Reduction of sulfur monoxide on a hexanuclear ruthenium complex

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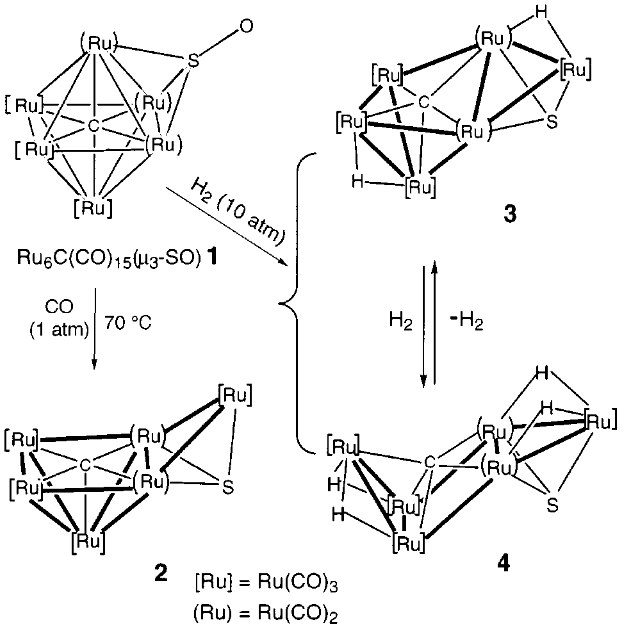
The sulfur monoxide unit, which originates from a gaseous SO_2 molecule trapped on a Ru_6-cluster, is easily reduced either by CO or H_2 to the sulfide ligand with concomitant skeletal cluster rearrangement, where the resulting cluster shape depends largely on the amount of the reducing agent taken up by the cluster.

Removal of SO_2 from combustion gases by reduction to sulfur is of great research interest because harmless S_8 is often a more desirable product than oxidized forms such as SO_4^{2-}.[1,2] The heterogeneous system, 0.5% Ru/γ-Al_2O_3, is one of the most active agents for the catalytic reduction of SO_2 with H_2 in the gas phase.† The presence of Al_2O_3 is crucial, since Ru metal alone has no catalytic activity.[3] It is likely that, aside from the role of Al_2O_3 as the carrier of fine metal particles, the Lewis acid character of Al_2O_3 assists in the reduction.[4,5] On the basis of the often-referred cluster–surface analogies,[6] reduction of SO_2 on high nuclearity metal clusters would be a good model for SO_2 reactions on metal particles.[1,7] Shriver and coworkers found that the cluster-bound SO_2 in the trinuclear cluster $[Fe_3H(CO)_9(SO_2)]^-$ is transformed to a μ3-SO ligand on reduction with Na·Ph_2CO, but prior acetylation of the ligating SO_2 to give an AcOSO ligand was necessary for its complete reduction to the sulfide complex $[Fe_3(CO)_9S]^{2-}$.

Although $[Fe_3(CO)_9(SO)]^{2-}$ represents the first example of a cluster-bound SO made by reductive cleavage of SO_2, addition of excess reducing agent to the isolated SO complex resulted in degradation of the cluster, and hence reactivity of this highly important intermediate could not be studied.[8] In the high nuclearity cluster complex, $[Ru_6C(CO)_{15}(\mu\text{-}SO_2)]^{2-}$, which we recently prepared, the bound SO_2 can easily be converted to an SO ligand, $Ru_6C(CO)_{15}(\mu_3\text{-}SO)$ **1**, by addition of a Lewis acid such as BF_3.[9] Herein we describe the first reduction-reactivity of the SO ligand on polynuclear cluster complexes, which may have relevance to a stepwise reduction of SO_2 on heterogeneous metal surfaces.

A dichloroethane solution of **1** was heated at 70 °C for 6 h under one atmosphere of CO. A dark-purple crystalline complex was isolated in 74% yield after chromatography on silica gel, and was structurally characterized as $Ru_6C(CO)_{16}S$ **2**.‡ As shown in Scheme 1, the reaction is accompanied by incorporation of an additional CO into the cluster, cleavage of two of the metal–metal bonds and swinging of the S-capped metal triangle to open the upper part of the original octahedral metal skeleton of **1** (Scheme 1). An 88-electron Os cluster having a related structure, $Os_6(CO)_{16}(\mu_4\text{-}S)(\mu_3\text{-}S)$, has been isolated by Adams and Yang as one of the products of the thermolysis of $HOs_3(CO)_{10}(\mu\text{-}SPh)$.[10]

The reduction of SO to S on the cluster was also achieved by reaction with H_2. A dichloroethane solution of complex **1** was allowed to react with H_2 (10 atm) and 1.5 equiv. CO in an autoclave. After 6 h at 70 °C, four complexes were isolated after silica-gel column chromatography: the known trinuclear complex, $Ru_3(CO)_9(\mu_2\text{-}H)_2(\mu_3\text{-}S)$ (12%),[11] red–purple crystalline $Ru_6C(CO)_{16}(H)_2S$ (**3**, 30%), dark-orange crystals of $Ru_6C(CO)_{16}(H)_4S$ (**4**, 9%), and a brown powder (*ca.* 15%) which appears to be a heptanuclear ruthenium complex containing sulfur and CO as determined by elemental analysis, IR, and ESMS. The new compounds **3** (Fig. 1) and **4** (Fig. 2) were characterized by single-crystal X-ray diffraction analyses.‡ Complex **3** has a shape analogous to that of **2** but, as a result of cleavage of an additional metal–metal bond [Ru3···Ru6 3.920(1) Å], the pentagonal unit is now very much distorted. Two new hydride ligands, which are bridging the Ru1–Ru3 and Ru5–Ru6 bonds, supply the electrons needed to break the



Scheme 1

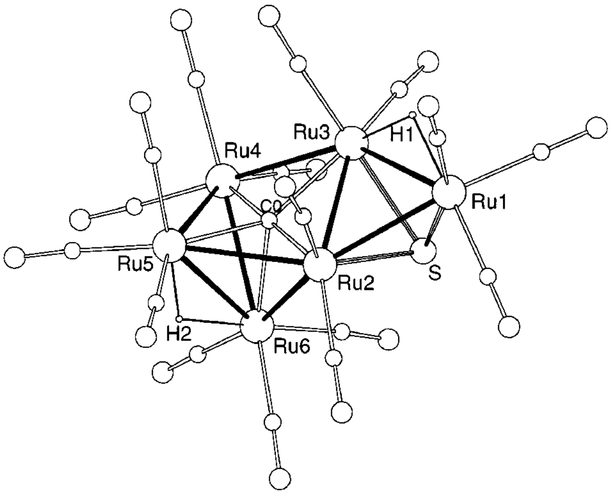


Fig. 1 X-Ray crystal structure of $Ru_6C(CO)_{16}(H)_2S$ **3**. Selected bond distances (Å): Ru1–Ru2 2.8071(5), Ru1–Ru3 2.8603(5), Ru2–Ru3 2.7308(5), Ru2–Ru5 2.8656(5), Ru2–Ru6 2.8765(5), Ru3–Ru4 2.9794(5), Ru3···Ru6 3.920(1), Ru4–Ru5 2.9261(5), Ru4–Ru6 2.8358(5), Ru5–Ru6 2.8249(5), Ru1–S 2.318(1), Ru2–S 2.383(1), Ru3–S 2.389(1).

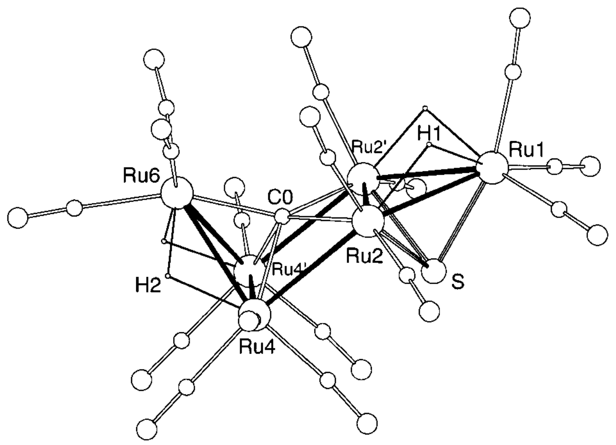


Fig. 2 X-Ray crystal structure of $Ru_6C(CO)_{16}(H)_4S$ **4**. Selected bond distances (Å): Ru1–Ru2 2.854(1), Ru2–Ru3 2.721(1), Ru2–Ru4 2.869(1), Ru4–Ru5 2.808(1), Ru4–Ru6 2.860(1), Ru2···Ru6 3.8939(1), Ru1–S 2.359(4), Ru2–S 2.375(3).

metal–metal bond. In complex **4**, two more hydrogen atoms are present and one more metal–metal bond (either Ru2–Ru5 or Ru2–Ru6 in **3**) has been broken. The solid-state molecular structure of **4** has a mirror plane that passes through Ru1, Ru6, and the carbide carbon atom (C0) of the chair-like cluster skeleton. The carbide ligand is well exposed, its distances from the metal square Ru2–Ru2′–Ru4–Ru4′ and the metal triangle Ru4–Ru4′–Ru6 are 0.39 and 0.80 Å, respectively. A carbon atom of this type has attracted much interest as being relevant to metal-surface bound carbon atoms in heterogeneous catalysis.[12]

Despite the large change in skeletal shape, complexes **3** and **4** are interconvertible cleanly, although slowly, at room temperature. The transformation was monitored by observing the characteristic IR bands of these complexes in the ν(CO) region. Keeping a dichloromethane solution of **3** under 15 atm H_2 at room temperature gave **4** in 80% conversion after 2 weeks, while formation of any other by-products was not detected. The reverse reaction was more facile. When a dichloromethane solution of **4** was allowed to stand under argon for 4 days, dihydrogen was released to generate **3** almost quantitatively. In contrast, **2** did not react with H_2 under similar conditions. The reactions are summarized in Scheme 1. Further, it may be mentioned that the trinuclear complex $Ru_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}S)$ obtained as a minor product in the present reaction of **1** with H_2 (*vide supra*) has a structure[11] similar to that of the S-capped metal triangle moiety in **4**. It is interesting that recent reports have described facile metal–metal bond cleavage on solid metal surfaces induced by adsorption of small molecules such as H_2.[13]

In conclusion, reduction of sulfur oxide to S on high nuclearity clusters should take place smoothly either by CO or H_2 once the cluster bound SO_2 is transformed to SO. The first step, reduction of SO_2 to SO, appears more difficult since $[Ru_6C(CO)_{15}(\mu\text{-}SO_2)]^{2-}$ or $Ru_6C(CO)_{16}(\mu\text{-}SO_2)$ do not react under similar conditions. Either much more severe conditions or assistance by a Lewis acid will be required for the initial reduction process.

Notes and references

† In homogeneous dinuclear metal systems, pioneering works for catalytic and stoichiometric reduction of SO_2 by H_2 have been reported by Kubas *et al.*[14,15] and Neher and Lorenz.[16]

‡ *Crystal data*: for **2**: $C_{17}O_{16}Ru_6S$, M = 1098.66, triclinic, space group $P\bar{1}$, a = 8.8781(4), b = 10.6179(5), c = 15.1237(11) Å, α = 83.354(5), β = 82.280(4), γ = 74.894(3)°, U = 1352.8(1) Å^3, Z = 2, T = 21 °C, μ = 34.15 cm^{-1}, for 6279 unique reflections R = 0.022 and GOF = 1.26.

For **3**: $C_{17}H_2O_{16}Ru_6S$, M = 1100.67, monoclinic, space group $P2_1/n$, a = 16.2771(14), b = 9.7107(7), c = 17.6042(9) Å, β = 96.174(5)°, U = 2766.4(3) Å^3, Z = 4, T = 21 °C, μ = 33.40 cm^{-1}, for 4739 unique reflections R = 0.023 and GOF = 1.17.

For **4**: $C_{17}H_4O_{16}Ru_6S{\cdot}CH_2Cl_2$, M = 1187.62, orthorhombic, space group $Pnnm$, a = 23.7389(26), b = 12.0440(7), c = 17.5965(12) Å, U = 3315.6(5) Å^3, Z = 4, T = 21 °C, μ = 29.51 cm^{-1}, for 2869 unique reflections R = 0.044 and GOF = 3.55. CCDC 182/1141. See http://www.rsc.org/suppdata/cc/1999/279/ for crystallographic files in .cif format.

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