

## Synthesis and X-Ray Structural Characterisation of $\text{Rh}_4(\mu\text{-CO})_4(\mu\text{-SO}_2)_3\text{-}[\text{P}(\text{OPh})_3]_4 \cdot \frac{1}{2}\text{C}_6\text{H}_6$ : A 'Butterfly' Cluster with an Unusual Bridging Mode for Sulphur Dioxide

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**Summary** The reaction of  $\text{SO}_2$  with  $\text{Rh}_4(\text{CO})_8[\text{P}(\text{OPh})_3]_4$  leads to the formation of a tetranuclear 'butterfly' cluster compound  $\text{Rh}_4(\mu\text{-CO})_4(\mu\text{-SO}_2)_3[\text{P}(\text{OPh})_3]_4$ , which has the sulphur dioxide ligand functioning in a novel bridging fashion bonding to two metal atoms through the sulphur and a third metal atom through one of the oxygen atoms.

ALTHOUGH considerable interest has been shown recently in the co-ordination chemistry of sulphur dioxide<sup>1</sup> few cluster compounds containing this ligand have been reported.<sup>2</sup> In all of these cluster compounds the  $\text{SO}_2$  ligand acts as a two-electron bridging ligand and co-ordinates to two metal atoms through the sulphur atom in a manner analogous to the more widely studied CO ligand. However, the significant differences in the electronic characteristics of these ligands together with their very different steric requirements suggested that the reactions of  $\text{SO}_2$  with metal cluster compounds might lead to the isolation of cluster compounds with unusual geometries and reactivities. The ability of  $\text{SO}_2$  to alter the preferred total number of electrons in trinuclear platinum clusters has previously been noted.<sup>3</sup>

When  $\text{SO}_2$  is bubbled through a solution of  $\text{Rh}_4(\text{CO})_8\text{-}[\text{P}(\text{OPh})_3]_4$  in benzene at room temperature for 15 min the solution takes on a yellow appearance, and the addition of hexane leads to the isolation of an air-stable orange crystalline solid (m.p. 123–127 °C). Analytical data and a molecular weight determination suggested that this compound was best formulated as  $\text{Rh}_4(\text{CO})_4(\text{SO}_2)_3[\text{P}(\text{OPh})_3]_4$ . Infrared data [ $\nu(\text{CO})(\text{CCl}_4)$  1968s, 1945m, and 1911 vs  $\text{cm}^{-1}$ ;  $\nu(\text{SO}_2)$  (Nujol) 1230s, 1102m, 1074s, and 977s  $\text{cm}^{-1}$ ] were consistent with presence of bridging CO and  $\text{SO}_2$  ligands,<sup>1</sup> but did not resolve the apparent co-ordinative unsaturation of the compound.

*Crystal data:*  $\text{C}_{78}\text{H}_{63}\text{O}_{22}\text{P}_4\text{Rh}_4\text{S}_2$ ,  $M = 1995$ , monoclinic,  $a = 21.924(8)$ ,  $b = 14.474(9)$ ,  $c = 51.398(25)$  Å,  $\beta = 94.48(4)^\circ$ ,  $U = 16261$  Å<sup>3</sup>;  $Z = 8$ ,  $D_c = 1.50$  g  $\text{cm}^{-3}$ ,  $F(000) = 8032$  electrons, graphite-monochromated Mo- $K_\alpha$  radiation ( $\lambda = 0.71069$  Å),  $\mu(\text{Mo-}K_\alpha) = 8.73$   $\text{cm}^{-1}$ , space group  $A2/a$  from successful refinement of structure. The diffracted intensities were measured to  $\theta_{\text{max}} = 20^\circ$  on an Enraf-Nonius CAD4 diffractometer and were not corrected for absorption. 3201 reflections  $I \geq 3\sigma(I)$  were used to solve (direct methods, Patterson and Fourier syntheses) the

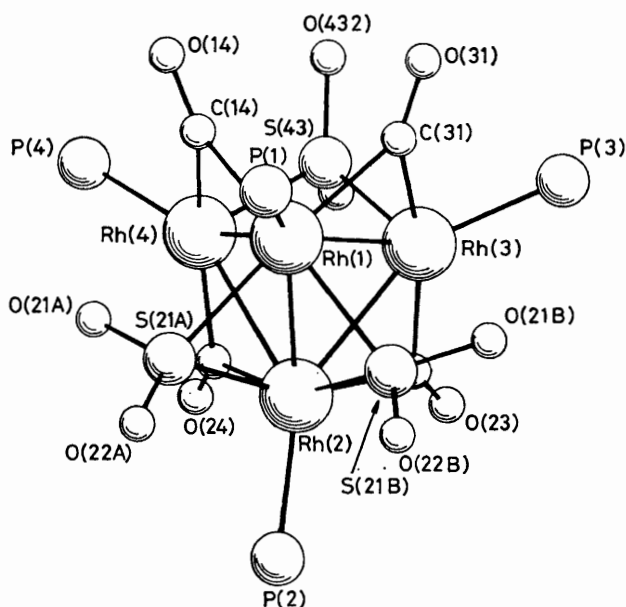


FIGURE 1. X-Ray structure of  $\text{Rh}_4(\mu\text{-CO})_4(\mu\text{-SO}_2)_3[\text{P}(\text{OPh})_3]_4 \cdot \frac{1}{2}\text{C}_6\text{H}_6$ ; hydrogen atoms, phenyl rings, and  $\text{C}_6\text{H}_6$  of solvation have been omitted for clarity. Distances and angles: Rh(1)–Rh(2) 2.782(2), Rh(1)–Rh(3) 2.719(2), Rh(2)–Rh(3) 2.716(2), Rh(2)–Rh(4) 2.711(2), Rh(3)–Rh(4) 3.073(3), Rh(1)–S(21B) 2.336(6), Rh(1)–S(21A) 2.358(6), Rh(2)–S(21B) 2.333(6), Rh(2)–S(21A) 2.317(6), Rh(3)–S(43) 2.249(6), Rh(4)–S(43) 2.236(6), S(43)–O(431) 1.48(2), S(43)–O(432) 1.43(1), S(21B)–O(22B) 1.43(2), S(21B)–O(21B) 1.50(2), S(21A)–O(21A) 1.47(1), S(21A)–O(22A) 1.44(2), Rh(3)–O(21B) 2.34(2), Rh(4)–O(21A) 2.29(1) Å;  $\angle\text{O}(431)\text{–S}(43)\text{–O}(432)$  114(1),  $\text{O}(21A)\text{–S}(21A)\text{–O}(22A)$  115(1),  $\text{O}(21B)\text{–S}(21B)\text{–O}(22B)$  113(1)°.

structure, which was refined (blocked matrix least squares) to  $R = 0.053$ .†

The molecular structure of  $\text{Rh}_4(\mu\text{-CO})_4(\mu\text{-SO}_2)_3[\text{P}(\text{OPh})_3]_4$  illustrated in Figures 1 and 2 shows several interesting features which were not apparent from the spectroscopic data. Firstly, the metal tetrahedral cluster present in  $\text{Rh}_4(\text{CO})_8[\text{P}(\text{OPh})_3]_4$  has opened out to give a 'butterfly' or 'hinged' cluster in  $\text{Rh}_4(\mu\text{-CO})_4(\mu\text{-SO}_2)_3[\text{P}(\text{OPh})_3]_4$ . The extent of this distortion may be defined by a long Rh(3)–Rh(4) bond of 3.073(3) Å compared to 2.711(2)–2.782(2) Å for the remaining five metal–metal bonds and a dihedral angle of 82.4° between the planes defined by Rh(1)Rh(2)Rh(3) and Rh(1)Rh(2)Rh(4). This dihedral angle is considerably smaller than those reported for other 'butterfly' cluster compounds, e.g.  $[\text{Rh}_4(\text{CO})_8(\text{PPh}_2)_4]^-$  (124°) and  $[\text{Fe}_4(\text{CO})_{13}\text{H}]^-$  (117°).<sup>4,5</sup> The long Rh(3)–Rh(4) bond is bridged by an  $\text{SO}_2$  ligand and the other two  $\text{SO}_2$  ligands bridge the Rh(1)–Rh(2) bond as shown in Figure 2. The four bridging carbonyl ligands span the remaining four metal–metal bonds in a slightly asymmetrical fashion with Rh(1)–C and Rh(2)–C bond lengths consistently 0.06–0.08 Å shorter than the Rh(3)–C and Rh(4)–C bond lengths. The co-ordination spheres about the metal atoms are completed by the triphenyl phosphite ligands.

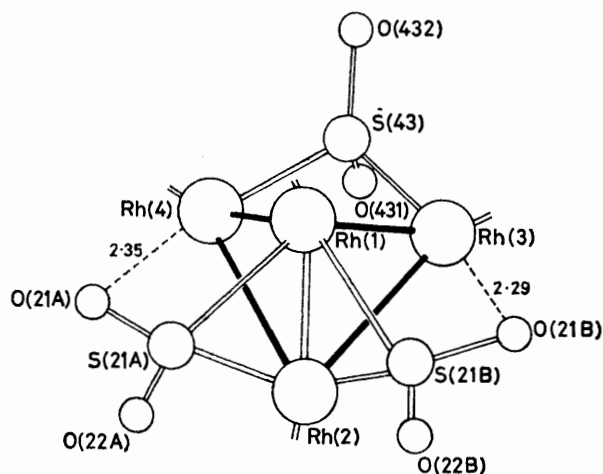
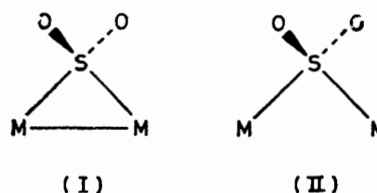


FIGURE 2. Illustration of the two types of  $\text{SO}_2$  bridging modes and the 'butterfly' cluster geometry.

A number of complexes have been reported which contain an  $\text{SO}_2$  ligand bound only through sulphur and bridging two metal atoms.<sup>2</sup> The metal–metal bond lengths in these complexes show an enormous variation (2.6–3.9 Å) and the bonding at the extremes of this range can be adequately represented by the canonical forms (I) and (II). In



$\text{Rh}_4(\text{CO})_4(\text{SO}_2)_3[\text{P}(\text{OPh})_3]_4$  the 0.291(4) Å difference in metal–metal bond lengths for the Rh(1)–Rh(2) and Rh(3)–Rh(4) sulphur dioxide-bridged bonds suggests that the former is best represented by (I) and the latter has a significant contribution from (II). Adoption of the extreme formulations for these bonds leads to 18 electron configurations at Rh(1) and Rh(2), but only 16 electron configurations at Rh(3) and Rh(4). This apparent electron deficiency is resolved by supplementary interactions between the lone pairs of the oxygen atoms, O(21A) and O(21B), of the  $\text{SO}_2$  ligands and Rh(3) and Rh(4). This interaction is clearly illustrated in Figure 2. The Rh(3)–O(21B) and Rh(4)–O(21A) bond lengths of 2.34(2) and 2.29(2) Å respectively are comparable to that reported for Rh–O in  $\text{Rh}(\text{NO})(\eta^2\text{-SO}_2)(\text{PPh}_3)_2$ .<sup>6</sup> The long Rh(3)–S(21B) and Rh(4)–S(21A) bond lengths of 2.823(6) and 2.800(6) Å suggest that there is little supplementary bonding interactions between these atoms.

This compound therefore provides the first example of the  $\text{SO}_2$  ligand utilising lone pairs on the sulphur and one of the oxygen atoms to function as a four-electron bridging ligand between three metal atoms. Furthermore, the opening up of the tetrahedral cluster which accompanies  $\text{SO}_2$  co-ordination appears to be a direct consequence of the

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

adoption of this co-ordination mode. Recently an example of SO<sub>2</sub> bridging two molybdenum atoms by bonding to one metal atom through an η<sup>2</sup>-S,O linkage and the second through an oxygen atom has been reported,<sup>7</sup> suggesting that SO<sub>2</sub> may prove to be a very flexible ligand in the context of cluster chemistry. The chemical implications of the unusual co-ordination mode found in Rh<sub>4</sub>(CO)<sub>4</sub>(SO<sub>2</sub>)<sub>3</sub>[P(OPh)<sub>3</sub>]<sub>4</sub> and the possibility that SO<sub>2</sub> might introduce similar geometric

changes in higher nuclearity cluster compounds are currently being investigated.

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