

## Synthesis and Structural Characterisation of a Novel Palladium Sulphur Dioxide Cluster Compound, $[\text{Pd}_5(\mu^2\text{-SO}_2)_2(\mu^3\text{-SO}_2)_2(\text{PMe}_3)_5]$

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General routes into palladium  $\text{SO}_2$  cluster compounds are described and the structure of the title compound has shown that the  $\text{SO}_2$  ligands can adopt unusual bridging modes.

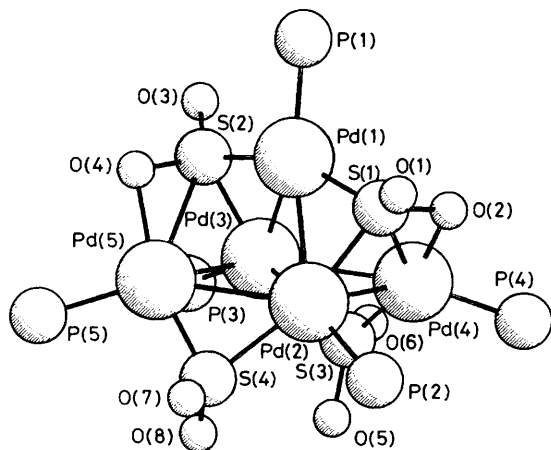
Carbon monoxide has played a dominant role in the development of the cluster chemistries of the platinum metals, largely because of its  $\pi$ -acid character, its small size, and its ability to undergo a range of reactions which lead to cluster aggregation.<sup>1</sup> In previous papers<sup>2</sup> we have demonstrated that  $\text{SO}_2$  represents a useful and flexible alternative  $\pi$ -acid ligand. Although a large number of  $\text{SO}_2$  cluster compounds of platinum have been studied, only one example of a related triangular palladium cluster, *viz.*  $[\text{Pd}_3(\mu^2\text{-SO}_2)_2(\text{CNBu}^t)_5]$ , has been structurally characterised.<sup>3</sup> The recently reported synthesis of  $[\text{Pd}_8(\text{CO})_8(\text{PMe}_3)_7]$ <sup>4</sup> prompted us to investigate whether this compound would provide a viable route into high nuclearity  $\text{SO}_2$  cluster compounds of palladium.

When  $\text{SO}_2$  was bubbled through a solution of  $[\text{Pd}_8(\text{CO})_8(\text{PMe}_3)_7]$  in  $\text{CH}_2\text{Cl}_2$  for two minutes and the solution allowed to stand for one hour, it was possible to isolate  $[\text{Pd}_5(\text{SO}_2)_4(\text{PMe}_3)_5]$  in *ca.* 50% yield as a red crystalline solid. The solid was recrystallised from  $\text{CH}_2\text{Cl}_2$ -hexane and single crystals of the compound suitable for *X*-ray diffraction study were obtained from  $\text{C}_6\text{H}_6$ -hexane. If the  $\text{SO}_2$  moieties were behaving as two electron bridging ligands in this compound then the total valence electron count for the cluster of 68 would be consistent with a trigonal bipyramidal geometry, isostructural and isoelectronic with  $[\text{Pt}_5\text{H}_8(\text{PR}_3)_5]$ .<sup>5,6</sup> The i.r. spectrum of the title compound, however, showed the presence of bands at 1262 and 1057  $\text{cm}^{-1}$  (Nujol mull) which can be assigned to  $\mu^2\text{-SO}_2$  and additional bands at 1184 and 1162  $\text{cm}^{-1}$ , which suggested that some of the  $\text{SO}_2$  ligands might be behaving in a unconventional fashion in this cluster compound.<sup>7</sup>

The structure of  $[\text{Pd}_5(\mu^2\text{-SO}_2)_2(\mu^3\text{-SO}_2)_2(\text{PMe}_3)_5]$ , illustrated in Figure (1),<sup>†</sup> is not the anticipated trigonal bipyramidal structure, because two of the  $\text{SO}_2$  ligands are acting as four-electron bridging ligands. They co-ordinate to two palladium atoms through the sulphur lone pair and to a third palladium atom through an oxygen lone pair. Although we have previously noted this co-ordination mode in  $\{\text{Rh}_4(\text{CO})_4(\mu^2\text{-SO}_2)(\mu^2\text{-SO}_2)(\mu^3\text{-SO}_2)_2[\text{P}(\text{OPh}_3)_4]\}$ ,<sup>8</sup> it has not been observed in platinum (or indeed any third-row transition metal)  $\text{SO}_2$  cluster compounds.

The cluster geometry can be described either in terms of a trigonal bipyramid with two long axial-equatorial

<sup>†</sup> Crystal data for  $[\text{Pd}_5(\mu^2\text{-SO}_2)_2(\mu^3\text{-SO}_2)_2(\text{PMe}_3)_5] \cdot \text{C}_6\text{H}_6 \cdot \text{C}_{21}\text{H}_{51}\text{O}_8\text{-P}_5\text{Pd}_5\text{S}_4$ ,  $M = 1246.8$ , trigonal space group  $P3_1$ ,  $a = 11.141(2)$ ,  $c = 29.365(4)$  Å,  $U = 3157$  Å<sup>3</sup>,  $Z = 3$ , crystal dimensions  $0.12 \times 0.15 \times 0.18$  mm,  $D_c = 1.97$  g  $\text{cm}^{-3}$ . A total of 3175 reflections were measured ( $2 < 2\theta < 40^\circ$ );  $R = 0.053$ ,  $R_w = 0.061$  for 1006 unique, observed reflections [ $I > 3\sigma(I)$ ]. Intensity data were collected on an Enraf-Nonius CAD-4F diffractometer using graphite monochromated radiation. The data were corrected for absorption ( $\mu = 24.85$   $\text{cm}^{-1}$ ). The structure was solved using Patterson and Fourier methods. The space group  $P3_2$  was also investigated but gave an  $R$  value higher by 0.5%. Blocked least-squares refinement; anisotropic thermal parameters for Pd, P, and S atoms. Disorder was observed for one of the phosphine ligands [P(1)] and it was necessary to model the four methyl carbon sites observed with carbon occupancies of 0.75. In the atom listings these sites are C(1), C(2), C(3), and C(31): Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



**Figure 1.** A view of  $[\text{Pd}_5(\mu^2\text{-SO}_2)_2(\mu^3\text{-SO}_2)_2(\text{PMe}_3)_5]$  along the basal plane. Selected geometric parameters: Pd(1)–Pd(2) 2.805(5), Pd(1)–Pd(3) 2.805(6), Pd(2)–Pd(3) 3.026(5), Pd(2)–Pd(4) 2.828(6), Pd(2)–Pd(5) 2.956(5), Pd(3)–Pd(4) 2.957(5), Pd(3)–Pd(5) 2.844(6), O(2)–Pd(4) 2.18(3), O(4)–Pd(5) 2.22(3) Å.

metal–metal bonds [3.410(5) Å] or a rhombus of palladium atoms with a fifth Pd bridging the internal Pd–Pd bond of the rhombus [3.026(5) Å]. The cluster approximates to  $C_2$  symmetry with the opposite edges of the rhombus having average lengths of 2.836(6) and 2.956(5) Å. The shorter palladium–palladium bonds are bridged by the  $\mu^2\text{-SO}_2$  ligands. The unique palladium atom [Pd(1)] forms bonds to the central palladium atoms with an average length of 2.805(5) Å. These bonds are bridged by  $\text{SO}_2$  ligands through the sulphur atoms. In addition, these ligands form bonds to the wing tip palladium atoms through lone pairs on the oxygens. Consequently, the total number of valence electrons in the cluster is 72. The structure can be understood in terms of the cluster condensation rules<sup>6</sup> and it is closely related to that reported for  $[\text{Pd}_m\text{Pt}_n(\text{PPh}_3)_5(\text{Bu}^i\text{CP})_3]^9$  ( $m = 2, n = 3; m = 5, n = 0$ ) which also have 72 valence electrons. In the latter, however, the central Pd–Pd bond is tristellated and the resultant structure has  $C_3$  symmetry. The structure of the palladium  $\text{SO}_2$  cluster

also differs significantly from that reported for  $[\text{Pt}_5(\mu\text{-CO})_2=(\mu\text{-SO}_2)_3(\text{CO})(\text{PPh}_3)_4]$  which was obtained from  $[\text{Pt}_5(\text{CO})_6(\text{PPh}_3)_4]$  and  $\text{SO}_2$ . The pentanuclear platinum clusters have an edge-bridged tetrahedral structure with conventional two electron bridging  $\text{SO}_2$  ligands.<sup>2</sup>

The cluster  $[\text{Pd}_4(\text{SO}_2)_3(\text{PCy}_3)_4]$  (Cy = cyclohexyl) has been synthesised directly from  $[\text{Pd}_2(\text{dba})_3]$  (dba = dibenzylidene acetone),  $\text{PCy}_3$ , and  $\text{SO}_2$ . It has a tetrahedral metal geometry with  $\mu^3\text{-SO}_2$  ligands bonded in an analogous fashion to that described above. The accuracy of the X-ray analysis for  $[\text{Pd}_4(\text{SO}_2)_3(\text{PCy}_3)_4]$  has been severely limited by extensive disorder problems.<sup>10</sup> Taken together, however, these results suggest an extensive range of  $\text{SO}_2$  cluster compounds of palladium in which the  $\mu^3$  bonding mode is prevalent.

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