the metal−metal bonding in the closely related the Os analog[44,45] of **2**, $[Os_2(\mu\text{-}S{-}S_2CN(C_2H_5)_2)_2(S_2CN(C_2H_5)_2)_3]^+$. In this case the two Os(III) centers are d^5 and therefore have an addition pair of electrons compared to complex **2**. These electrons occupy the $\pi^*(b_{3g})$ molecular orbital, and hence the metal−metal bonding would be described as a net single Os−Os σ bond which would be expected to be longer than the double bond of complexes **1** and **2**. The relatively long (2.792 Å) Os−Os distance is consistent with this analysis.

The simple bonding scheme presented here may have some applicability to the binding in the layered ReS_2 structure. However, although the solid state material ReS_2 can be considered as formally having Re_2S_{10} units, the metal−metal bonding network and analysis is more complex and has been discussed by Burdett[68] and Whangbo.[69]

Extended Hückel calculations were carried out in order to further understand the bonding and see how it changed upon formation of the disulfide bond in going from $Re^{IV}{}_2(\mu\text{-}S)_2(S_2CNR_2)_4$, **1**, to $[Re^{III}{}_2(\mu\text{-}S{-}S_2CNR_2)_2(S_2CNR_2)_3]^+$, **2**. Strong similarities are observed in the orbital patterns of the two complexes, consistent with their similar Re−Re bond distances and the qualitative scheme discussed above.

The metal−ligand character of the frontier orbitals should be particularly informative as these orbitals are likely key participants in the internal redox reactions. The large sulfur component in the HOMO of complex **1** is consistent with (a) the observed initial oxidation at sulfur and (b) subsequent bond formation at this atom as seen in the conversion of **1** to **2** and **1** to **4** in the presence of an oxidant and appropriate ligand (dtc and "S_2", respectively). While the HOMO of **1** has a substantial sulfur component, the LUMO is metal-centered. Internal electron transfer from the filled orbital of **1** to the metal-centered empty orbital may therefore be "induced" by reactions that mildly perturb the electronic levels. Clearly, reactions with external oxidants appear sufficient to induce the internal electron transfer leading to metal reduction. In tetrathiometalates the energy of the ligand to metal charge transfer (from HOMO to LUMO) has been correlated with the ease of induced internal electron transfer.[22] A similar situation may prevail in the dinuclear rhenium species where the HOMO−LUMO gap may be similarly small. Specifically, for **1-Me** the lowest visible transition appears at ~750 nm (~13 300 cm^{-1}).

Electrochemistry. Electrochemical analysis of $Re_2(\mu\text{-}S)_2(S_2CN(CH_3)_2)_4$, **1-Me**, and $[Re_2(\mu\text{-}S{-}S_2CN(CH_3)_2)_2(S_2CN(CH_3)_2)_3]^+$, **2-Me**$^+$, proved useful in establishing mechanistic details of their interconversion (by induced internal electron transfer) and in determining the purity of **1-Me**.

Sulfur contamination of **1** is consistent with both the "clean" ^1H NMR spectrum obtained for the crude samples and the isolation of the dimer-of-dimers, $[(Re_2(\mu\text{-}S)(S_2CN(C_4H_9)_2)_4)_2(\mu\text{-}S_4)][PF_6]_2$ **4**, by chemical oxidation of crude **1**. The complexity of the ^1H NMR spectra of bulk samples of the dimer of dimers, **4**, suggests that a variety of products may have been formed possibly all dimers-of-dimers, bridged by different sulfur chain lengths, or a mixture of dimers of dimers and simple dimers. Another possibility is that the dimer-of-dimers exists in a variety of different conformations that do not rapidly interconvert on the NMR time scale.

Interestingly, the olive green product, **1-Me**$^+$, obtained by electrolysis of **1-Me** is related to **4** in that the $Re_2(\mu\text{-}S)_2$ centers of each compound are one electron more oxidized than the parent dimer. Moreover, both species, upon reaction with tetramethylthiuram disulfide, yield **2**. However, **1-Me**$^+$ does not seem to rapidly dimerize, and probably exists long enough to react with tetramethylthiuram disulfide as a simple dimer, as suggested by the chemical reversibility of both the first and second one-electron oxidations of **1-Me**. Furthermore, the cyclic voltammogram of the olive-green species generated by electrolysis (**1-Me**$^+$) is very similar to that of the parent dimer, **1-Me**. These results do not exclude, however, the possibility that dimerization is an equilibrium process. Results of EPR

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[67] Cotton, F. A. *Chemical Applications of Group Theory*, 3rd ed.; Wiley-International: New York, 1990.

[68] Burdett, J. K.; Hughbanks, T. *Inorg. Chem.* **1985**, *24*, 1741.

[69] Whangbo, M.-H.; Canadell, E. *J. Am. Chem. Soc.* **1993**, *114*, 9587.

spectroscopy are consistent with dimerization of **1-Me**$^+$, as no EPR signal was observed for the olive green species at room temperature, although other explanations for the absence of the EPR signal are possible. From molecular orbital calculations and the existence of **4**, it seems reasonable that the oxidation is based in the bridging sulfido ligand and that dimerization to form a sulfur–sulfur bonded dimer of dimers similar to **4** without the S–S bridge would be possible.

The electrochemical results establish that, for the reaction between **1-Me** and tetramethylthiuram disulfide giving **2-Me**$^+$, an external oxidant with a potential great enough to first oxidize **1-Me** to **1-Me**$^+$ is necessary. **1-Me**$^+$ is then further oxidized by reaction with tetramethylthiuram disulfide undergoing internal electron transfer. Tetramethylthiuram disulfide alone (irreversible $E_c = -1.5$ V vs SCE at 50 mV/s scan rate) is not potent enough to induce reaction of **1-Me**. However, ferrocenium hexafluorophosphate and iodine have oxidizing potentials high enough to induce reaction of **1-Me** with thiuram disulfide to form **2-Me**, which has been verified experimentally.

The isosbestic point observed by spectrophotometrically monitoring the reaction between **1-Me**$^+$ and tetramethylthiuram disulfide excludes any long-lived intermediates in this process, even though the reaction is expected to be complex, including both external and internal oxidation. Taube and others have shown that external *oxidation* of a ligand and internal electron transfer are independent and sequential in induced internal redox reactions of cobalt complexes.[70] A proposed mechanism consistent with kinetic data for the induced internal electron transfer reaction between $[MoS_4]^{2-}$ and organic disulfides to form $[Mo_2S_2(\mu\text{-}S)_2(S_2)_2{}^{2-}]$ also invokes oxidation of ligands prior to internal electron transfer from the metal center.[15] While our data for the transformation of **1-Me**$^+$ to **2-Me** cannot establish that the oxidation of **1-Me**$^+$ by thiuram disulfide takes place prior to internal electron transfer, our data for the *reduction* of **2-Me**$^+$ to **1-Me** clearly show that external reduction by two electrons does indeed occur prior to internal electron transfer and loss of dithiocarbamate.

Structural Relationship between 1, 2, and ReS$_2$. Figure 12 shows the Re_2S_{10} and Re_2S_{12} cores of complexes **1** and **2** viewed perpendicular to the Re–Re bond below a representation of the solid state material ReS_2 drawn to the same scale. Interestingly, the meso diastereoisomer may be viewed as two sulfur monolayers of five atoms sandwiching the two rhenium atoms (Figure 4). Note the striking similarities in the S–Re–S layering appearance in the rhenium–sulfur core of the molecular complexes and ReS_2. This layer arrangement and the multiple bonded nature of $Re^{IV}{}_2(\mu\text{-}S)_2$ gives the same general appearance as a portion of layered ReS_2. Another feature common to complexes **1**, **2**, and ReS_2 is the short Re–Re distance. Clearly, these aspects of the ReS_2 lattice are reproduced in the far simpler molecular complexes.

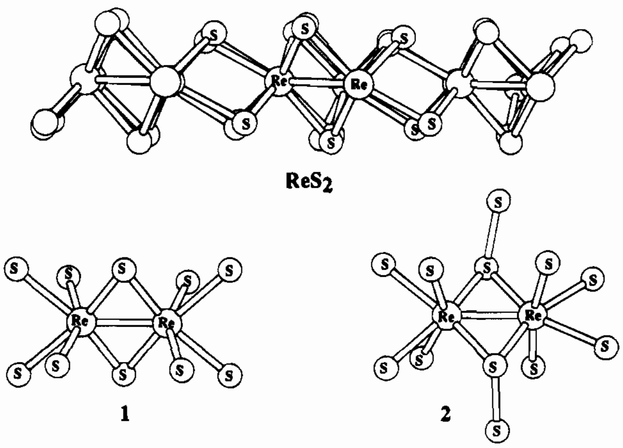

Figure 12. Re_2S_{10} and Re_2S_{12} core of complexes **1** and **2**, perpendicular to the Re–Re bond, and a portion of the solid state material ReS_2 showing the similarities in the S–Re–S layering and Re–Re interaction.

Conclusions

The rhenium sulfur chemistry described here demonstrates the application of induced redox chemistry as a nonintuitive synthetic approach to lower valent rhenium sulfide complexes starting from tetrathioperrhenate. A dramatic three-electron *reduction* per metal center in the conversion of $ReS_4{}^-$ to $Re_2(\mu\text{-}S)_2(S_2CNR_2)_4$ induced via an *oxidant* has been demonstrated and explained. Furthermore, the addition of a greater than a stoichiometric quantity of *oxidant* ligand precursor (TDS) to affect the *reduction* has been satisfactorily explained in terms of the need for oxidizing equivalents. The synthesis of mono-, di-, and tetranuclear complexes has been demonstrated. In a general sense, solvents, reactant ratios, and/or reagents such as Lewis acids added may now be selected to give a variety of metal sulfide complexes starting from readily available d^0 tetrathiometalates.

The multiple metal–metal bonding in complexes **1** and **2** has been described and gives a picture that is consistent with the induced internal electron transfer reactions and with the short Re–Re distance in the dinuclear cores. The structural relationship between the Re_2S_{10} cores of **1** and **2** and ReS_2 reveals the similarity in local structure between the solid state and molecular systems.

The electrochemical studies have established the potentials required for induced internal electron transfer in the interconvertible pair of complexes, **1-Me** and **2-Me**$^+$. In addition, some mechanistic details about the interconversion have been elucidated. Specifically, in the oxidatively induced internal electron transfer reaction of **1-Me** to form **2-Me**$^+$, one-electron oxidation of **1-Me** is followed by a relatively slow reaction with TDS. In the reductively induced internal redox reaction of **2-Me**$^+$ to form **1-Me**, two sequential one-electron reductions are followed by a chemical reaction (an EEC process). Combined with other work the studies reported in this paper establish induced internal electron transfer process as useful and controllable reactions in the synthesis of lower valent transition metal sulfide complexes.

Acknowledgment. We gratefully acknowledge Dr. Cynthia S. Day of Crystalytics Co. for carrying out the X-ray diffraction studies and Dr. K. Hegetschweiler of Eidgenössische Technische Hochschule, Zürich, for the mass spectroscopy studies.

Supplementary Material Available: Complete crystallographic reports giving tables of fractional coordinates, anisotropic thermal parameters, and complete bond distances and angles for compounds **1-*i*-Bu**, **[2-Me][O$_3$SCF$_3$]**, **[3-Me][Cl]**, and **[4-*i*-Bu][PF$_6$]$_2$** (70 pages). Ordering information is given on any current masthead page.

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[70] Taube, H. *Electron Transfer Reactions of Complex Ions in Solution*; Academic Press: New York, 1970; p 73.