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Synthesis and structural characterisation of the novel tetranuclear cluster compound $[Pd_4(\mu\text{-}SO_2)_2(\mu_3\text{-}S)(CO)(PBz_3)_4]$ ($Bz = C_6H_5CH_2$) †

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The synthesis, spectroscopic characterisation and single crystal structure are reported for the novel tetranuclear cluster compound $[Pd_4(\mu\text{-}SO_2)_2(\mu_3\text{-}S)(CO)(PBz_3)_4]$, obtained when $[Pd_2(\mu\text{-}dba)(\mu\text{-}SO_2)(PBz_3)_2]$ (dba = dibenzylideneacetone, Bz = benzyl) is reacted with COS which fragments to give independent CO and S ligands on a tetrahedral cluster.

The past two decades have seen much research in the area of transition metal cluster chemistry. This was initially stimulated by their potential as models for catalytic activity on surfaces. More recently, increased interest has been shown in their properties as homogeneous catalysts[1] and their use as building blocks for bigger structures (clusters of clusters).[2] In the latter context, Hor and coworkers have demonstrated that μ-sulfido platinum compounds derived from COS may be used to generate a large range of heterometallic clusters and aggregates.[3,4] Since the first report on the coordination properties of the platinum sulfido-dimer $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$,[3] several heterometallic clusters and aggregates have been successfully prepared from this compound (*e.g.* $[Cu\{Pt_2(\mu\text{-}S)_2(PPh_3)_4\}_2]$, $[Pt_2(\mu\text{-}S)_2(PPh_3)_4\text{-}BiCl_3]$ and $[Ag_2Pt_2Cl_2(\mu\text{-}S)_2(PPh_3)_4])$.[4] The chemistry of analogous palladium compounds is less well developed, although the compound $[Ag_2Pd_2(dppf)_2(\mu\text{-}S)_2]$ has been reported recently.[5] The development of this area has been limited by the absence of suitable sulfido-precursors.

We have recently reported[6] that the dimer $[Pd_2(\mu\text{-}SO_2)(\mu\text{-}dba)(PBz_3)_2]$ **1** (dba = dibenzylideneacetone, Bz = benzyl) is formed when $[Pd_2(dba)_3]$ is reacted with PBz_3 in the presence of SO_2. This dimer is unusual in retaining one dba molecule which bridges two palladium centres. The dba ligand is relatively labile and this has stimulated a systematic study of the reactions of **1**. In this communication the synthesis and structural characterisation are reported for $[Pd_4(\mu\text{-}SO_2)_2(\mu_3\text{-}S)(CO)(PBz_3)_4]$ **2** which is obtained in the reaction between **1** and COS. This compound is a potential building block for the synthesis of higher nuclearity heterometallic clusters.

When COS gas was bubbled through a solution of **1** (100 mg, 0.09 mmol) in toluene (25 cm^3) for 10 minutes, the colour of the reaction mixture changed from yellow to deep red.‡ The solvent was removed under reduced pressure and the crude product washed with methanol to remove free dba. The crude product was recrystallised from a toluene–methanol mixture at −25 °C giving red crystals of **2** and spectroscopic and X-ray structural analyses§ have confirmed the formulation $[Pd_4(\mu\text{-}SO_2)_2(\mu_3\text{-}S)(CO)(PBz_3)_4]$. The IR spectrum of **2** showed $\nu(SO_2)$ vibrations which had shifted to lower wavenumbers (1033, 1051 and 1180 cm^{-1}) in comparison to those of the starting material (1054 and 1195 cm^{-1}). An intense band at 2030 cm^{-1} was observed and tentatively assigned to terminal CO. No peaks corresponding to dba were observed. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **2** showed two doublets at δ 21.6 with a coupling constant of 57.6 Hz and at δ 15.7 with a coupling constant of 101.7 Hz. A third signal was observed at δ 7.6 which consists of a doublet of triplets with coupling constants of 101.7 Hz for the doublet and of 57.6 Hz for the triplets. The ratio of intensities of these 3 signals is 2 : 1 : 1 respectively.¶ These spectroscopic data together with elemental analyses‡ suggested that **2** is a tetranuclear compound with three inequivalent phosphine environments and with bridging SO_2 and terminal CO ligands. The formulation $[Pd_4(\mu\text{-}SO_2)_2(\mu_3\text{-}S)(CO)(PBz_3)_4]$ was confirmed by a single crystal X-ray analysis (see Fig. 1) which showed that **2** has a distorted tetrahedral Pd_4 core. It contains two edge-bridging SO_2 ligands, one terminal CO and has one cluster face capped by a triply bridging S atom. The COS has reacted dissociatively with **1** releasing CO and S which act as independent ligands in **2**. This reaction was unexpected but not unprecedented. Werner[7] has shown that the palladium compound $[Pd(PMe_3)_3H]^+$ reacts with COS to yield $[Pd_3(PMe_3)_6(\mu_3\text{-}S)_2]BF_4$. Similarly the complex $[Pt(COS)(PPh_3)_2]$ is converted into the dimer $[Pt_2(\mu\text{-}S)(CO)(PPh_3)_3]$ under refluxing conditions.[8]

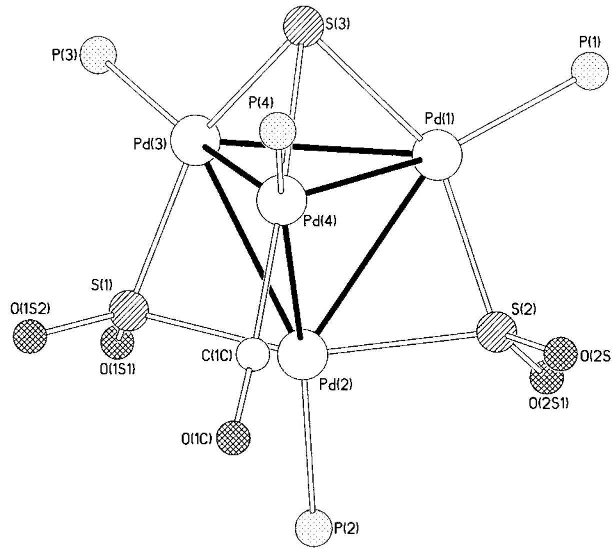

Fig. 1 The molecular structure of $[Pd_4(\mu\text{-}SO_2)_2(\mu_3\text{-}S)(CO)(PBz_3)_4]$ **2** with the phosphine substituents omitted for clarity. Important bond lengths (Å): Pd(1)–Pd(2) 2.8741(6), Pd(1)–Pd(3) 2.9404(6), Pd(1)–Pd(4) 2.7735(6), Pd(2)–Pd(3) 2.8614(6), Pd(2)–Pd(4) 2.7851(6), Pd(3)–Pd(4) 2.7416(6), Pd(1)–S(3) 2.4179(14), Pd(3)–S(3) 2.3759(14), Pd(4)–S(3) 2.2865(14), Pd(1)–S(2) 2.2147(14), Pd(2)–S(2) 2.3475(14), Pd(2)–S(1) 2.3019(14), Pd(3)–S(1) 2.2276(14), Pd(1)–P(1) 2.2805(14), Pd(2)–P(2) 2.3267(14), Pd(3)–P(3) 2.2791(14), Pd(4)–P(4) 2.3089(14), Pd(4)–C(1C) 1.938(6).

The Pd–Pd bond lengths in **2** lie between 2.7416(6) and 2.9404(6) Å and are within the range of previously reported

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† *Supplementary data available*: discussion of the ^{31}P NMR spectrum of $[Pd_4(\mu\text{-}SO_2)_2(\mu_3\text{-}S)(CO)(PBz_3)_4]$. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/653/, otherwise available from BLDSC (No. SUP 57488, 3 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).

SO_2-containing palladium clusters. The shorter lengths involve those between Pd(4) and the other three palladium atoms, an effect which may be attributed to the π-electron-withdrawing properties of the terminal carbonyl to which it is bonded. The longest Pd–Pd bond length is between Pd(3) and Pd(1) (2.9404(6) Å). There are very few reported examples of palladium clusters with triply-bridging sulfide ligands.[7,9] The Pd–S distances in these clusters range from 2.312(6) to 2.374(2). Even though the range of distances found for μ_3-S in **2** is wider (from 2.2865(14) to 2.4179(14) Å) they are consistent with the previously reported structural data.

There are two skeletal geometries observed for tetrametallic Group 10 clusters: tetrahedral and butterfly. The former is associated with an electron count of 60 while the latter generally has an electron count of 58.[10] Cluster **2** has a polyhedral electron count of 58 and a somewhat surprising tetrahedral geometry. To our knowledge, there are only four other tetrahedral palladium cluster compounds structurally characterised. These clusters are: $[Pd_4(\mu\text{-}CO)_8(P^nBu_3)_4]$[11] and $[Pd_4(\mu_3\text{-}CR)(\mu\text{-}X)_3(P^tBu_3)_4]$ (R = H, X = Cl; R = F, X = Br)[12,13] with a polyhedral electron count of 60, and $[Pd_4(\mu\text{-}CO)_2(phen)_4]^{4+}$ with 56.[14] On the other hand, three examples of 58 electron butterfly cluster compounds are known: $[Pd_4(\mu\text{-}CO)_5(PMePh_2)_4]$, $[Pd_4(\mu\text{-}CO)_5(PPh_3)_4]$ and $[Pd_4(\mu\text{-}SO_2)_2(\mu_3\text{-}SO_2)(MeCN)(PPh_3)_4]$.[15] A geometric distortion taking a perfect tetrahedron into a butterfly-type geometry would explain the unexpected electron count. The range of bond lengths in the cluster (arising from the different bridging groups) makes it difficult to identify a specific tetrahedron to butterfly distortion. However, it is noteworthy that the Pd(1)–Pd(3) bond is significantly longer than the other Pd–Pd bond lengths.

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Notes and references

‡ Selected data for compound **2**·C_6H_5Me: yield 51 mg (62%) (Found: C, 56.4; H, 4.7. $C_{92}H_{92}O_5P_4Pd_4S_3$ requires: C, 57.5; H, 4.8%). ν_{max}/cm^{-1} 1033 (SO_2), 1051 (SO_2), 1180 (SO_2), 2030 (CO). ^{31}P-{^{1}H} NMR δ_P (C_6D_6): 21.6 (d, 2P, $^3J_{P(B)-P(X)}$ 57.6), 15.7 (d, 1P, $^3J_{P(A)-P(X)}$ 101.7), 7.6 (dt, 1P, $^3J_{P(B)-P(X)}$ 57.6, $^3J_{P(A)-P(X)}$ 101.7 Hz).

§ Crystal data for **2**·C_6H_5Me: $C_{92}H_{92}O_5P_4Pd_4S_3$, $M = 1923.32$, triclinic, $P\bar{1}$, $a = 15.2388(16)$, $b = 16.7003(17)$, $c = 18.7170(12)$ Å, $\alpha = 101.682(9)$, $\beta = 104.990(7)$, $\gamma = 104.678(7)°$, $V = 4264.1(7)$ Å^3, $Z = 2$, $D_c = 1.498$ g cm^{-3}, μ(Mo-Kα) = 1.030 mm^{-1}, $F(000) = 1952$, $T = 198(2)$ K. 16668 reflections measured. The final R_1 was 0.040 and wR_2 was 0.092 for 14823 ($R_{int} = 0.023$) independent observed absorption. The positions of the palladium, phosphorus and sulfur atoms were determined by direct methods and subsequent difference-Fourier synthesis revealed the positions of the remaining non-hydrogen atoms. Refinements were performed on SHELXTL based on F^2.[16] The hydrogen atoms were placed in calculated positions with displacement parameters equal to 1.2 U_{eq}. Anisotropic displacement parameters were assigned to all non-hydrogen atoms, with the exception of the solvent molecule. CCDC reference number 186/1331.

¶ A discussion of the ^{31}P-{^{1}H} NMR data is available as SUP 57488.

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