Redox and Non-redox Reactivity of Dihydrogen Sulfide at a Triply Bonded Dimetal Core: Hydrido, Hydrosulfido and *gem*-Dithiolato Complexes of Dirhenium

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While H_2S oxidatively adds to the electron-rich Re–Re triple bond of $Re_2X_4(\mu\text{-dppm})_2$ (X = Cl or Br; dppm = $Ph_2PCH_2PPh_2$) to give $Re_2(\mu\text{-H})(\mu\text{-SH})X_4(\mu\text{-dppm})_2$, non-redox reactions occur upon reaction of H_2S with *cis*-$Re_2(\mu\text{-O}_2CR)_2Cl_2(\mu\text{-dppm})_2$ (R = Me or Et) in the presence of $HBF_4\cdot Et_2O$ to give either *cis*-$Re_2(\mu\text{-SH})_2Cl_2(\mu\text{-dppm})_2$, when thf (tetrahydrofuran) or $CHCl_3$ is used as the solvent, or the *gem*-dithiolato complexes *cis*-$Re_2(\mu\text{-S}_2CR'R'')_2Cl_2(\mu\text{-dppm})_2$ and *cis*-$Re_2(\mu\text{-S}_2CHR'')_2Cl_2(\mu\text{-dppm})_2$ in the presence of ketones (R'R''CO) and aldehydes (R''CHO).
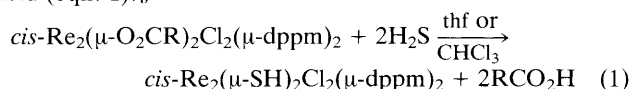
There has been a growing interest in the use of H_2S as a source of H_2 and organosulfur compounds,[1] although the isolation of H_2S complexes themselves have proved to be rather difficult[2,3] and only very recently has the first H_2S complex been structurally characterized.[3] Interestingly, the reactions of H_2S with dimetal complexes that contain metal–metal multiple bonds and which can serve as multi-electron redox reagents,[4,5] have not been described, although these hold the potential for some interesting chemistry that may not be accessible with other systems. In the present report, we describe the preliminary results of studies that encompass the reactions of

H_2S with triply bonded dirhenium(II) compounds and which yield products that are the results of either redox or non-redox behaviour at the electron-rich M≡M bond.

When deoxygenated thf solutions of the complexes $Re_2X_4(\mu\text{-dppm})_2$ (X = Cl or Br; dppm = $Ph_2PCH_2PPh_2$)[5] are exposed to a stream of gaseous H_2S for a few minutes and then stirred for *ca.* 5 h, the green–brown dirhenium(III) complexes $Re_2(\mu\text{-H})(\mu\text{-SH})X_4(\mu\text{-dppm})_2$ (**1a**, X = Cl; **1b**, X = Br) are obtained in isolated yields of 70–80%. The structure of these diamagnetic compounds has been established by an X-ray structure determination on **1b**; the Re–Re distance is

2.4566(7) Å.† The presence of μ-H and μ-SH ligands has been confirmed by ^{1}H NMR spectroscopy (CD_2Cl_2) which reveals resonances for the μ-*H* and μ-S*H* ligands at δ −6.34 (m, 1H) and δ +16.1 (m, 1H) for **1a**, and δ −7.30 (m, 1H) and δ + 16.2 (m, 1H) for **1b**, respectively. This represents the first case of the oxidative addition of the S–H unit across an electron-rich triple bond ($σ^2π^4δ^2δ*^2$ configuration).

In contrast to this reaction course, we observe quite different behaviour when the dirhenium(II) complexes of the type *cis*-Re$_2$(μ-O$_2$CR)$_2$Cl$_2$(μ-dppm)$_2$ **2**[6] are treated with H$_2$S.‡ The carboxylato species **2** can be activated by strong acid (HBF$_4$·Et$_2$O or HPF$_6$·H$_2$O) in non-aqueous solvents through labilization of the carboxylate groups. This generates the reactive, weakly solvated [Re$_2$Cl$_2$(μ-dppm)$_2$]$^{2+}$ moiety the enhanced electrophilic character of which, compared to the more readily oxidized neutral Re$_2$X$_4$(μ-dppm)$_2$,[5] results in non-redox reactions with H$_2$S, the actual reaction course being dependent on the solvent used. When a suspension of **2** (0.30 g; *ca.* 0.2 mmol) in deoxygenated thf or CHCl$_3$ (6 ml) is treated with HBF$_4$·Et$_2$O (0.15 ml) and then with a stream of gaseous H$_2$S the green hydrosulfido complex *cis*-Re$_2$(μ-SH)$_2$Cl$_2$(μ-dppm)$_2$ **3** precipitates in essentially quantitative yield (eqn. 1).§

$$cis\text{-}Re_2(\mu\text{-}O_2CR)_2Cl_2(\mu\text{-}dppm)_2 + 2H_2S \xrightarrow{\text{thf or}} \\ CHCl_3$$
$$cis\text{-}Re_2(\mu\text{-}SH)_2Cl_2(\mu\text{-}dppm)_2 + 2RCO_2H \quad (1)$$

The single crystal X-ray structure of **3** is shown in Fig. 1.¶ The complex possesses a cradle-like geometry[7] in which the two μ-SH ligands have replaced the carboxylate bridges. The Re–Re distance of 2.2577(5) Å is in accord with the retention of a Re≡Re bond.[4–6] The ^{1}H NMR spectrum (CD_2Cl_2 at room temp.) does not reveal a clearly discernible S-*H* resonance, although the IR spectrum (Nujol mull) of **3** shows a sharp and clearly defined, albeit weak, ν(S–H) mode at 2451 cm^{-1}. The ^{31}P{^{1}H} NMR spectrum shows relatively broad resonances at

1a X = Cl
1b X = Br

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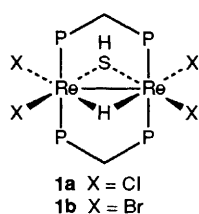
† Structural refinement is complicated by the presence of a badly disordered lattice diethyl ether molecule. At the present stage of refinement (R = 0.053 and R_w = 0.070) the bridging hydrido ligand and hydrogen on the bridging hydrosulfido ligand have not been located. Full structural details will be published in due course.

‡ Satisfactory elemental microanalyses were obtained for all compounds.

§ This same reaction course ensues in the absence of added HBF$_4$ but the reaction is slower and the product less pure. Presumably, the H$_2$S saturated solutions are sufficiently acidic to facilitate the slow release of RCO$_2$H with concomitant coordination of HS$^-$.
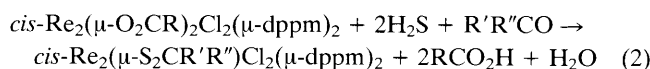
¶ *Crystal data* for Re$_2$(μ-SH)$_2$Cl$_2$(μ-dppm)$_2$·0.5CH$_2$Cl$_2$ **3** at +20 °C: space group $P2_1/c$ with a = 23.280(3), b = 13.040(2), c = 16.582(3) Å, β = 94.43(2)°, Z = 4, D_c = 1.748 g cm^{-3}. An empirical absorption correction was applied and all hydrogen atoms were included. The final residuals were R = 0.033 (R_w = 0.037) and GOF = 1.425 for 5275 data with I > 3.0σ(I).

Crystal data for Re$_2$(μ-S$_2$CMe$_2$)Cl$_2$(μ-dppm)$_2$·CH$_2$Cl$_2$ **4** at +20 °C: space group $P2_1/n$ with a = 13.093(5), b = 23.807(9), c = 18.832(4) Å, β = 106.29(2)°, Z = 4, D_c = 1.654 g cm^{-3}. An empirical absorption correction was applied and all hydrogen atoms were included. The final residuals were R = 0.053 (R_w = 0.069) and GOF = 1.941 for 5555 data with I > 3.0σ(I).

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

δ *ca.* −6.5 and δ *ca.* −3.8 in accord with the retention of pairs of chemically inequivalent dppm phosphorus atoms in solution as is the case in the solid-state structure (Fig. 1).

When acetone is used in place of thf and CHCl$_3$ as the solvent, the reaction proceeds to give the green *gem*-dithiolato complex *cis*-Re$_2$(μ-S$_2$CMe$_2$)Cl$_2$(μ-dppm)$_2$ **4** in *ca.* 85% yield, the identity of which was established by X-ray crystallography.¶ This complex also possesses a cradle-like geometry, with a bridging S$_2$CMe$_2$ ligand replacing the two μ-SH units (Fig. 2). The Re–Re distance of 2.2544(6) Å is identical to that in **3**. This complex, which has virtual C_{2v} symmetry, shows a singlet at δ −10.1 in its ^{31}P{^{1}H} and ^{31}P NMR spectra (CD_2Cl_2 at room temp.). We find that the use of other ketones and aldehydes in place of acetone leads to a range of *gem*-dithiolato complexes *cis*-Re$_2$(μ-S$_2$CR′R″)Cl$_2$(μ-dppm)$_2$ [see eqn. (2)], so this is a simple and quite general route to species of this type (isolated yields 60–80%).

$$cis\text{-}Re_2(\mu\text{-}O_2CR)_2Cl_2(\mu\text{-}dppm)_2 + 2H_2S + R'R''CO \rightarrow \\ cis\text{-}Re_2(\mu\text{-}S_2CR'R'')Cl_2(\mu\text{-}dppm)_2 + 2RCO_2H + H_2O \quad (2)$$

[R′ = H when R″ = H, Me or Et; R′ = Me when R″ = Me, Et, Pr or Pr^i; R′ = R″ = Et or Ph; R′,R″ = cyclopentyl or cyclohexyl]

Although **3** is converted into **4** when treated with a mixture of HBF$_4$·Et$_2$O and H$_2$S in acetone, it does not do so in the absence of H$_2$S or the absence of HBF$_4$·Et$_2$O, thereby indicating that it may not be an intermediate in the direct conversion of *cis*-Re$_2$(μ-O$_2$CR)$_2$Cl$_2$(μ-dppm)$_2$ into **4**. Rather, the formation of **4** most likely involves the direct attack of the *gem*-dithiol upon the weakly solvated [Re$_2$Cl$_2$(μ-dppm)$_2$]$^{2+}$ moiety since *gem*-dithiols (along with thioketones or thioaldehydes) are formed by the reactions of H$_2$S with ketones and aldehydes under acidic and basic conditions.[8]

Complexes that contain the methanedithiolato bridge μ-S$_2$CH$_2$ are quite well documented and several have been structurally characterized.[9–11] However, examples of *gem*-dithiolato ligand bridges of the type μ-S$_2$CXY are surprisingly
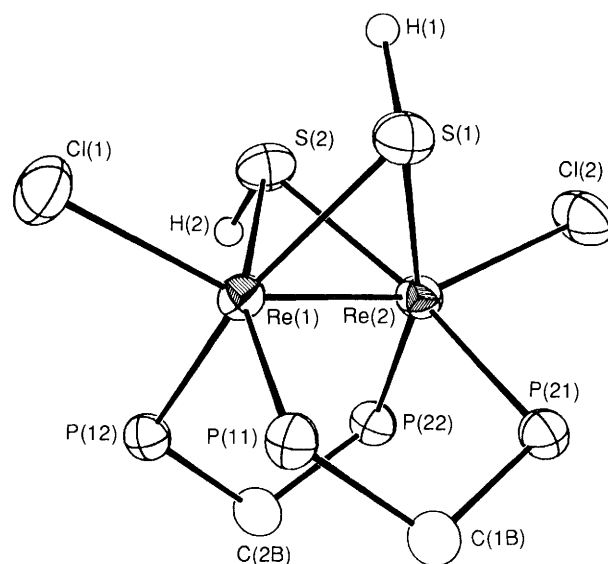
Fig. 1 ORTEP representation of the structure of the dirhenium complex in crystals of Re$_2$(μ-SH)$_2$Cl$_2$(μ-dppm)$_2$·0.5CH$_2$Cl$_2$ **3** with the phenyl group atoms of the dppm ligands omitted. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and bond angles (°): Re(1)–Re(2) 2.2577(5), Re(1)–Cl(1) 2.525(2), Re(1)–S(1) 2.495(2), Re(2)–S(1) 2.475(2), Re(1)–P(11) 2.392(2), Re(1)–P(12) 2.395(2); Re(2)–Re(1)–Cl(1) 153.82(6), P(11)–Re(1)–P(12) 97.12(8), S(1)–Re(1)–S(2) 74.85(9), S(1)–Re(1)–P(11) 91.30(8), Re(2)–Re(1)–S(1) 62.54(6), Re(1)–S(1)–Re(2) 54.03(5).
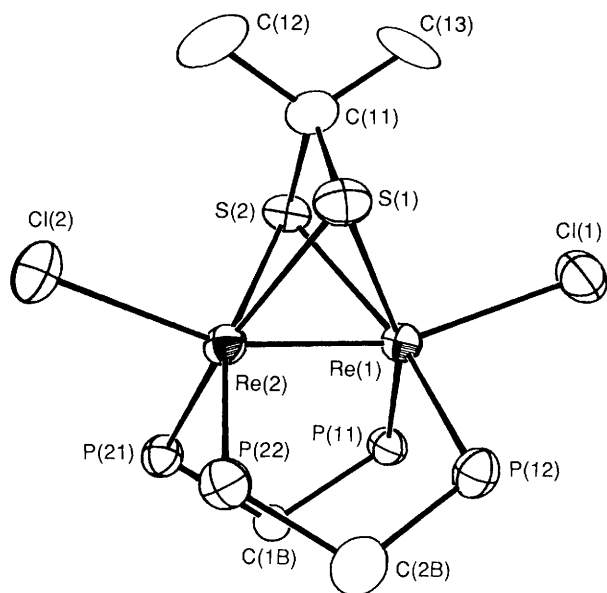
Fig. 2 ORTEP representation of the structure of the dirhenium complex in crystals of $Re_2(\mu\text{-}S_2CMe_2)Cl_2(\mu\text{-}dppm)_2\cdot CH_2Cl_2$ **4** with the phenyl group atoms of the dppm ligands omitted. Thermal ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) and bond angles (°): Re(1)–Re(2) 2.2544(6), Re(1)–Cl(1) 2.501(3), Re(1)–S(1) 2.471(3), Re(2)–S(1) 2.485(3), Re(1)–P(11) 2.399(3), Re(1)–P(12) 2.397(3); Re(2)–Re(1)–Cl(1) 160.74(7), P(11)–Re(1)–P(12) 99.98(9), S(1)–Re(1)–S(2) 68.81(9), S(1)–Re(1)–P(12) 96.3(1), Re(2)–Re(1)–S(1) 63.27(7), Re(1)–S(1)–Re(2) 54.12(6).

scarce, although a few examples exist in cyclopentadienyl-molybdenum chemistry in the cases where X = Me when Y = OH,[12] NH_2,[12] Me[9a] or Ph.[9b] However, none of these compounds has been structurally characterized by X-ray crystallography although there is one example of a structurally characterized 2,4-dithiametallacyclobutane complex, $(\eta\text{-}C_5Me_5)(Me_3P)Ir(S_2CMe_2)$, that contains a chelating S_2CMe_2 ligand.[13] Our work provides the first series of $\mu\text{-}gem$-dithiolate complexes in which a wide variety of alkyl substituents have been incorporated and which can be prepared in high yield in such a simple and straightforward fashion. This work demonstrates the effectiveness of the triply bonded dirhenium unit as a template for new metal–sulfur chemistry, the scope of which is under further investigation. This strategy provides an entry

into the chemistry of compounds that contain the previously unknown metal–metal bonded $Re(\mu\text{-}SH)_2Re$ and $Re(\mu\text{-}S_2CR'R'')Re$ moieties.

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