A New Sulfur-Rich Rhenium(III) Complex, Re($S_2CC_6H_5$)($S_3CC_6H_5$)$_2$, and Seven-Coordinate Complexes Formed by Reversible Sulfur Abstraction Reactions, Re($S_2CC_6H_5$)$_3$(PPh_3) and [Re($S_2CC_6H_5$)$_3$(CN)]$^-$

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Induced internal electron transfer involving tetrathiometalate anions of V, Mo, W, and Re has been established.[1] Reactions of VS_4^{3-}, MoS_4^{2-}, and ReS_4^- with oxidants yield products with the metal in a lower oxidation state than in the starting tetrathiometalate. Most work dealing with internal redox reactions has involved tetraalkylthiuram disulfide, $(R_2NCS_2)_2$, as the oxidant.[1] To gain a better understanding of ligand influences, we have studied the reaction of dithiobenzoate disulfide, $(C_6H_5CS_2)_2$, with MoS_4^{2-} and ReS_4^-. The ligand/oxidant has a major effect on the final product leading, in the case of Re, to an unprecedented four-electron reduction of a single metal center.

Reaction of $(C_6H_5CS_2)_2$ with $[Et_4N]_2MoS_4$ in acetonitrile produces the known compound $[Mo^{IV}(S_2CC_6H_5)_4]$.[2] However, reaction of a 1:2 ratio of red-violet $[Et_4N]ReS_4$ to red $(C_6H_5CS_2)_2$, stirred at room temperature for 2 days in dry CH_3CN under an argon atmosphere, forms the new green, neutral, “sulfur-rich” mononuclear rhenium(III) complex $[Re(S_2CC_6H_5)(S_3CC_6H_5)_2]$, **1**, in 93% yield.[3] This reaction is a striking example of an internal redox reaction in which Re(VII) is reduced by four electrons to Re(III):

$$[Re^{VII}S_4]^- + 2(C_6H_5CS_2)_2 \rightarrow [Re^{III}(S_2CC_6H_5)(S_3CC_6H_5)_2] + 2\text{“S”} + (C_6H_5CS_2)^-$$

In this reaction 2 equiv of $(C_6H_5CS_2)_2$ are also reduced by four electrons to form $C_6H_5CS_2^-$ (one free). The eight electrons required to balance the reaction come from the oxidation of all of the sulfides (S^{2-}) in ReS_4^- to S^0. This S^0 includes free sulfur (identified as a reaction byproduct) and one sulfur atom in the perthio bond of each $(S_3CC_6H_5)^-$ ligand. The four-electron reduction of the single rhenium metal center is an unprecedented step in induced internal electron transfer reactions.

Single crystals of **1** were obtained by layering a CH_2Cl_2 solution with hexane. X-ray diffraction analysis established the six-coordinate structure shown in Figure 1.[4] The Re(III) center has distorted octahedral coordination, with one chelating dithiobenzoate and two chelating perthiobenzoate ligands. The distortion is largely attributable to the small bite of the $(S_2CC_6H_5)^-$ ligand.[5] All bond angles and lengths are unexceptional.[1e,6−10] The phenyl ligands are twisted out of the S−Re−S−C or S−Re−S−S−C planes (20.2° [C_2−C_{12}], 26.1° [C_1−C_{11}], and 12.5° [C_3−C_{13}], respectively).

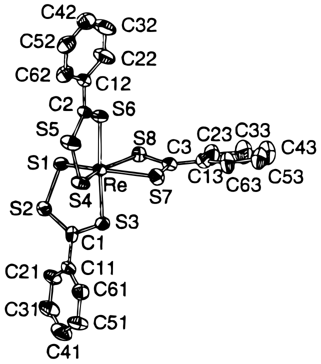

Figure 1. Neutral, octahedral $[Re(S_2CC_6H_5)(S_3CC_6H_5)_2]$. Bond lengths (Å) and angles (deg): Re−S_1 = 2.222(2), Re−S_3 = 2.344(2), Re−S_7 = 2.502(2), S_1−S_2 = 2.125(3), C_1−S_2 = 1.713(7), C_1−S_3 = 1.660(7), C_3−S_7 = 1.677(7), C_1−C_{11} = 1.462(10), S_3−Re−S_6 175.83(7), S_1−Re−S_7 155.59(8), S_1−Re−S_4 111.01(8), S_1−Re−S_3 89.31(7), S_7−Re−S_8 67.8(7), Re−S_1−S_2 109.63(11), S_1−S_2−C_1 104.27(26), S_2−C_1−S_3 122.87(44), Re−S_3−C_1 112.19(27), Re−S_8−C_3 91.01(26), S_7−C_3−S_8 110.57(42).

This octahedral, d^4, rhenium(III) complex is diamagnetic, as no paramagnetic shifts are observed in the ^1H or ^{13}C NMR spectra.[11] Cyclic voltammetry of **1** in CH_2Cl_2 reveals two reversible, one-electron oxidations at 950 mV and 1.36 V ($E_{1/2}$ vs SCE). These are assigned to the formation of Re(IV) and Re(V) complexes, respectively, accessing the $5d^3$ and $5d^2$ systems.

Complex **1** displays reversible chemical reactivity with respect to sulfur-abstracting agents. Upon addition of a 3:1 ratio of either PPh_3 or $[Et_4N]CN$ to a CH_2Cl_2 solution of **1**, the S−S stretch at 544 cm^{-1} disappears, indicative of sulfur atom abstraction. Single crystals were grown by layering CH_2Cl_2 solutions with hexane. X-ray diffraction analysis revealed two

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(3) Anal. Found (calcd): C, 35.89 (35.52); H, 1.95 (2.13); S, 36.00 (36.12).

(4) Crystal data for $Re(S_2CC_6H_5)(S_3CC_6H_5)_2$: monoclinic $P2_1/c$, $Z = 4$, $a = 20.041(4)$ Å, $b = 10.580(2)$ Å, $c = 12.022(2)$ Å, $\beta = 105.54(3)°$, $V = 2455.9(8)$ Å^3 at 293 K. $R_w(F^2) = 0.125$ for 271 variables and 5216 independent reflections; $R_1 = 0.044$ for 3958 reflections having $F_o^2 > 2\sigma(F_o^2)$.

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(11) ^{13}C NMR (CD_2Cl_2, 299.1 K): δ 125.18 (s, 1C), 128.17 (s, 1C), 128.91 (s, 1C), 132.36 (s, 1C), 133.82 (s, 1C), 134.05 (s, 1C), 135.50 (s, 1C), 143.38 (s, 1C), 234.80 (s, 1C), 239.42 (s, 1C). ^1H NMR (CD_2Cl_2, 303 K): δ 7.40, 7.55, 7.70, 8.04 (m, 6). IR (KBr pellet): 997 [ν(C=S)], 544 [ν(S−S)], 399 cm^{-1} [ν(Re−S)]. UV−vis/NIR (CH_2Cl_2, nm): 907 (ϵ = 355 M^{-1} cm^{-1}), 617 (ϵ = 7411 M^{-1} cm^{-1}), 466 (ϵ = 16 340 M^{-1} cm^{-1}), 391 (ϵ = 14 713 M^{-1} cm^{-1}), 315 (ϵ = 31 629 M^{-1} cm^{-1}), 277 (shoulder, ϵ = 24 648 M^{-1} cm^{-1}).

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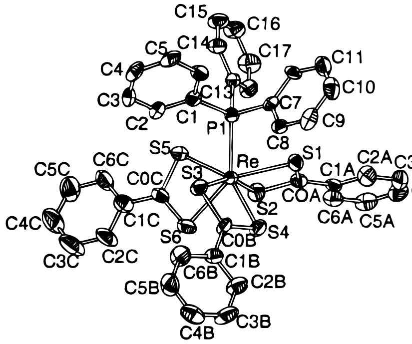

Figure 2. The neutral capped octahedron $[Re(S_2CC_6H_5)_3(PPh_3)]$, with PPh_3 as the capping ligand. Bond lengths (Å) and angles (deg): $Re{-}P_1 = 2.400(3)$, mean $Re{-}S = 2.438$, mean $C{-}S = 1.681$, mean $(S)C{-}C_{Ph} = 1.465$, mean $P{-}C = 1.834$, $P_1{-}Re{-}S_1$ 77.68(9), $P_1{-}Re{-}S_2$ 119.85(9), $S_2{-}Re{-}S_4$ 97.30(10), $S_2{-}Re{-}S_3$ 158.26(10), $S_1{-}Re{-}S_5$ 128.25(9), $S_1{-}Re{-}S_2$ 68.31(10), mean $Re{-}S{-}C$ 90.59, mean $S{-}C{-}S$ 109.61, $S{-}C{-}C_{Ph}$ 125.05, mean $Re{-}P_1{-}C = 115.92$.

new complexes, purple $[Re(S_2CC_6H_5)_3(PPh_3)]$, **2**, and blue $[Et_4N][Re(S_2CC_6H_5)_3(CN)]$, **3**, both seven-coordinate rhenium(III) compounds with all excess sulfur removed.[12,13] As shown in Figure 2, the neutral complex **2** is a capped octahedron, with PPh_3 as the capping ligand.[14] Bond angles and lengths are unexceptional.[15,16] A technetium xanthate analog of this structure has been reported, $[Tc(S_2COC_4H_9)_3(PPh_3)]$, although prepared by an unrelated route from $(TcOCl_4)^-$, PPh_3, and excess $K(S_2COCH_2CH_3)$.[15] The anionic complex **3** is a distorted pentagonal bipyramid, with CN^- in the equatorial plane and S_2 and S_3 in the axial positions (Figure 3).[17] Bond angles and lengths are unexceptional.[18,19] The starting complex (and its perthio bonds) can be regenerated by refluxing either **2** or **3** with excess sulfur. UV−vis and IR spectra show quantitative regeneration of **1**.

Sulfur abstraction accompanied by formation and isolation of a seven-coordinate complex is unprecedented.[8,15] Addition and removal of sulfur with Ni(II), Zn(II), Pd(II), and Pt(II) complexes does not change the coordination number of the metal center.[20] However, a green material was isolated by reaction of Ph_3P with $[Ni(S_2CC_6H_5)(S_3CC_6H_5)]$,[20d] which was possibly a Ph_3P adduct of $[Ni(S_2CC_6H_5)_2]$. In addition, $[Mo^{IV}O(S_2CC_6H_5)_2(PPh_3)]$ was isolated in low yield from the reaction of $[Mo^{IV}O(S_2CC_6H_5)(S_3CC_6H_5)]$ with a large excess of Ph_3P.[21]

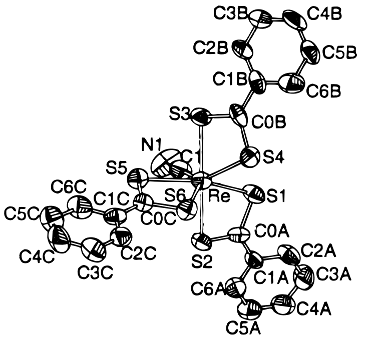

Figure 3. The distorted pentagonal-bipyramidal $[Re(S_2CC_6H_5)_3(CN)]^-$ anion. Bond lengths (Å) and angles (deg): $Re{-}C_1 = 2.077(16)$, $C_1{-}N_1 = 1.149(16)$, mean $Re{-}S = 2.423$, mean $C{-}S = 1.676$, mean $(S)C{-}C_{PH} = 1.458$, $N_1{-}C_1{-}Re$ 173.48(1.42), $S_1{-}Re{-}S_2$ 68.06(12), $S_4{-}Re{-}S_1$ 76.74(12), $S_4{-}Re{-}C_1$ 135.52(40), $S_4{-}Re{-}S_2$ 121.18(13), $S_3{-}Re{-}S_6$ 114.67(13), $C_1{-}Re{-}S_5$ 78.54(42), $S_5{-}Re{-}S_2$ 95.48(12), $S_1{-}Re{-}S_5$ 155.31(40), $S_6{-}Re{-}C_1$ 142.28(40), $S_3{-}Re{-}S_2$ 163.20(12), mean $S{-}C{-}S$ 108.32, mean $S{-}C{-}C_{Ph} = 125.83$, mean $Re{-}S{-}C$ 91.55.

In summary, reaction of $[ReS_4]^-$ with $(C_6H_5CS_2)_2$ produces a unique sulfur-rich rhenium(III) complex, $[Re(S_2CC_6H_5)(S_3CC_6H_5)_2]$. Sulfur (in the sulfur-rich ligands) can be quantitatively extracted with Ph_3P or CN^-, to form new seven-coordinate rhenium complexes in high yield. Sulfur addition quantitatively regenerates the starting complex. The influence of the ligand/oxidant on the resulting product can be seen by comparing the reaction between $[Re^{VII}S_4]^-$ and $(R_2NCS_2)_2$, which yields the dimer $[Re^{IV}_2(\mu\text{-}S)_2(R_2NCS_2)_4]$.[1e] The electron-donating ability of the chelating ligand may influence the oxidation state of the product. Dithiocarbamate is a better electron donor than dithiobenzoate,[22] stabilizing a higher oxidation state on the metal [i.e., Re(IV) vs Re(III)]. The ability of dithiocarbamate to stabilize higher metal oxidation states is also seen in the reaction between $[Mo^{VI}S_4]^{2-}$ and $(R_2NCS_2)_2$, which yields $[Mo^{V}S_2(R_2NCS_2)_3]$,[1d] instead of the hypothetical isomer $[Mo^{III}(S_2CC_6H_5)(S_3CC_6H_5)_2]$, which would be the analog of the $[Re^{III}(S_2CC_6H_5)(S_3CC_6H_5)_2]$ complex reported here.[23] Clearly, the nature of the metal and ligand both influence the course of the internal redox reactions.

Supporting Information Available: Experimental details (Tables S1, S7, and S12), atomic parameters (Tables S2, S8, S13), bond lengths and angles (Tables S3, S9, and S14), anisotropic displacement parameters (Tables S4, S10, and S15), H parameters (Tables S5, S11, and S16), and least-squares planes (Table S6) (29 pages). Ordering information is given on any current masthead page.

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[12] 1:1 and 1:2 ratios were tried but resulted in incomplete reactions. Only the 1:3 reaction went to completion.

[13] A 1:3 reaction ratio also resulted in formation of $[Re(S_2CC_6H_5)_3CN]^-$, as characterized via IR and UV−vis.

[14] Crystal data for $Re(S_2CC_6H_5)_3(PPh_3)$: triclinic $P\bar{1}$, $Z = 2$, $a = 10.112(2)$ Å, $b = 13.123(3)$ Å, $c = 15.509(3)$ Å, $\alpha = 68.44(3)°$, $\beta = 70.74(3)°$, $\gamma = 72.74(3)°$, $V = 1770.5(6)$ Å^3 at 293 K. $R_w(F^2) = 0.114$ for 424 variables and 6213 independent reflections; $R_1 = 0.057$ for 4737 reflections having $F_o^2 > 2\sigma(F_o^2)$.

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[17] Crystal data for $[Re(S_2CC_6H_5)_3CN][(CH_3CH_2)_4N]$: triclinic $P\bar{1}$, $Z = 4$, $a = 14.208(3)$ Å, $b = 15.511(3)$ Å, $c = 16.663(3)$ Å, $\alpha = 106.62(3)°$, $\beta = 107.14(3)°$, $\gamma = 96.96(3)°$, $V = 3276.8(11)$ Å^3 at 293 K. $R_w(F^2) = 0.128$ for 742 variables and 11496 independent reflections; $R_1 = 0.062$ for 6560 reflections having $F_o^2 > 2\sigma(F_o^2)$.

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[23] In each case only one redox isomer is formed, i.e. $[Mo^{V}S_2(R_2NCS_2)_3]$ instead of $[Mo^{III}(S_2CC_6H_5)(S_3CC_6H_5)_2]$ in the $[Mo^{VI}S_4]^{2-}/(R_2NCS_2)_2$ reaction and $[Re^{III}(S_2CC_6H_5)(S_3CC_6H_5)_2]$ instead of $[Re^{V}S_2(R_2NCS_2)_3]$ in the $[ReS_4]^-/(C_6H_5CS_2)_2$ reaction.