Redox Reactions Between Metal–Metal Multiple Bonds and Carbon Disulfide

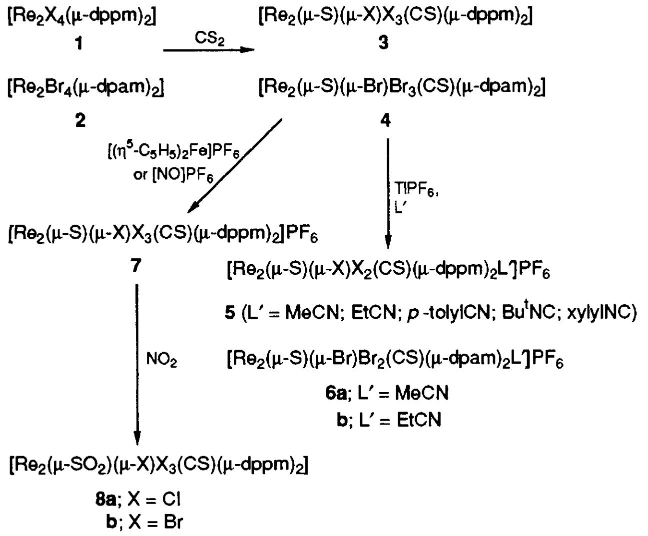
Ju-sheng Qi, Paul W. Schrier, Phillip E. Fanwick and Richard A. Walton*

Department of Chemistry, Purdue University, West Lafayette, IN 47907, USA

Carbon disulfide is reduced by triply bonded complexes of the type $[Re_2X_4(\mu\text{-}LL)_2]$ [X = Cl or Br; LL = $Ph_2PCH_2PPh_2$ (dppm) or $Ph_2AsCH_2AsPh_2$ (dpam)] to afford the edge-shared bioctahedral dirhenium(III) species $[Re_2(\mu\text{-}S)(\mu\text{-}X)X_3(CS)(\mu\text{-}LL)_2]$, which can in turn be converted to salts of the type $[Re_2(\mu\text{-}S)(\mu\text{-}X)X_2(CS)(\mu\text{-}LL)_2L']PF_6$ (L′ = MeCN, EtCN, *p*-toylCN, Bu^{t}NC or xylylNC) by reaction with $TlPF_6$ and L′ and to the $\mu\text{-}SO_2$ complexes $[Re_2(\mu\text{-}SO_2)(\mu\text{-}X)X_3(CS)(\mu\text{-}LL)_2]$ (LL = dppm) by treatment with $NOPF_6$ in dichloromethane.

We are currently examining the use of the electron-rich metal–metal triple bond ($\sigma^2\pi^4\delta^2\delta^{*2}$ configuration)[1,2] as a redox reagent towards a variety of unsaturated organic substrates including heteroalkenes. While the interaction of carbon disulfide with transition metal complexes can lead to a variety of insertion and redox reactions,[3] such behaviour has not previously been encountered in metal–metal multiple bond chemistry,[1,2] although the addition of CS_2 to the triply bonded compounds $[(\eta^5\text{-}C_5R_5)_2Mo_2(CO)_4]$ (R = H or Me) has been reported[4] to yield a $\eta^2\text{-}CS_2$ complex. We now describe the first example of the two-electron reduction of CS_2 at a multiply bonded dimetal unit.

When the triply bonded dirhenium(II) complexes $[Re_2X_4(\mu\text{-}dppm)_2]$[5] **1** and $[Re_2Br_4(\mu\text{-}dpam)_2]$[6] **2** are treated with CS_2 at room temperature for one day, the diamagnetic, olive green, insoluble complexes $[Re_2(\mu\text{-}S)(\mu\text{-}X)X_3(CS)(\mu\text{-}dppm)_2]$ **3** and $[Re_2(\mu\text{-}S)(\mu\text{-}Br)Br_3(CS)(\mu\text{-}dpam)_2]$ **4** are formed (Scheme 1), in which the thiocarbonyl and sulfido ligands are incorporated



Scheme 1 dppm = $Ph_2PCH_2PPh_2$; dpam = $Ph_2AsCH_2AsPh_2$; X = Cl or Br

into the final products.† The presence of a terminal CS group was established by a single intense ν(CS) mode near 1290 cm^{-1} in the IR spectra of these products (recorded as a Nujol mull). These complexes generally have low solubility in common solvents, but their solubility is enhanced considerably following their derivatization to salts of the type $[Re(\mu\text{-}S)(\mu\text{-}X)X_2(CS)(\mu\text{-}LL)_2L']PF_6$ (**5**, LL = dppm; **6**, LL = dpam) upon their reaction with L′ and $TlPF_6$ (Scheme 1). The structural identity of these compounds has been confirmed by an X-ray crystal structure determination on the derivative where X = Br, LL = dpam and L′ = EtCN **6b** with a crystal grown from CH_2Cl_2–$Pr^i{}_2O$. This diamagnetic complex, which shows a ν(CS) mode in its IR spectrum at 1314 cm^{-1}, possesses an edge-shared bioctahedral geometry (Fig. 1).‡ The Re–Re bond distance of 2.956(2) Å is *ca.* 0.3 Å greater than those in metal–metal bonded dirhenium(III) complexes such as $[Re_2(\mu\text{-}Cl)_2Cl_4(\mu\text{-}dppm)_2]$[7] and in carbonyl-containing edge-shared bioctahedral species like $[Re_2(\mu\text{-}Cl)(\mu\text{-}CO)Cl_3(\mu\text{-}dppm)_2(CO)]$,[8] both of which are prepared from $[Re_2Cl_4(dppm)_2]$. Although complex **6b** possesses bridging ligands (Br^- and S^{2-}) that are larger than those in these chloride systems, this does not of itself explain this large Re···Re bond lengthening.[9] Rather, we believe that this distance may be rationalized using the Walsh diagram[10] for the model system $[Re_2(\mu\text{-}Cl)_2Cl_8]^q$, where q represents the charge. For the compound $[Re_2(\mu\text{-}Cl)_2Cl_4(\mu\text{-}dppm)_2]$, the ground-state configuration can be represented as $\sigma^2\pi^2\delta^{*2}\delta^2$ (*i.e.* a net double bond) based upon an EHMO treatment,[10] which accords with the experimentally determined Re–Re distance of 2.616(1) Å.[7] As the bridge angles open up, as they do in the case of **6b**, for which the Re–S–Re and Re–Br–Re

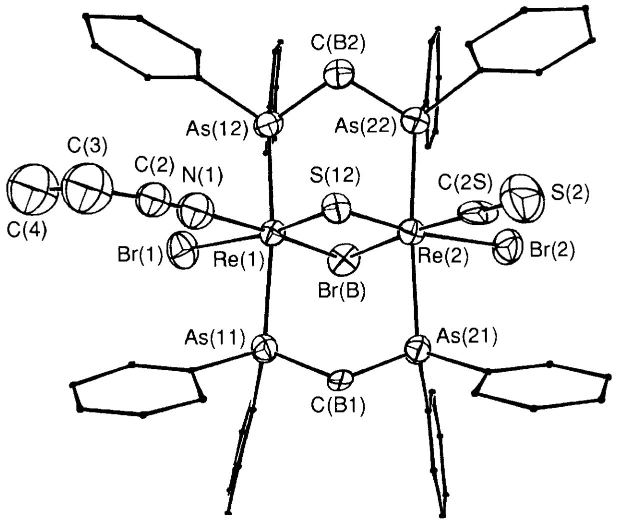


Fig. 1 ORTEP representation of the structure of the $[Re_2(\mu\text{-}S)(\mu\text{-}Br)Br_2(CS)(\mu\text{-}dpam)_2(NCEt)]^+$ cation in **6b**·CH_2Cl_2. Thermal ellipsoids are drawn at the 50% probability level except for the phenyl carbon atoms which are circles of arbitrary radius. Selected bond distances (Å) and bond angles (°): Re(1)–Re(2) 2.956(2), Re(1)–Br(1) 2.551(4), Re(1)–Br(B) 2.526(4), Re(1)–S(12) 2.240(8), Re(1)–N(1) 2.12(3), Re(2)–Br(2) 2.546(4), Re(2)–Br(B) 2.590(4), Re(2)–S(12) 2.263(8), Re(2)–C(2S) 2.02(3), S(2)–C(2S) 1.40(4); Re(1)–S(12)–Re(2) 82.1(3), Re(1)–Br(B)–Re(2) 70.57(9), Br(1)–Re(1)–N(1) 79.9(7), N(1)–Re(1)–S(12) 84.4(8), S(12)–Re(1)–Br(B) 105.0(2), Br(1)–Re(1)–Br(B) 90.7(1), Re(2)–C(2S)–S(2) 174(3).

angles are 82.1(3) and 70.57(9)°, π^* can drop below δ leading to the ground-state electron configuration $\sigma^2\pi^2\delta^{*2}\pi^{*2}$ and a bond order less than one. The destabilization of δ relative to π^* results from the interaction of the former with the filled nonbonding orbitals on the bridging ligands.[10] The interaction with S^{2-} may be particularly important in the present case since an increase in the Re–Re distance of this magnitude has not previously been seen in any structurally characterized dirhenium(III) complexes which possess the $[Re_2(\mu\text{-}dppm)_2]$ unit.[5c,11]

A one-electron oxidation at $E_{\frac{1}{2}}$(ox) *ca.* +0.40 V (*vs.* Ag/AgCl) which is found in the cyclic voltammograms of solutions of **3** and **4** in 0.1 mol dm^{-3} $Bu^n{}_4NPF_6$–CH_2Cl_2 can be accessed chemically by the use of CH_2Cl_2 solutions of $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$. By this means we have oxidized **3** to paramagnetic $[Re_2(\mu\text{-}S)(\mu\text{-}X)X_3(CS)(\mu\text{-}dppm)_2]PF_6$ **7**.§ While these same complexes are also produced when $[NO]PF_6$ is the oxidant, they rapidly convert to the μ-SO_2 complexes $[Re_2(\mu\text{-}SO_2)(\mu\text{-}X)X_3(CS)(\mu\text{-}dppm)_2]$ **8** if the reaction medium is not rigorously deoxygenated (Scheme 1). The structure of the chloro complex **8a** (crystals grown from $C_2H_4Cl_2$–CH_2Cl_2–$Pr^i{}_2O$), which is shown in Fig. 2,‡ resembles those of complexes **3**–**6** (Fig. 1), except that a bridging μ-SO_2 unit has replaced the μ-S ligand and the Re–Re bond distance has shortened to 2.628(1) Å. The disparity in the ligand sets about the two rhenium atoms in this complex induces an asymmetry in the bonding of the SO_2 ligand such that the Re–S distances differ by *ca.* 0.15 Å. This behaviour resembles that encountered previously in the structures of the carbonyl complexes $[Re_2(\mu\text{-}CO)(\mu\text{-}Cl)Cl_2(CO)(\mu\text{-}dppm)_2(PR_3)]PF_6$ (R = Me or OEt),[12] in which the μ-CO ligand is asymmetrically bound to the two rhenium centres. Formally, we can consider complexes **8**, like **3**–**6**, to be dirhenium(III) derivatives and the shortening in the Re–Re bond by *ca.* 0.3 Å to result from a

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† Yields 70–80%. Satisfactory elemental microanalyses were obtained for all compounds.

‡ *Crystal data* for **6b**·CH_2Cl_2 at +20 °C: triclinic, space group $P\bar{1}$ with a = 12.653(2), b = 16.901(7), c = 17.368(7) Å, α = 65.88(4), β = 78.91(2), γ = 72.12(3)°, Z = 2, D_c = 1.981 g cm^{-3}. An empirical absorption correction was applied. The final residuals were R = 0.062 (R_w = 0.073) for 3786 data with $I > 3.0\sigma(I)$.

Crystal data for **8a**·$C_2H_4Cl_2$·CH_2Cl_2 at +20 °C: space group $P\bar{1}$ with a = 11.231(1), b = 14.316(2), c = 19.854(2) Å, α = 86.67(1), β = 80.30(1), γ = 81.03(1)°, Z = 2, D_c = 1.68 g cm^{-3}. An empirical absorption correction was applied. The final residuals were R = 0.044 (R_w = 0.070) and GOF = 2.144 for 6416 data with $I > 3\sigma(I)$.

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.

§ These complexes are EPR-active (X-band spectra in CH_2Cl_2–toluene at −160 °C) and have magnetic moments of 1.7 (±0.1) μ_B (Evans method in CH_2Cl_2).

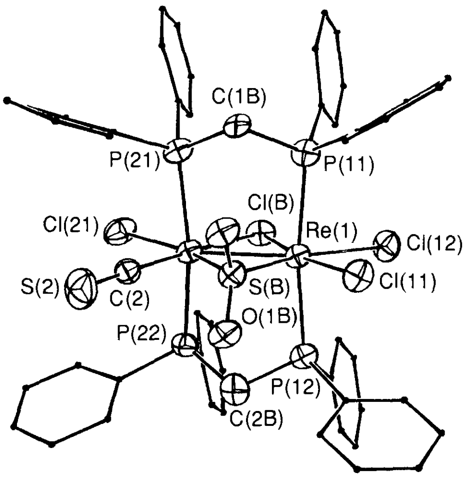

Fig. 2 ORTEP representation of the structure of the $[Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_3(CS)(\mu\text{-dppm})_2]$ molecule in **8a**$\cdot C_2H_4Cl_2\cdot CH_2Cl_2$. Thermal ellipsoids are drawn at the 50% probability level except for the phenyl carbon atoms which are circles of arbitrary radius. Selected bond distances (Å) and bond angles (°): Re(1)–Re(2) 2.628(1), Re(1)–Cl(11) 2.386(2), Re(1)–Cl(12) 2.415(2), Re(1)–Cl(B) 2.433(2), Re(1)–S(B) 2.251(2), Re(2)–Cl(21) 2.400(2), Re(2)–Cl(B) 2.460(2), Re(2)–S(B) 2.406(2), Re(2)–C(2) 1.947(8), S(2)–C(2) 1.476(9), S(B)–O(1B) 1.457(6), S(B)–O(2B) 1.463(6); Re(1)–S(B)–Re(2) 68.63(6), Re(1)–Cl(B)–Re(2) 64.98(5), Cl(11)–Re(1)–S(B) 77.02(8), C(2)–Re(2)–S(B) 72.4(2), Re(2)–C(2)–S(2) 176.5(6), O(1B)–S(B)–O(2B) 110.9(4).

change in ground-state electronic configuration from $\sigma^2\pi^2\delta^{*2}\pi^{*2}$ (in **3**–**6**) to $\sigma^2\pi^2\delta^{*2}\delta^2$ (in **8**). The loss of the non-bonding sulfur orbitals upon oxidation of μ-S to μ-SO_2 could lead to a relative stabilization of the metal-based δ orbital so that it drops below π^*.[10]

While full details of the mechanism for the conversion of **7** to **8** (Scheme 1) remain to be established, we believe this reaction involves the attack of NO_2 on **7**. The NO_2 is produced by the reaction of NO (the byproduct of the oxidation of **3** to **7**) with small amounts of adventitious O_2 in the system, *i.e.* NO_2 is the actual oxygen transfer reagent for the conversion of μ-S to μ-SO_2. In support of this contention we find that when **3** and **7** are treated with NO_2, **8** is formed in essentially quantitative yield in both cases. We observe no reaction between O_2 and complexes **3**–**6**. The isolation of **8** in its reduced form rather than as $[Re_2(\mu\text{-}SO_2)(\mu\text{-}X)X_3(CS)(\mu\text{-dppm})_2]^+$ accords with the electrochemical properties of **8** [$E_{1/2}(\text{ox}) = +1.12$ V, $E_{1/2}(\text{red})(1) = -0.20$ V and $E_{1/2}(\text{red})(2) = -1.05$ V *vs.* Ag/AgCl in 0.1 mol dm^{-3} $Bu^n{}_4NPF_6$–CH_2Cl_2] which show that in its oxidized form it is a very potent one-electron oxidant.

The formation of the complexes $[Re_2(\mu\text{-}S)(\mu\text{-}X)X_3(CS)(\mu\text{-}LL)_2]$ **3** and **4** and their closely related derivatives **5** and **6** constitutes the first examples where multiply bonded dimetal complexes have brought about a 2-electron reduction of CS_2, and the CS and S^{2-} fragments have been incorporated into the resulting products in which the dimetal unit is preserved. This provides a convenient entry to the mixed sulfide–halide and sulfur dioxide–halide units $[Re(\mu\text{-}S)(\mu\text{-}X)Re]^{n+}$ and $[Re(\mu\text{-}SO_2)(\mu\text{-}X)Re]^{n+}$, further aspects of whose chemistry are currently being investigated.

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