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# Synthesis and Structural Characterization of Novel Terminal and Bridging Re(V)−Sulfido Complexes

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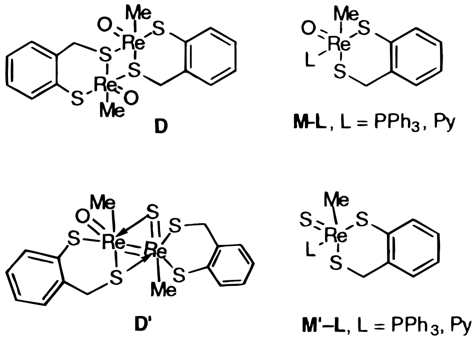
Transition metal sulfur complexes play important roles in biology and industry.[1,2] Metal-assisted cleavage of C−S bonds has been of particular interest since this process is believed to be involved in the catalytic hydrodesulfurization of fossil fuels. As part of our ongoing studies of rhenium-catalyzed sulfur atom transfer reactions, we reported recently the synthesis of novel Re(V) complexes containing a bisthiolato ligand (complexes **D** and **M**−**L**, Chart 1).[3] We then became interested in synthesizing the sulfur analogues of these complexes (Re═S in place of Re═O) since they form key catalytic intermediates. Many anionic terminal Re(V)−sulfido complexes are known, and some of them tend to oligomerize under certain conditions.[4−6] Conversion of metal−oxo to metal−sulfido complexes has usually been realized with $H_2S$,[2,7] although $CS_2$ has also been used.[8] These reagents proved ineffective in our studies, but the use of $P_4S_{10}$ gave very promising results. Here, we report the synthesis of the first example of a neutral terminal Re(V)−sulfido complex and a mixed oxo(sulfido)dimeric Re(V) complex. They are complexes M′−PPh$_3$ and D′ of Chart 1.

**Chart 1**



When the green mononuclear complex **M**−PPh$_3$ (256 mg, 0.4 mmol) was treated with $P_4S_{10}$ (143 mg, 0.32 mmol) in toluene at 25 °C, a rapid reaction was indicated by the color of the solution changing to red, eq 1. The newly formed product, **M′**−PPh$_3$, was isolated in 56% yield (column chromatography with 5% EtOAc in hexane as eluent). The material was characterized by analysis and spectroscopy.[9]

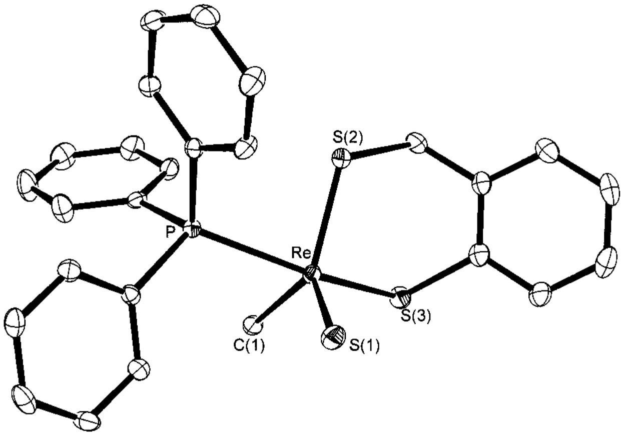


**Figure 1.** Perspective view of **M′**−PPh$_3$ with thermal ellipsoids at the 30% probability level. Selected bond lengths (pm) and bond angles (deg): Re−S(1) = 209.8(2), Re−S(2) = 226.1(2), Re−S(3) = 231.4(2), Re−P = 244.5(2); S(3)−Re−P = 156.8(1), S(3)−Re−S(1) = 107.4(1), S(3)−Re−C(1) = 79.5(2), S(3)−Re−S(2) = 90.9(1).

$$\frac{1}{2}\,\mathbf{D} \xrightarrow{\mathrm{PPh_3}} \mathbf{M}-\mathrm{PPh_3} \xrightarrow{\mathrm{P_4S_{10}}} \mathbf{M'}-\mathrm{PPh_3} \qquad (1)$$

The single-crystal X-ray determination of **M′**−PP$_3$ is summarized by the ORTEP diagram shown in Figure 1.[10] The monomeric complex exhibits a distorted trigonal bipyramidal geometry around the rhenium atom. Atoms C(1), S(1), and S(2) define the equatorial plane while atoms S(3) and P occupy the apical positions. The S(3)−Re−P angle spans 156.78(3)°, differing significantly from linearity. As a result of the trans location of atoms P and S(3), the Re−S(3) distance of 231.35(10) pm is somewhat longer than the 226.09(9) pm Re−S(2) bond distance; both, however, are well within the range of typical rhenium−sulfur distances. The Re═S bond to the sulfide ligand is significantly shorter, 209.75(10) pm, consistent with similar Re═S distances found in anionic Re(V) complexes.[11] The rhenium−

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(9) Spectroscopic data for **M′**−PPh$_3$ are as follows. $^1$H NMR: $\delta$ 7.73−7.41 (m, 15H), 7.29 (t, 1H, $J$ = 7.6 Hz), 7.25 (m, 2H), 7.15 (t, 1H, $J$ = 7.6 Hz), 4.98 (d, 1H, $J$ = 11.6 Hz), 3.75(d, 3H, $J$ = 8.4 Hz), 2.63 (d, 1H, $J$ = 11.6 Hz) ppm. $^{13}$C NMR: $\delta$ 146.74, 138.91, 134.58, 132.34, 131.61, 131.09, 128.83, 128.66, 128.41, 126.45, 49.66, 16.06 ppm. $^{31}$P NMR: $\delta$ 23.42 ppm. Elem. anal. C 48.80 (found for $RePS_3C_{26}H_{24}$, 47.98), H 3.88 (3.72), S 14.14 (14.78).

(10) X-ray crystal data for $C_{29}H_{27}PReS_3\cdot{}^1/_2C_6H_6$ (**M′**−PPh$_3$): monoclinic, $P2_1/n$, $a$ = 9.2936(5) Å, $b$ = 22.2088(12) Å, $c$ = 13.0576(7) Å, $\beta$ = 91.237(1)°, $V$ = 2694.5(3) Å$^3$, $Z$ = 4, $T$ = 173(2) K, $D_{\mathrm{calcd}}$ = 1.698 Mg/m$^3$, $R(F)$ = 2.46% for 4280 independent observed ($I = 2\sigma(I)$) reflections ($4 \leq 2\theta \leq 53°$). X-ray crystal data for $C_{16}H_{18}ORe_2S_5$ (**D′**): monoclinic, $P2_1/c$, $a$ = 11.2214(6) Å, $b$ = 12.8234(7) Å, $c$ = 13.7784(8) Å, $\beta$ = 90.423(1)°, $V$ = 1982.61(19) Å$^3$, $Z$ = 4, $T$ = 193(2) K, $D_{\mathrm{calcd}}$ = 2.543 Mg/m$^3$, $R(F)$ = 2.03% for 3334 independent observed ($I = 2\sigma(I)$) reflections ($4 \leq 2\theta \leq 52°$). All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. In the case of **M′**−PPh$_3$, the asymmetric unit also contains one half of a solvate benzene molecule. All software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-Ray Systems, Madison, WI).

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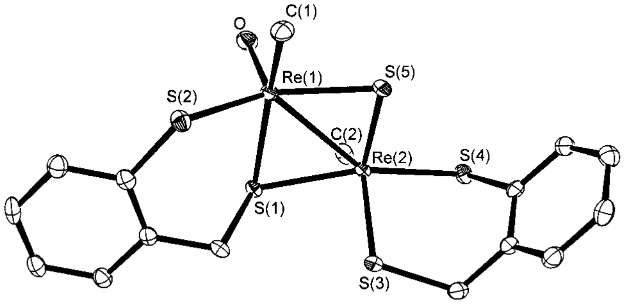

**Figure 2.** Perspective view of **D′** with thermal ellipsoids at the 30% probability level. Selected bond lengths (pm) and bond angles (deg): Re(1)−S(5) = 230.7(1), Re(1)−S(1) = 238.3(1), Re(1)−O = 167.5(3), Re(1)−Re(2) = 277.7(1), Re(2)−S(5) = 219.0(1), Re(2)−S(1) = 232.8(2); S(2)−Re(1)−S(5) = 134.2(1), S(4)−Re(2)−S(1) = 156.7(1), S(4)−Re(2)−S(5) = 94.0(1), S(4)−Re(2)−S(3) = 91.1(1), S(4)−Re(2)−C(2) = 81.5(2).

phosphorus and rhenium−carbon distances are in good agreement with the corresponding bonds in similar compounds.

Numerous attempts to extend the same approach to synthesize a sulfur analogue directly from **D** using $P_4S_{10}$ always led to an insoluble material. We then adopted a different strategy toward the synthesis of a sulfur analogue of **D**, shown in eq 2. Our approach was to convert the dimer to the monomeric pyridine complex first, and then treat this with $P_4S_{10}$ to replace Re═O by Re═S. When the yellow dimer **D** was treated with 2.2 equiv of pyridine per **D** in toluene at room temperature, the green mononuclear pyridine complex was formed slowly. Further treatment with $P_4S_{10}$ resulted in the formation of a red complex, which was isolated by column chromatography.

$$\frac{1}{2}\mathbf{D} \xrightarrow{C_5H_5N} \mathbf{M}\text{−Py} \xrightarrow{P_4S_{10}} [\mathbf{M'}\text{−Py}] \rightarrow \frac{1}{2}\mathbf{D'} + \text{Py} \qquad (2)$$

We were able to grow single crystals of this complex which on X-ray structural analysis was found to be a mixed oxo(sulfido)-dimeric Re(V) complex, **D′**, but it was devoid of pyridine, suggesting its loss upon isolation of the stable solid material, as shown in the last step of reaction 2. The structure is shown in Figure 2.[12] The dimer is held together by a bridging sulfide ligand, a bridging sulfur atom of one bidentate ligand only, and by a rhenium−rhenium bond. Each rhenium atom is therefore six-coordinate, but not octahedral in that the rhenium−rhenium bond axis is not directed toward one of the ideal octahedral apexes. Ignoring the rhenium−rhenium bond, the local geometry about atom Re(1) is best described as being that of a severely distorted square-planar arrangement, whereas the geometry about atom Re(2) is best represented as that of a severely distorted trigonal bipyramid. In the case of Re(1), the atoms S(1), S(2), S(5), and C(1) form the basal plane with the least squares a 15 pm deviation from planarity. The Re(1)−O vector forms a 88.4° angle to this plane. The trigonal bipyramidal approach would put atoms S(1), C(1), and O in the equatorial plane and atoms S(2) and S(5) in the apical positions. The S(2)−Re(1)−S(5) angle measuring 134.16(5)° clearly cannot be attributed to this geometry. The Re(1)−S(1) distance of 238.28(11) pm is slightly longer than the Re(1)−S(2) bond, 232.88(11) pm, owing to the coordination of S(1) to the second rhenium atom. The Re(1)−S(5) separation of 230.72(13) pm is markedly shorter than the other rhenium(1)−sulfur distances but still falls in the usual range of single rhenium−sulfur bonds, 230−240 pm. The geometry about Re(2) is best characterized as that of a trigonal bipyramid, with atoms S(3), S(5), and C(2) forming the equatorial plane and atoms S(1) and S(4) located at the apexes. The geometry is distorted as illustrated by the S(1)−Re(2)−S(4) angle value of 156.71(4)°, which is far from being linear. An alternative view of the Re(2) environment as square pyramidal would place atoms S(1), S(3), S(4), and C(2) in the basal plane with the least-squares deviation from planarity of 26 pm and atom S(5) at the apex. The Re(2)−S(5) vector comprises a 82.8° angle with the basal plane. The latter two numbers significantly deviate from the ideal values of 0° and 90°. The Re(2)−S(4) bond length of 231.18(12) pm is somewhat longer than the Re(2)−S(3) distance of 225.02(11) pm due to the trans positions of atoms S(4) and S(1). The Re(2)−S(5) bond measured 219.01(10) pm, indicative of the multiple character of the bond. The rhenium−rhenium bond was found to be 277.73(3) pm, a value on the shorter end for reported single bonds and on the longer end for reported double bonds.[13−16] In comparison, the nonbonded Re−Re distance in **D** is 371 pm.[3]

The formation of **D′** is best explained as follows: unlike the phosphine terminal sulfido complex, **M′**−$PPh_3$, which is stable by itself, the analogous pyridine complex is not stable and hence likely to dimerize with loss of ligand under the reaction conditions. Indeed, high oxidation state sulfido complexes of transition metals are known to dimerize or oligomerize, as has been well documented in the literature.[1,4] Hence it is likely that the pyridine-bound terminal sulfido complex reacts with another pyridine oxo complex to generate a dimer. This complex can slowly lose pyridine to form **D′**. Since the bridging sulfur is closer to Re(2) than Re(1) by 12 pm, and the Re−Re distance is 277.73(3) pm, the particular resonance structure shown for **D′** in Chart 1 is probably the best depiction.

In summary, we have reported here the synthesis and characterization of the first example of a neutral terminal Re(V)−sulfido complex. Also we have shown that in suitable cases $P_4S_{10}$ can be successfully used to effect metal−oxo to metal−sulfido conversion. We are currently studying the extension of this approach to other Re═S complexes and the reactivity of these complexes.

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**Supporting Information Available:** Experimental procedures for the synthesis of **D′** and **M′**-$PPh_3$ and spectroscopic and X-ray diffraction data for the two complexes (19 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) $^1$H NMR for **D′**: $\delta$ 8.22 (d, 1H, $J$ = 7.6 Hz), 7.65 (d, 1H, $J$ = 7.6 Hz), 7.36 (m, 2H), 7.08 (m, 2H), 6.95 (m, 2H), 5.09 (d, 1H, $J$ = 12.0 Hz), 4.83 (d, 1H, $J$ = 12.0 Hz), 3.41 (s, 3H), 3.05 (d, 1H, $J$ = 12.0 Hz), 3.04 (d, 1H, $J$ = 12.0 Hz), 2.93 (s, 3H) ppm.

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