294 *Organometallics* **1997,** *16,* 294−296

Syntheses of Dinuclear Rhenium Complexes with Disulfido and Sulfido Ligands[†]

M. Rakowski DuBois,* Balaji R. Jagirdar, S. Dietz, and B. C. Noll

Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309

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Summary: New dinuclear cyclopentadienylrhenium derivatives with four bridging sulfur ligands have been synthesized and characterized. The disulfide ligands in $[Cp'Re(\mu\text{-}S_2)]_2Cl_2$ *have been found to react with dihydrogen, acetylene, and ethene under mild conditions.*

Heterogeneous metal sulfides show extensive catalytic activity.[1−3] Soluble, molecular metal sulfide complexes have the potential to undergo related reactions and to provide insights into structural and electronic features which are important in determining the reactivity. For example, certain sulfido-bridged cyclopentadienylmolybdenum complexes react with molecular hydrogen under mild conditions to form products with highly reactive hydrosulfido ligands.[4,5] In recent work we have begun to study related molecular complexes which may involve more reactive M-S bonds,[6] and our syntheses of new cyclopentadienylrhenium complexes with sulfur ligands are reported here. Several CpRe derivatives with sulfido or polysulfido ligands have been reported previously,[7−10] but to our knowledge, previous examples of quadruply bridged Re dimers such as those described here have not been characterized.

The reaction of $Cp'ReCl_4$[11] ($Cp' = EtMe_4C_5$) with 2 equiv of bis(trimethylsilyl) sulfide[12] leads to the formation of a product of formulation $[Cp'ReS_2Cl]_2$, **1**, isolated in 80% yield.[13,14] The ^1H NMR spectrum for **1** confirms that the cyclopentadienyl ligands are equivalent, but provides no other information regarding the structure of the product. Single crystals of **1** were obtained from a pentane/dichloromethane solution, and an X-ray diffraction study was carried out.[15] A perspective drawing of the complex, and selected bond distances are given in Figure 1. The dication is a centrosymmetric dimer of Re(IV) ions bridged by two η^2-disulfide ligands. A disorder was observed in the arrangement of these ligands. The disorder was modeled by a second pair of disulfide ligands in the same plane rotated by an angle of 22° with final occupancies of 0.62 for the major orientation and 0.38 for the minor position. Only the major orientation of disulfide ligands is shown in Figure 1.

The $Re_2(\mu\text{-}S_2)_2$ core in **1** appears to be unique for dirhenium derivatives, as we have not found previous examples of a dinuclear Re complex with $\mu\text{-}\eta^2\text{-}S_2$ ligands. However the $M_2(\mu\text{-}S_2)_2$ unit has been identified in a number of other metal complexes.[16−20] A large number of $Cp_2M_2S_4$ compounds have also been characterized

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[†] Preliminary aspects of this work were presented at the 1995 International Chemical Congress of Pacific Basin Societies, Honolulu, HI, Dec 1995.

[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1997.

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(12) A product formulated as $[Cp'ReS(Cl)_2]_2$ has been isolated from the reaction of $Cp'ReCl_4$ with 1 equiv of $(Me_3Si)_2S$.[13]

(13) Complete details of syntheses, spectroscopic data, and elemental analyses for the new compounds are given in the Supporting Information.

(14) To a solution of $Cp'ReCl_4$ (0.40 g, 0.84 mmol) in CH_2Cl_2 was added $(Me_3Si)_2S$ (0.36 mL, 1.71 mmol), and the solution was stirred under N_2 at room temperature for ca. 18 h. The brown solution was then refluxed for 6 h. Solvent was removed in vacuo, and the product, **1**, was recrystallized from CH_2Cl_2/pentane at low temperature. Yield: 0.32 g, 87%. ^1H NMR ($CDCl_3$): 2.46 (q, Cp−CH_2); 2.44, 2.43 (2 s, CpMe); 1.18 (t, $CpCH_2CH_3$). FAB$^+$ mass spectrum (*m*/*e*): 835 (P − Cl); 798 (P − 2Cl); 766 (P − 2Cl − S); 734 ($Cp'_2Re_2S_2$).

(15) Crystallographic data for $[Me_4EtCpReS_2]_2Cl_2$, **1**: $C_{22}H_{34}Cl_2Re_2S_4$, fw 870.03, monoclinic, $P2_1/n$, $a = 8.596(2)$ Å, $b = 9.804(2)$ Å, $c = 15.726(3)$ Å, $\beta = 90.64°$, $V = 1325.2(5)$ Å^3, $Z = 2$, $T = 293$ K. Full-matrix refinement (based on F_o^2, SHELXL-93) of the positional and anisotropic thermal parameters for the non-hydrogen atoms converged with $R_1 = 0.0410$ and $wR_2 = 0.0743$ for 2320 independent reflections with $I > 2.0\sigma(I)$.

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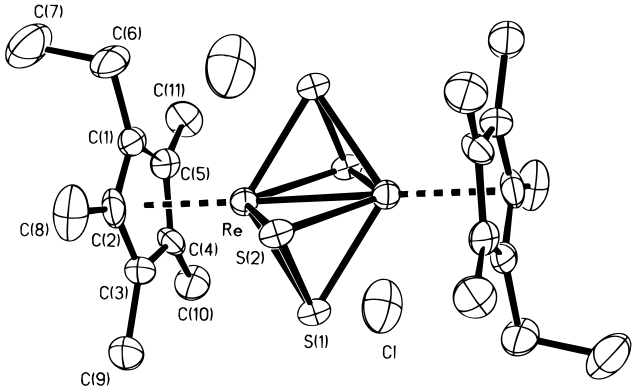
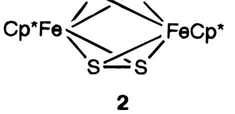


Figure 1. Perspective drawing and numbering scheme for $[Cp'Re(\mu\text{-}S_2)]_2Cl_2$, **1**. Selected bond distances: Re−Rea, 2.613(2) Å; Re−S(1), 2.358(7) Å; Re−S(2), 2.365(7) Å; S(1)−S(2), 2.228(10) Å.

previously;[21] within this class, the structures of $[CpFe(\mu\text{-}S_2)]_2^{2+}$, **2**,[22] and $(Cp^*Mo)_2(\mu\text{-}S_2)(\mu\text{-}S)_2$, **3**,[23] are most



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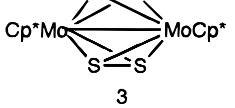

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closely related to that of **1**. The Re−Re distance in the dication is consistent with some degree of metal−metal bonding.[24] In other quadruply bridged dimers short metal−metal distances have been found to be quite similar regardless of metal oxidation states[25] and not good indicators of bond order.

Each of the $\mu\text{-}\eta^2\text{-}S_2$ ligands in **1** appears to undergo an additional weak interaction with the Cl^- counterions. The Cl−S1′ distance is 2.65 Å, and the Cl−S2 distance is 2.78 Å. These interactions suggest that the S_2 ligands are quite electrophilic in character. Close intermolecular interactions have been observed previously between halide-containing counterions and the $\mu\text{-}S_2$ ligands in $[M(\mu\text{-}S_2)S_2CNR)_2]_2^{2+}$, M = Mo and W.[16] Other types of metal−S_2 complexes with intermolecular interactions with halides have also been described.[26]

A final feature of note in the structure of **1** is that the S−S distance in the $\mu\text{-}S_2$ ligands is significantly lengthened to 2.228(10) Å compared to values near 2.00 Å for S_2 ligands in other complexes. This long S−S bond could result from the interactions of the S_2 ligands with the chloride counterions, but we note that such lengthening is not observed in the BF_4^---S_2 and I^---S_2 ligands of the Mo and W dithiocarbamate complexes described above.[16] Average sulfur−sulfur distances in these complexes were 1.99 and 2.03 Å, respectively.

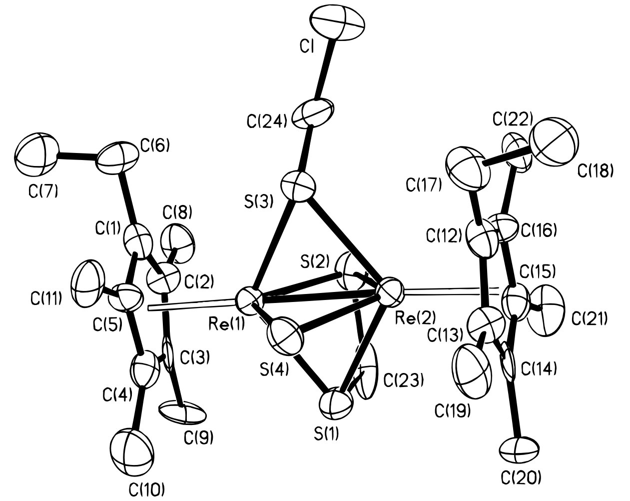

Figure 2. Perspective drawing and numbering scheme for the cation $[(Cp'Re)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2Cl)]^+$, **4**. Selected bond distances: Re1−Re2, 2.5652(10) Å; Re1−S1, 2.383(4) Å; Re1−S2, 2.432(4) Å; Re1−S3, 2.389(4) Å; Re1−S4, 2.410(4) Å; Re2−S1, 2.404(4) Å; Re2−S2, 2.420(5) Å; Re2−S3, 2.403(5) Å; Re2−S4, 2.398(4) Å.

A second minor product has been isolated from the reaction of $Cp'ReCl_4$ with 2 equiv of $(Me_3Si)_2S$ in refluxing dichloromethane.[27] Crystallization of **1** left a green supernatant from which **4** was isolated in 6−8% yield. The ^1H NMR spectrum of **4** showed four Cp−Me resonances, indicating that one of the planes of symmetry in **2** had been lost. In addition, two new singlets which integrated for 2 H each were observed at 3.45 and 7.49 ppm. The FAB^+ mass spectrum for **4** showed a strong fragment centered at *m/e* 863 with an isotope ratio that was consistent with the formulation of $[Cp'_2Re_2S_4(CH_2)_2Cl]^+$. The data suggested that fragments from the dichloromethane solvent have been incorporated into the dinuclear Re product. An X-ray diffraction study was carried out in order to determine the structural details of the complex.[28a]

Complex **4** was found to be a monocationic derivative of another quadruply bridged Re(IV) dimer.[28b] A perspective drawing of the cation and selected bond distances are shown in Figure 2. The metal ions are bridged by an η^2-methanedithiolate ligand, a sulfido ligand, and a chloromethanethiolate ligand. The synthesis and spectroscopic data for the analogous complex

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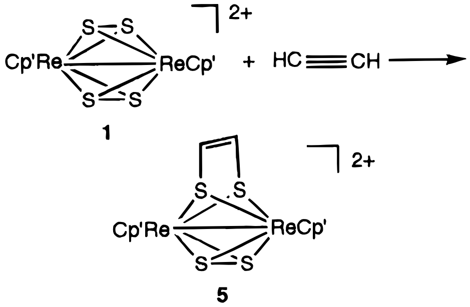
[27] $Cp'ReCl_4$ (0.30 g, 0.63 mmol) was reacted with $(Me_3Si)_2S$ (0.28 mL, 1.33 mmol) under similar conditions as described for the synthesis of **1**; the deep green supernatant solution formed during the crystallization of **1** was separated. Upon slow evaporation of solvent, deep green needles of **4** were obtained. Yield: 0.018 g, 6.4%. ^1H NMR ($CDCl_3$): 7.51 (br s, S_2CH_2); 3.45 (s, SCH_2Cl); 2.36, 2.35 (2 s, Cp−Me); 2.30 (q, Cp−CH_2); 1.29 (t, Cp−CH_2CH_3). FAB^+ mass spectrum (*m/e*): 895 (P, very weak); 863 (P − S).

[28] (a) Crystallographic data for $[(Cp'Re)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2Cl]$-SH, **4**: $C_{24}H_{40}ClRe_2S_5$, fw = 896.70, orthorhombic, $P2_12_12_1$, $a = 11.140(2)$ Å, $b = 13.993(3)$ Å, $c = 18.439(4)$ Å, V = 2874.3(10) Å^3, $Z = 4$, 299(2) K. Full-matrix refinement (based on F_o^2, SHELX-93) of the positional and anisotropic thermal parameters for the non-hydrogen atoms converged with $R_1 = 0.0440$, and $wR_2 = 0.0698$ for 3133 independent reflections with $I > 2\sigma(I)$. (b) The counterion for **4** appears to be the SH^- anion on the basis of mass spectral data and elemental analyses.[13] In the structural study the hydrogen atom on the anion was located by difference map (see Supporting Information).

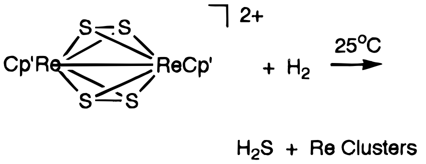
of molybdenum $[(Cp^*Mo)_2(S_2CH_2)(\mu\text{-}S)(\mu\text{-}SCH_2Cl)]^+$ have been reported previously.[29] Further work will be necessary to learn more about the mechanism for the formation of **4**. The formation of methanedithiolate and chloromethanethiolate ligands by reactions of nucleophilic molybdenum sulfide complexes with chlorinated solvents has been observed in earlier work,[4b,29] and a nucleophilic intermediate initially generated in the reaction with $(Me_3Si)_2S$ may be involved in the formation of **4**.

Convenient reagents for a preliminary assessment of ligand-based reactivity of discrete metal sulfur complexes are acetylene and ethylene. While activated acetylenes have been found to react with many different metal sulfido complexes in a variety of ways,[30−35] the addition of the *unsubstituted* alkyne to disulfido or to adjacent sulfido ligands to form the ethenedithiolate ligand has been observed only for a very few highly reactive systems.[36−38] The analogous addition of ethene to form ethanedithiolate ligands appears to be even rarer.[37c,38,39] The disulfido ligands in the rhenium complex **1** reacted readily with these unsaturated molecules, e.g., eq 1.[40] The spectroscopic data for **5** are consistent with the structure shown.[13] Similar dithiolate formation has been observed in the reaction of **1** with ethylene.[13]



(1)

The activation of dihydrogen by **3**[5a] and related derivatives[4,5] to give products with hydrosulfido ligands is an unusual capability which makes these complexes uniquely suited to study model reactions of hydrogen addition on metal sulfide surfaces. We report here that the rhenium derivative **1** also reacts with hydrogen under very mild conditions (1 atm, 25 °C). However in this case, a product with hydrosulfido ligands has not been isolated, and instead, the reaction leads to the facile elimination of hydrogen sulfide which has been identified by both ^1H NMR and GC−mass spectroscopic data, eq 2. The major rhenium cluster formed in this reaction shows limited stability and has not yet been completely identified, but a pattern at $m/e = 1134$ in the mass spectrum provides evidence for a trinuclear $Cp'_3Re_3S_4$ product. The hydrogenolysis of bridging sulfur ligands in di- or polynuclear metal complexes is a very unusual reaction which has direct relevance to the catalytic activity of heterogeneous metal sulfides. In the latter systems the reaction with hydrogen at high temperatures also results in the elimination of hydrogen sulfide, and this is the primary means of generating the anion vacancies believed to be necessary for substrate activation on the catalyst surface.[41] The similarities in the reactivity of the molecular system described here, accessible under very mild conditions, should permit us to explore mechanistic features of these important processes.



(2)

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Supporting Information Available: Text and tables giving syntheses, spectroscopic data, and elemental analyses for new complexes, tables listing details of data collection and refinement, complete bond distances and angles, and positional and thermal parameters for **1** and **4**, and an ORTEP diagram (21 pages). Ordering information is given on any current masthead page.

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[40] Complex **1** (0.15 g, 0.17 mmol) was dissolved in CH_3CN, and the solution was degassed in several freeze−pump−thaw cycles on a vacuum line. Two equivalents of acetylene were condensed into the reaction flask, and the solution was stirred for 4 days at room temperature. Solvent was removed in vacuo, and the crude product, **6**, was recrystallized from CH_3CN/Et_2O to give red brown microcrystals. Yield: 0.10 g, 65%. ^1H NMR (CD_3CN): 6.64 (s, SC_2H_2S); 2.45, 2.43 (2 s, Cp−Me); 2.34 (q, $Cp{-}CH_2$); 1.36 (t, $Cp{-}CH_2CH_3$). EI mass spectrum (*m*/*e*): 824 (P − 2Cl); 798 ($Cp'_2Re_2S_4$).

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