General Synthetic Route for SO₂ Cluster Compounds of Platinum and the Structural Characterisation of $Pt_5(\mu\text{-}CO)_2(\mu\text{-}SO_2)_3(CO)(PPh_3)_4$

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The reaction of 1 atm of SO_2 at 60 °C with toluene solutions of platinum carbonyl cluster compounds provides a general synthetic route for platinum SO_2 cluster compounds.

Although the co-ordination chemistry of the SO_2 ligand has received considerable attention recently,[1] few cluster compounds containing this ligand have been reported.[2] For example, in the case of platinum only two trinuclear cluster compounds have been reported *viz.* $Pt_3(\mu\text{-}SO_2)_3(PPh_3)_3$[3] and $Pt_3(\mu\text{-}Ph)(\mu\text{-}PPh_2)(\mu\text{-}SO_2)(PPh_3)_3$.[4] The former was prepared only in sufficient quantities for a single crystal X-ray analysis by allowing solutions of $Pt(SO_2)_2(PPh_3)_2$ to stand for several months, and the latter serendipitously from the thermolysis of $Pt(\eta^2\text{-}C_4H_6)(SO_2)(PPh_3)_2$. We now report a general route to platinum-SO_2 cluster compounds and illustrate their usefulness as intermediates in the interconversion of platinum carbonyl cluster compounds.

The platinum cluster compounds $Pt_3(\mu\text{-}CO)_3(PPh_3)_4$, Pt_4-$(\mu\text{-}CO)_5(PMe_2Ph)_4$, and $Pt_5(\mu\text{-}CO)_5(CO)(PPh_3)_4$[5,6] react readily with SO_2 at 1 atm and 60 °C in toluene to give the following cluster compounds selectively and in high yields: $Pt_3(\mu\text{-}SO_2)_3$-$(PPh_3)_3$ (1), $Pt_4(\mu\text{-}SO_2)_5(PMe_2Ph)_4$ (2), and $Pt_5(\mu\text{-}CO)_2(\mu\text{-}SO_2)_3$-$(CO)(PPh_3)_4$ (3). Table 1 summarises some physical properties and i.r. data for these compounds, which have been obtained

Table 1. Colours and i.r. stretching frequencies[a] for the SO_2 cluster compounds.

| Compound	Colour	$\nu(SO_2)/cm^{-1}$
$Pt_3(SO_2)_3(PPh_3)_3$ (1)	orange	1276s, 1260ms, 1086vs
$Pt_4(SO_2)_5(PMe_2Ph)_4$ (2)	deep red	1258m, 1077vs
$Pt_5(CO)_3(SO_2)_3$-$(PPh_3)_4$ (3)[b]	orange-red	1240mw, 1087vs, 1070vs

[a] Recorded as Nujol mulls. [b] $\nu(CO)$ 2050m, 1940sh, 1909m cm^{-1}.

as air stable crystalline solids. The i.r. data are in each case consistent with the presence of SO_2 acting as a bridging ligand between two metal atoms through the sulphur atom.[7]

$Pt_3(\mu\text{-}SO_2)_3(PPh_3)_3$ (1) was shown to have a *triangulo*-cluster geometry identical with that reported by Moody and Ryan[3] on the basis of powder diffraction experiments and $^{31}P\{^1H\}$ n.m.r. studies.† Spectroscopic measurements have suggested that $Pt_4(\mu\text{-}SO_2)_5(PMe_2Ph)_4$ (2) has the same 'butterfly' metal cluster geometry as that reported for $Pt_4(\mu\text{-}CO)_5$-$(PMe_2Ph)_4$.[5] It was of interest, however, to undertake a single crystal X-ray analysis of the pentanuclear cluster (3) in order to establish which bridging carbonyls had been replaced by the SO_2 ligands.
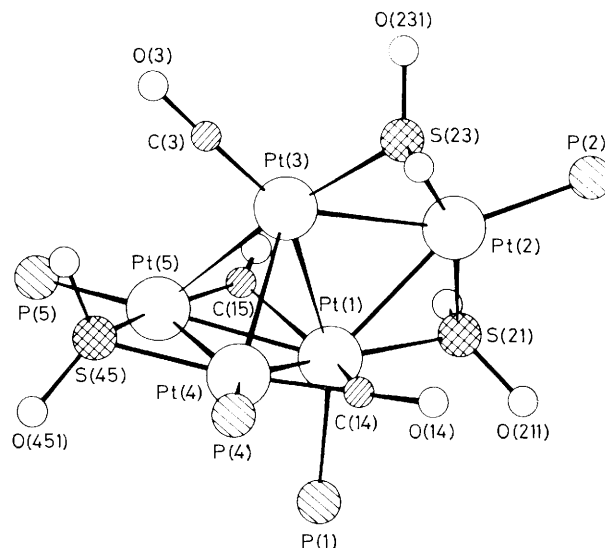
Crystal data: $C_{80}H_{72}Cl_4O_{10}P_4Pt_5S_3$ $[Pt_5(CO)_3(SO_2)_3(PPh_3)_4$.2-$CH_2Cl_2.Me_2CHOH$, recrystallised from CH_2Cl_2-$Me_2CHOH]$, $M = 2530.8$, triclinic, space group $P\bar{1}$, $a = 13.991(6)$, $b = 14.625(5)$, $c = 21.285(4)$ Å, $\alpha = 84.07(2)$, $\beta = 83.34(3)$, and $\gamma = 70.76(4)°$, $U = 4074(3)$ Å^3, $Z = 2$, $D_c = 2.06$ g cm^{-3}, $F(000)$ 2 396, $\mu(Mo\text{-}K_\alpha)$ 93.4 cm^{-1}; current R 0.059 (R' 0.079) for 7033 independent reflections $(2\theta \leqslant 40°, I \geqslant 3\sigma(I)$, CAD4 diffractometer, Mo-K_α X-radiation, $\lambda = 0.710$ 69 Å).‡

The molecular structure of $Pt_5(\mu\text{-}CO)_2(\mu\text{-}SO_2)_3(CO)(PPh_3)_4$ (3) which is illustrated in Figure 1 is related to that reported for $Pt_5(\mu\text{-}CO)_5(CO)(PPh_3)_4$ (4)[6] but differs in a number of

$$Pt_5(\mu\text{-}CO)_5(CO)(PPh_3)_4$$

(4)
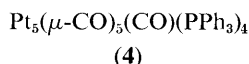
interesting and detailed respects. The unbridged Pt–Pt bond lengths radiating from Pt(3) in (3) are 0.05—0.12 Å shorter than the corresponding bond lengths in the parent carbonyl complex (4). Indeed, the lengths of the Pt(3)–Pt(5) and Pt(3)–Pt(4) bonds, *viz.* 2.808(1) and 2.877(1) Å respectively, are sufficiently similar to the remaining Pt–Pt bond lengths in (3) [2.751(1)—2.825(1) Å] to warrant an unambiguous description of the cluster as *edge-bridged-tetrahedral*. In (4) the relatively long Pt(3)–Pt(5) and Pt(3)–Pt(4) bond lengths [av. 2.918(1) Å] led to the suggestion[6] that the cluster may be more correctly described in terms of two orthogonal *triangulo*-clusters which share a common metal atom.

The classification of (3) and (4) as edge-bridged-tetrahedra is consistent with a recent theoretical analysis of the bonding in platinum phosphine cluster compounds which proposes that the total number of valence electrons in the platinum

† $^{31}P\{^1H\}$ n.m.r. data (to low field of TMP) (TMP = trimethyl-phosphate): δ 61.4 p.p.m. [$^1J(^{195}Pt,^{31}P)$ 4 073, $^2J(^{195}Pt,^{31}P)$ 425, and $^3J(^{31}P,^{31}P)$ 51 Hz] in CH_2Cl_2 solution with external D_2O lock. Powder diffraction study on $Pt_3(SO_2)_3(PPh_3)_3$.SO_2.toluene: tetragonal, $a = 24.39$, $c = 9.42$ Å [reported[3] $a = 24.272(7)$, $c = 9.454(3)$ Å].

‡ 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.

Figure 1. The molecular structure of $Pt_5(\mu\text{-}CO)_2(\mu\text{-}SO_2)_3(CO)$-$(PPh_3)_4$ (3). For reasons of clarity the phenyl rings have been omitted from the illustration. Important bond lengths include: Pt(1)–Pt(3) 2.751(1), Pt(3)–Pt(4) 2.877(1), Pt(3)–Pt(5) 2.808(1), Pt(1)–Pt(2) 2.826(1), Pt(2)–Pt(3) 2.784(1), Pt(4)–Pt(5) 2.793(1), Pt(1)–Pt(4) 2.763(1), Pt(1)–Pt(5) 2.766(1), Pt(1)–S(21) 2.313(5), Pt(2)–S(21) 2.244(5), Pt(2)–S(23) 2.274(6), Pt(3)–S(23) 2.227(6), Pt(4)–S(45) 2.305(5), Pt(5)–S(45) 2.264(5), and S–O (av.) 1.45(2) Å.
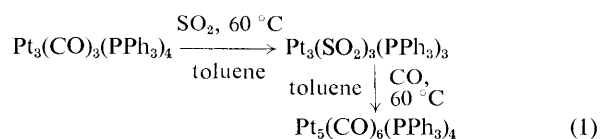
cluster compounds is four less than that observed for a carbonyl cluster compound with the same metal skeletal geometry but derived primarily from conical $M(CO)_3$ fragments. This generalisation is effectively illustrated by examples (1)—

(1)	Tetrahedral	$Rh_4(CO)_{12}$ [60 valence electrons (v.e.)]
		$Pt_4H_8(PR_3)_4$ (56 v.e.)
(2)	Butterfly	$Os_4(CO)_{12}H_3I$ (62 v.e.)
		$Pt_4(CO)_5(PR_3)_4$ (58 v.e.)
(3)	Trigonal bipyramid	$Os_5(CO)_{15}H^-$ (72 v.e.)
		$Pt_5H_8(PR_3)_5$ (68 v.e.)
(4)	Edge-bridged-tetrahedron	$Os_5(CO)_{16}H_2$ (74 v.e.)
		(3) and (4) (70 v.e.)

(4). The theoretical basis of this generalisation has been discussed by us in detail elsewhere.[7]

It is noteworthy that the reaction of (4) with SO_2 under the mild conditions described above leads only to the replacement of carbonyl ligands which are attached to Pt(2) or the opposite edge of the tetrahedron. The relative inertness of the carbonyl ligands which bridge Pt(1)–Pt(5) and Pt(1)–Pt(4) could arise from steric rather than electronic grounds since these carbonyl ligands are well shielded by the ligand atoms on adjacent metal atoms and Pt(3).[8] The presence of bridging CO and SO_2 ligands within the same molecule does present an internal check on the effects of replacing CO by SO_2 on the Pt–Pt bond lengths. In (3) the lengths of the Pt–Pt bonds bridged by CO do not differ significantly from those in (4). However, those bonds which are bridged by SO_2 are consistently 0.1 Å longer than the comparable bond lengths in (4). This effect can be attributed to the lower π-acidity of SO_2.

The bond strengths of the bridging CO and SO_2 ligands in the platinum cluster compounds appear to be roughly com-

$$Pt_3(CO)_3(PPh_3)_4 \xrightarrow[\text{toluene}]{SO_2,\ 60\ °C} Pt_3(SO_2)_3(PPh_3)_3$$

$$\text{toluene} \Bigg\downarrow \begin{array}{c} CO, \\ 60\ °C \end{array}$$

$$Pt_5(CO)_6(PPh_3)_4 \qquad (1)$$

parable since the SO_2 ligands in (**1**)—(**3**) may be expelled when CO is passed through toluene solutions of the complexes at 60 °C. This property has been utilised to provide an effective and high yield route for interconverting platinum carbonyl cluster compounds as in equation (1).

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