A General Synthetic Route for Platinum Sulphur Dioxide Cluster Compounds and the *X*-Ray Structural Characterisation† of Di-μ-carbonyl-carbonyl-tri(μ-sulphur dioxide)-tetrakis(triphenylphosphine)pentaplatinum–Dichloromethane–Propan-2-ol (1/2/1), $[Pt_5(CO)(\mu\text{-}CO)_2(\mu\text{-}SO_2)_3(PPh_3)_4]\cdot 2CH_2Cl_2\cdot Me_2CH(OH)$

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Some or all of the carbonyl ligands in platinum carbonyl phosphine clusters may be replaced by sulphur dioxide under mild conditions to give high yields of clusters containing the bridging sulphur dioxide ligand. In some cases ligand substitution is accompanied by a change in cluster structure which gives rise to high-yield routes for altering the nuclearity of platinum carbonyl clusters. In particular the reaction of sulphur dioxide with $[Pt_4(\mu\text{-}CO)_5(PMe_2Ph)_4]$ gave the trinuclear cluster $[Pt_3(\mu\text{-}SO_2)_3(PMe_2Ph)_3]$ rather than the tetranuclear cluster reported by us in an earlier communication. The molecular structure of $[Pt_5(CO)(\mu\text{-}CO)_2(\mu\text{-}SO_2)_3(PPh_3)_4]\cdot 2CH_2Cl_2\cdot Me_2CH(OH)$ has been determined by single-crystal *X*-ray techniques. The compound crystallises in the triclinic space group $P\bar{1}$ with two formula units in a unit cell with a = 13.991(6), b = 14.625(5), c = 21.285(4) Å, α = 84.07(2), β = 83.34(3), and γ = 70.76(4)°. The structure was solved to *R* 0.059 (*R'* 0.079) from 7 033 observed independent reflections [$F^2 \geqslant 3.0\sigma(F^2)$] collected in the range $3 \leqslant 2\theta \leqslant 45°$. The molecule has an edge-bridged tetrahedral skeletal geometry with Pt–Pt in the range 2.751(1)—2.877(1) Å. The cluster has one terminal carbonyl and four triphenylphosphine ligands and two edges of the cluster are bridged by carbonyl ligands and three by sulphur dioxide. The other two edges are unbridged. Detailed analysis of the structure has clarified the nature of the bonding in pentanuclear platinum clusters and enabled the structure of a previously incorrectly characterised platinum arsine cluster to be reformulated.

Although the co-ordination chemistry of sulphur dioxide has been extensively studied,[1,2] there have been relatively few structurally characterised examples of metal cluster compounds containing co-ordinated SO_2.[3,4] Three such clusters have been reported for platinum. A few crystals of the *triangulo*-cluster $[Pt_3(\mu\text{-}SO_2)_3(PPh_3)_3]$ were isolated by Moody and Ryan[5] in 1977 and recently we have reported the structures of $[Pt_3(\mu\text{-}SO_2)_3\{P(C_6H_{11})_3\}_2(dppp)]$ [dppp = 1,3-bis(diphenylphosphino)propane][6] and $[Pt_3(\mu\text{-}SO_2)(\mu\text{-}Ph)(\mu\text{-}PPh_2)(PPh_3)_3]$.[7] In this paper we report a general synthetic route for platinum phosphine sulphur dioxide clusters and the single-crystal *X*-ray analysis of one such cluster. Since our preliminary communication of this work[8] Ritchey and Moody[9] have reported the synthesis of some *triangulo*-platinum sulphur dioxide clusters by similar routes.

Results and Discussion

Electronically SO_2 is a better σ donor than CO, but whereas CO has two effective π-acceptor orbitals, SO_2 only has one and CO is therefore a better π acceptor.[10,11] In electronic terms therefore CO and SO_2 do not differ too widely, which suggested that SO_2 might replace CO in preformed carbonyl clusters. This was indeed found to be the case and the platinum cluster compounds $[Pt_3(\mu\text{-}CO)_3(PR_3)_3]$, $[Pt_3(\mu\text{-}CO)_3(PR_3)_4]$, $[Pt_4(\mu\text{-}CO)_5(PR_3)_4]$, and $[Pt_5(CO)(\mu\text{-}CO)_5(PR_3)_4]$ all reacted readily with SO_2 at 1 atm (10^5 N m^{-2}) and 60 °C in toluene solution.

Reaction of $[Pt_3(\mu\text{-}CO)_3(PR_3)_3]$ *with* SO_2.—Solutions of $[Pt_3(\mu\text{-}CO)_3(PR_3)_3]$, where R = cyclohexyl ($C_6H_{11}$),[12] Bu^n,[13] and CH_2CH_2CN,[13] reacted readily with SO_2 at 60 °C in toluene or acetone (R = CH_2CH_2CN) solutions to give products which were characterised as $[Pt_3(\mu\text{-}SO_2)_3(PR_3)_3]$ on the basis of analytical, i.r.,[2] and most conclusively $^{31}P\text{-}\{^1H\}$ n.m.r. evidence. The relevant coupling constants are given in Table 1. The coupling constants for the carbonyl precursors are given in Table 2.

Comparison of Tables 1 and 2 shows that for the SO_2-bridged clusters, $^1J(^{195}Pt\text{–}^{31}P)$ is *ca.* 700 Hz smaller than in the analogous CO-bridged cluster. This coupling constant has been related[14] to the *s* character of the Pt–P bond, which is affected by the electronic properties of the bridging ligand. In this case the reduced (Pt–P) *s* character may be attributed to the better σ-donor and weaker π-acceptor properties of SO_2 compared with CO.

Reaction of $[Pt_3(\mu\text{-}CO)_3(PPh_3)_4]$ *with* SO_2.—A solution of $[Pt_3(\mu\text{-}CO)_3(PPh_3)_4]$ reacted readily with SO_2 at 60 °C in toluene solution to give a product which was characterised as $[Pt_3(\mu\text{-}SO_2)_3(PPh_3)_3]\cdot SO_2\cdot C_7H_8$ on the basis of analytical, i.r., and $^{31}P\text{-}\{^1H\}$ n.m.r. evidence [$^1J(^{195}Pt\text{–}^{31}P)$ = 4 073, $^2J(^{195}Pt\text{–}^{31}P)$ = 425, $^3J(^{31}P\text{–}^{31}P)$ = 51 Hz]. As discussed above, this compound had previously been obtained in trace amounts by Moody and Ryan[5] and characterised by a single-crystal *X*-ray analysis.

It is noteworthy that replacement of CO by SO_2 in the cluster has led to a change in electron count from 44 to 42, consistent with the lower π-acceptor ability of SO_2. The factors which determine the electron count of a trinuclear platinum cluster have been discussed in detail by Dedieu and Hoffmann[15] and ourselves.[16]

It was of interest to study the reverse reaction of $[Pt_3(\mu\text{-}SO_2)_3(PPh_3)_3]$ with CO since there is obviously insufficient phosphine to enable the carbonyl precursor to be regenerated. The carbonyl cluster $[Pt_3(\mu\text{-}CO)_3(PPh_3)_3]$ has been shown to

† *Supplementary data available* (No. SUP 56526, 5 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Coupling constants (Hz) for some *triangulo*-triplatinum sulphur dioxide clusters

	$^1J(^{195}Pt-^{31}P)$	$^2J(^{195}Pt-^{31}P)$	$^3J(^{31}P-^{31}P)$
$[Pt_3(\mu-SO_2)_3\{P(C_6H_{11})_3\}_3]$	3 760	330	49
$[Pt_3(\mu-SO_2)_3(PBu^n{}_3)_3]$	3 673	361	49
$[Pt_3(\mu-SO_2)_3\{P(CH_2CH_2CN)_3\}_3]$	3 785	367	51

Table 2. Coupling constants (Hz) for some *triangulo*-triplatinum carbonyl clusters

	$^1J(^{195}Pt-^{31}P)$	$^2J(^{195}Pt-^{31}P)$	$^3J(^{31}P-^{31}P)$
$[Pt_3(\mu-CO)_3\{P(C_6H_{11})_3\}_3]$	4 412	430	58
$[Pt_3(\mu-CO)_3(PBu^n{}_3)_3]$	4 425	444	60
$[Pt_3(\mu-CO)_3\{P(CH_2CH_2CN)_3\}_3]$	4 489	466	61

be unstable with respect to phosphine exchange[17] and is perhaps therefore not a very likely product. Indeed $[Pt_3(\mu-SO_2)_3(PPh_3)_3]$ reacts with CO in toluene solution at 60 °C to give $[Pt_5(CO)(\mu-CO)_5(PPh_3)_4]$ as a reddish-brown crystalline solid.[18,19] Sequential replacement of CO and SO_2 therefore provides a facile and high-yield route for the conversion of $[Pt_3(\mu-CO)_3(PPh_3)_4]$ into $[Pt_5(CO)(\mu-CO)_5(PPh_3)_4]$ (see Scheme 1). The same transformation has recently been achieved by Bender and Braunstein[20] by passing a solution of $[Pt_3(\mu-CO)_3(PPh_3)_4]$ down a Kieselgel column.

$$[Pt_3(\mu-CO)_3(PPh_3)_4] \xrightarrow[PhMe]{SO_2} [Pt_3(\mu-SO_2)_3(PPh_3)_3] \xrightarrow{CO,\ PhMe} [Pt_5(CO)(\mu-CO)_5(PPh_3)_4]$$

Scheme 1.

Reaction of $[Pt_4(\mu-CO)_5(PMe_2Ph)_4]$ *with* SO_2.—A solution of the tetranuclear $[Pt_4(\mu-CO)_5(PMe_2Ph)_4]$ cluster, which has a 'butterfly' structure, also reacted with SO_2 in toluene solution at 60 °C to give a red crystalline solid. Although analytical and i.r. data were insufficient to unambiguously identify the cluster, a high-field n.m.r. spectrum conclusively indicated that the SO_2 had not simply replaced the bridging CO ligands as reported in our original communication,[8] but had in fact brought about cluster degradation to give $[Pt_3(\mu-SO_2)_3(PMe_2Ph)_3]$. The measured coupling constants were: $^1J(^{195}Pt-^{31}P) = 3\,974$, $^2J(^{195}Pt-^{31}P) = 388$, $^3J(^{31}P-^{31}P) = 50$ Hz. The reduction in cluster nuclearity is possibly related to the poorer π-acceptor ability of SO_2 relative to CO or alternatively may be a consequence of the greater steric requirements of the angular SO_2 ligand.

The reaction of $[Pt_3(\mu-SO_2)_2(PMe_3Ph)_3]$ with CO was also of interest because $[Pt_3(\mu-CO)_3(PMe_2Ph)_3]$ has not been isolated.[21] Whilst the phosphine ratio is such that $[Pt_4(\mu-CO)_5(PMe_2Ph)_4]$ could conceivably have been regenerated, the reaction of $[Pt_3(\mu-SO_2)_3(PMe_2Ph)_3]$ with CO in toluene at 60 °C gave $[Pt_5(CO)(\mu-CO)_5(PMe_2Ph)_4]$, as shown by analytical data and its i.r. spectrum which was very similar to that of the other known $[Pt_5(CO)(\mu-CO)_5(PR_3)_4]$ clusters.[19]

The sequence shown in Scheme 2 therefore provides an

$$[Pt_4(\mu-CO)_5(PMe_2Ph)_4] \xrightarrow[PhMe]{SO_2} [Pt_3(\mu-SO_2)_3(PMe_2Ph)_3] \xrightarrow{CO,\ PhMe} [Pt_5(CO)(\mu-CO)_5(PMe_2Ph)_4]$$

Scheme 2.

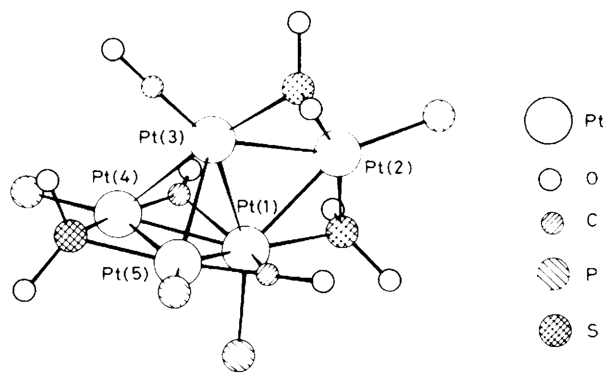

Figure. Crystal structure of $[Pt_5(CO)(\mu-CO)_2(\mu-SO_2)_3(PPh_3)_4]$

alternative route for the interconversion of platinum clusters. Clearly the pathways for the interconversion of the various platinum clusters have low activation energies and it is difficult to predict the nuclearity of a cluster which will be obtained from a given reaction.

Reaction of $[Pt_5(CO)(\mu-CO)_5(PPh_3)_4]$ *with* SO_2.—When SO_2 was bubbled through a toluene solution of $[Pt_5(CO)(\mu-CO)_5(PPh_3)_4]$ at 60 °C for 30 min, a slightly darker red solution was obtained from which an orange-red crystalline solid could be isolated. This compound analysed correctly for $[Pt_5(CO)_3(SO_2)_3(PPh_3)_4]$ and the i.r. spectrum showed bands characteristic of terminal and bridging CO and bridging SO_2 ligands. The $^{31}P-\{^1H\}$ n.m.r. spectrum of this compound was extremely complex and defied any simple analysis.

Since the structure of $[Pt_5(CO)_3(SO_2)_3(PPh_3)_4]$ could not be determined from the available spectroscopic data a single-crystal *X*-ray structural analysis of this compound was undertaken. The relevant details are given in the Experimental section.

Crystal and Molecular Structure of $[Pt_5(CO)(\mu-CO)_2(\mu-SO_2)_3(PPh_3)_4]\cdot 2CH_2Cl_2\cdot Me_2CH(OH)$.—The molecular structure of $[Pt_5(CO)(\mu-CO)_2(\mu-SO_2)_3(PPh_3)_4]$ determined from the *X*-ray crystallographic analysis is illustrated in the Figure and selected intramolecular bond lengths and angles are given in Tables 3 and 4 respectively. The fractional atomic co-ordinates are given in Table 5.

The molecular structure of $[Pt_5(CO)(\mu-CO)_2(\mu-SO_2)_3(PPh_3)_4]$ is related to that of the parent carbonyl cluster,[18,19] but differs in a number of interesting and detailed respects. The unbridged Pt–Pt bond lengths radiating from Pt(3) in $[Pt_5(CO)(\mu-CO)_2(\mu-SO_2)_3(PPh_3)_4]$ are 0.05—0.12 Å shorter than the corresponding bond lengths in $[Pt_5(CO)(\mu-CO)_5$-

Table 3. Interatomic distances (Å) in $[Pt_5(CO)(\mu-CO)_2(\mu-SO_2)_3(PPh_3)_4]$

Pt–Pt		C–O	
Pt(1)–Pt(2)	2.826(1)	C(3)–O(3)	1.20(3)
Pt(1)–Pt(3)	2.751(1)	C(14)–O(14)	1.24(3)
Pt(1)–Pt(4)	2.763(1)	C(15)–O(15)	1.14(3)
Pt(1)–Pt(5)	2.766(1)		
Pt(2)–Pt(3)	2.784(1)	S–O	
Pt(3)–Pt(4)	2.877(1)	S(21)–O(211)	1.46(2)
Pt(3)–Pt(5)	2.808(1)	S(21)–O(212)	1.44(2)
Pt(4)–Pt(5)	2.793(1)	S(23)–O(231)	1.44(2)
		S(23)–O(232)	1.44(2)
Pt–P		S(45)–O(451)	1.45(2)
Pt(1)–P(1)	2.344(6)	S(45)–O(452)	1.45(2)
Pt(2)–P(2)	2.274(6)		
Pt(4)–P(4)	2.275(6)	Pt–S	
Pt(5)–P(5)	2.283(7)	Pt(1)–S(21)	2.313(6)
		Pt(2)–S(21)	2.244(6)
Pt–C		Pt(2)–S(23)	2.274(7)
Pt(3)–C(3)	1.81(3)	Pt(3)–S(23)	2.227(7)
Pt(1)–C(14)	2.18(3)	Pt(4)–S(45)	2.305(6)
Pt(1)–C(15)	2.27(2)	Pt(5)–S(45)	2.264(7)
Pt(4)–C(14)	1.91(3)		
Pt(5)–C(15)	1.97(2)		

$(PPh_3)_4]$ which are summarised in Table 6. Indeed, the Pt(3)–Pt(5) and Pt(3)–Pt(4) bond lengths [2.808(1) and 2.877(1) Å respectively] are sufficiently similar to the remaining Pt–Pt bonds in $[Pt_5(CO)(\mu-CO)_2(\mu-SO_2)_3(PPh_3)_4]$ to warrant an unambiguous description of the cluster as *edge-bridged tetrahedral*. In $[Pt_5(CO)(\mu-CO)_5(PPh_3)_4]$ the relatively long Pt(3)–Pt(5) and Pt(3)–Pt(4) bond lengths [average 2.918(1) Å] led to the suggestion [18] that the cluster may be more correctly described in terms of two orthogonal *triangulo*-clusters which share a common metal atom. The 70-electron count in these two pentanuclear clusters is consistent with our recent theoretical analysis of the bonding in platinum clusters.[22]

It is noteworthy that the reaction of $[Pt_5(CO)(\mu-CO)_5(PPh_3)_4]$ with SO_2 leads only to the replacement of carbonyl ligands which are attached to Pt(2) or the opposite edge of the tetrahedron. The inertness of the carbonyl ligands which bridge Pt(1)–Pt(5) and Pt(1)–Pt(4), even under more forcing reaction conditions (3 h reflux in toluene under SO_2), 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).

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 $[Pt_5(CO)(\mu-CO)_2(\mu-SO_2)_3(PPh_3)_4]$ the Pt–Pt bond lengths bridged by CO do not differ significantly from those in $[Pt_5(CO)(\mu-CO)_5(PPh_3)_4]$. Those bonds which are bridged by SO_2 are consistently 0.1 Å longer than the corresponding bond lengths in the parent carbonyl. This effect can be attributed either to the lower π-acidity of SO_2 or to its greater steric requirements. The Pt–Pt bonds bridged by SO_2 in $[Pt_5(CO)(\mu-CO)_2(\mu-SO_2)_3(PPh_3)_4]$ are also approximately 0.1 Å longer than those in $[Pt_3(\mu-SO_2)_3(PPh_3)_3]$.[6] Again this could be a consequence of either steric or electronic factors or a combination of the two.

A definite measure of the lower π-acidity of sulphur dioxide relative to carbon monoxide is provided by a comparison of the i.r. spectra of $[Pt_5(CO)(\mu-CO)_2(\mu-SO_2)_3(PPh_3)_4]$ and $[Pt_5(CO)(\mu-CO)_5(PPh_3)_4]$. The terminal ν_{CO} band in the former occurs some 50 cm^{-1} higher than the corresponding band in the parent carbonyl.

Synthesis and Characterisation of $[Pt_5(CO)(\mu-CO)_5(AsPh_3)_4]$ *and its Reaction with* SO_2 *to give* $[Pt_5(CO)(\mu-CO)_2(\mu-SO_2)_3(AsPh_3)_4]$.—In 1970, Chatt and Chini [23] reported that the reduction of $[Pt(AsPh_3)_2Cl_2]$ with hydrazine under CO gave a red cluster which they formulated as $[Pt_4(CO)_5(AsPh_3)_4]$ on the basis of analytical data. An analogous cluster has recently been prepared by Goel *et al.*[24] by reaction of *trans*-$[PtH_2(AsBu^t_3)_2]$ with CO.

A sample of $[Pt_4(CO)_5(AsPh_3)_4]$ was prepared by the literature method [23] in order to attempt to characterise it more fully. This was in fact relatively straightforward since the i.r. spectrum of the sample was almost identical to that of $[Pt_5(CO)(\mu-CO)_5(PPh_3)_4]$. This strongly suggested that the arsine cluster should be reformulated as $[Pt_5(CO)(\mu-CO)_5(AsPh_3)_4]\cdot C_6H_6$. (The analytical data do not adequately discriminate between the two structures.)

Confirmatory evidence was obtained by reaction of the proposed $[Pt_5(CO)(\mu-CO)_5(AsPh_3)_4]$ with SO_2 in toluene solution at 60 °C. A red solid analysing for $[Pt_5(CO)_3(SO_2)_3(AsPh_3)_4]$ with an i.r. spectrum very similar to that of $[Pt_5(CO)(\mu-CO)_2(\mu-SO_2)_3(PPh_3)_4]$ was isolated, which strongly suggested that the arsine and phosphine clusters are isostructural.

Experimental

Reactions were routinely carried out, using standard Schlenk-line procedures, under an atmosphere of pure, dry dinitrogen and using dry dioxygen-free solvents. Microanalyses (C and H) were carried out by Mr. M. Gascoyne and his staff of this laboratory. Infrared spectra were recorded as Nujol mulls using a Pye-Unicam SP2000 spectrometer.

Proton-decoupled ^{31}P n.m.r. spectra were recorded using Bruker WH-90 and AM-250 spectrometers and referenced with respect to external trimethyl phosphate in D_2O. The machine operating frequencies were 36.43 and 101.26 MHz respectively for ^{31}P. All samples were run in deuteriated solvents.

The following compounds were prepared by literature procedures: $[Pt_3(\mu-CO)_3\{P(C_6H_{11})_3\}_3]$,[12] $[Pt_3(\mu-CO)_3(PBu^n_3)_3]$,[13] $[Pt_3(\mu-CO)_3\{P(CH_2CH_2CN)_3\}_3]$,[13] $[Pt_3(\mu-CO)_3(PPh_3)_4]$,[23] $[Pt_4(\mu-CO)_5(PMe_2Ph)_4]$,[23] and $[Pt_5(CO)(\mu-CO)_5(PPh_3)_4]$.[18]

Synthesis of $[Pt_3(\mu-SO_2)_3\{P(C_6H_{11})_3\}_3]$.—A solution of $[Pt_3(\mu-CO)_3\{P(C_6H_{11})_3\}_3]$ (0.20 g, 0.13 mmol) in toluene (25 cm^3) was heated to 60 °C and SO_2 bubbled through for 20 min. Concentration of the solution followed by addition of hexane precipitated $[Pt_3(\mu-SO_2)_3\{P(C_6H_{11})_3\}_3]$ as an orange microcrystalline solid. Yield 0.12 g (56%) (Found: C, 41.0; H, 6.4. $C_{54}H_{99}O_6P_3Pt_3S_3$ requires C, 40.0; H, 6.1%). I.r. (cm^{-1}): ν_{SO_2} 1 248mw, 1 082vs, and 1 072s. $^{31}P-\{^1H\}$ N.m.r. in C_6D_6: $\delta(^{31}P)$ 35.3 p.p.m. with $^1J(^{195}Pt-^{31}P)$ = 3 760, $^2J(^{195}Pt-^{31}P)$ = 330, and $^3J(^{31}P-^{31}P)$ = 49 Hz.

Synthesis of $[Pt_3(\mu-SO_2)_3(PBu^n_3)_3]$.—A solution of $[Pt_3(\mu-CO)_3(PBu^n_3)_3]$ (0.25 g, 2.0 mmol) in toluene (25 cm^3) was heated to 60 °C and SO_2 bubbled through for 20 min. Concentration of the solution to very low volume, addition of a small amount of methanol followed by cooling to −40 °C led to the formation of $[Pt_3(\mu-SO_2)_3(PBu^n_3)_3]$ as an orange crystalline solid. Yield 0.18 g (66%) (Found: C, 31.9; H, 6.3. $C_{36}H_{81}O_6P_3Pt_3S_3$ requires C, 31.2; H, 5.9%). I.r. (cm^{-1}): ν_{SO_2} 1 262ms, 1 255s, and 1 085vs. $^{31}P-\{^1H\}$ N.m.r. in C_6D_6: $\delta(^{31}P)$ 28.9 p.p.m. with $^1J(^{195}Pt-^{31}P)$ = 3 673, $^2J(^{195}Pt-^{31}P)$ = 361, and $^3J(^{31}P-^{31}P)$ = 49 Hz.

Synthesis of $[Pt_3(\mu-SO_2)_3\{P(CH_2CH_2CN)_3\}_3]$.—A solution of $[Pt_3(\mu-CO)_3\{P(CH_2CH_2CN)_3\}_3]$ (0.20 g, 0.16 mmol) in acetone (35 cm^3) was heated to 50 °C and SO_2 was bubbled through for 20 min when an orange-red solution was obtained. Concentration of the solution followed by addition of propan-2-

Table 4. Interbond angles (°) in $[Pt_5(CO)(\mu\text{-}CO)_2(\mu\text{-}SO_2)_3(PPh_3)_4]$

Pt-Pt-Pt	
Pt(2)-Pt(1)-Pt(3)	59.89(3)
Pt(2)-Pt(1)-Pt(4)	107.46(4)
Pt(3)-Pt(1)-Pt(4)	62.91(4)
Pt(3)-Pt(1)-Pt(5)	61.20(3)
Pt(4)-Pt(1)-Pt(5)	60.69(3)
Pt(1)-Pt(2)-Pt(3)	58.72(3)
Pt(1)-Pt(3)-Pt(2)	61.39(3)
Pt(1)-Pt(3)-Pt(4)	58.75(3)
Pt(1)-Pt(3)-Pt(5)	59.68(3)
Pt(2)-Pt(3)-Pt(4)	105.47(4)
Pt(2)-Pt(3)-Pt(5)	117.09(4)
Pt(4)-Pt(3)-Pt(5)	58.84(3)
Pt(1)-Pt(4)-Pt(3)	58.34(3)
Pt(1)-Pt(4)-Pt(5)	59.72(3)
Pt(3)-Pt(4)-Pt(5)	59.35(3)
Pt(1)-Pt(5)-Pt(3)	59.13(3)
Pt(1)-Pt(5)-Pt(4)	59.60(3)
Pt(3)-Pt(5)-Pt(4)	61.81(3)
Pt-Pt-P	
Pt(2)-Pt(1)-P(1)	140.9(2)
Pt(3)-Pt(1)-P(1)	158.1(2)
Pt(4)-Pt(1)-P(1)	97.9(3)
Pt(5)-Pt(1)-P(1)	101.1(2)
Pt(1)-Pt(2)-P(2)	151.1(2)
Pt(3)-Pt(2)-P(2)	150.0(2)
Pt(1)-Pt(4)-P(4)	150.3(2)
Pt(3)-Pt(4)-P(4)	126.2(2)
Pt(5)-Pt(4)-P(4)	150.0(2)
Pt(1)-Pt(5)-P(5)	144.8(2)
Pt(3)-Pt(5)-P(5)	134.4(2)
Pt(4)-Pt(5)-P(5)	152.5(2)
Pt-Pt-CO(terminal)	
Pt(1)-Pt(3)-C(3)	151.0(8)
Pt(2)-Pt(3)-C(3)	146.5(8)
Pt(4)-Pt(3)-C(3)	104.0(8)
Pt(5)-Pt(3)-C(3)	91.7(8)
Pt-CO(bridging)-Pt	
Pt(1)-C(14)-Pt(4)	84.6(10)
Pt(1)-C(15)-Pt(5)	81.1(8)
Pt-Pt-CO(bridging)	
Pt(2)-Pt(1)-C(14)	83.5(7)
Pt(2)-Pt(1)-C(15)	97.4(6)
Pt(3)-Pt(1)-C(14)	77.8(7)
Pt(3)-Pt(1)-C(15)	72.8(6)
Pt(4)-Pt(1)-C(14)	43.5(7)
Pt(4)-Pt(1)-C(15)	104.7(6)
Pt(5)-Pt(1)-C(14)	103.9(7)
Pt(5)-Pt(1)-C(15)	44.8(6)
Pt(1)-Pt(4)-C(14)	51.9(8)
Pt(3)-Pt(4)-C(14)	78.7(8)
Pt(5)-Pt(4)-C(14)	111.1(8)
Pt(1)-Pt(5)-C(15)	54.1(7)
Pt(3)-Pt(5)-C(15)	75.6(7)
Pt(4)-Pt(5)-C(15)	112.7(7)
Pt-S-Pt	
Pt(1)-S(21)-Pt(2)	76.6(2)
Pt(2)-S(23)-Pt(3)	76.4(2)
Pt(4)-S(45)-Pt(5)	75.4(2)
Pt-Pt-S	
Pt(2)-Pt(1)-S(21)	50.6.2)
Pt(3)-Pt(1)-S(21)	108.1(2)
Pt(4)-Pt(1)-S(21)	150.4(2)
Pt(5)-Pt(1)-S(21)	142.7(2)
Pt(1)-Pt(2)-S(21)	52.8(2)
Pt(1)-Pt(2)-S(23)	106.9(2)
Pt(3)-Pt(2)-S(21)	109.0(2)
Pt(3)-Pt(2)-S(23)	51.0(2)
Pt(1)-Pt(3)-S(23)	110.9(2)
Pt(2)-Pt(3)-S(23)	52.6(2)
Pt(4)-Pt(3)-S(23)	121.6(2)
Pt(5)-Pt(3)-S(23)	169.6(2)
Pt(1)-Pt(4)-S(45)	111.2(2)
Pt(3)-Pt(4)-S(45)	88.8(2)
P-Pt-C(bridging)	
P(1)-Pt(1)-C(14)	95.8(7)
P(1)-Pt(1)-C(15)	104.5(6)
P(4)-Pt(4)-C(14)	98.6(8)
P(5)-Pt(5)-C(15)	94.4(7)
P-Pt-S	
P(1)-Pt(1)-S(21)	93.8(2)
P(2)-Pt(2)-S(21)	100.3(2)
P(2)-Pt(2)-S(23)	100.0(2)
P(4)-Pt(4)-S(45)	98.4(2)
P(5)-Pt(5)-S(45)	100.5(2)
C(bridging)-Pt-C(bridging)	
C(14)-Pt(1)-C(15)	145.0(9)
C(terminal)-Pt-S	
C(3)-Pt(3)-S(23)	97.9(9)
C(bridging)-Pt-S	
C(14)-Pt(1)-S(21)	108.4(7)
C(15)-Pt(1)-S(21)	98.5(6)
C(14)-Pt(4)-S(45)	162.7(8)
C(15)-Pt(5)-S(45)	164.7(7)
S-Pt-S	
S(21)-Pt(2)-S(23)	159.6(2)
Pt-C-O(terminal)	
Pt(3)-C(3)-O(3)	174.0(24)
Pt-C-O(bridging)	
Pt(1)-C(14)-O(14)	126.3(20)
Pt(4)-C(14)-O(14)	148.5(21)
Pt(1)-C(15)-O(15)	127.8(20)
Pt(5)-C(15)-O(15)	151.0(22)
Pt-S-O	
Pt(1)-S(21)-O(211)	115.4(8)
Pt(1)-S(21)-O(212)	113.7(7)
Pt(2)-S(21)-O(211)	117.3(8)
Pt(2)-S(21)-O(212)	113.2(7)
Pt(2)-S(23)-O(231)	119.4(10)
Pt(2)-S(23)-O(232)	115.6(10)
Pt(3)-S(23)-O(231)	116.1(10)
Pt(3)-S(23)-O(232)	107.1(10)
Pt(4)-S(45)-O(451)	115.5(8)
Pt(4)-S(45)-O(452)	114.7(9)
Pt(5)-S(45)-O(451)	115.2(8)
Pt(5)-S(45)-O(452)	116.2(9)
O-S-O	
O(211)-S(21)-O(212)	115.1(11)
O(231)-S(23)-O(232)	115.4(14)
O(451)-S(45)-O(452)	114.4(12)

ol led to the precipitation of $[Pt_3(\mu\text{-}SO_2)_3\{P(CH_2CH_2CN)_3\}_3]$ as an orange solid. Yield 0.17 g (78%) (Found: C, 25.3; H, 3.0; N, 8.9. $C_{27}H_{36}N_9O_6P_3Pt_3S_3$ requires C, 23.9; H, 2.7; N, 9.3%). I.r. (cm^{-1}): 1 253m and 1 085s. $^{31}P\text{-}\{^1H\}$ N.m.r. in $(CD_3)_2CO$: $\delta(^{31}P)$ 24.3 p.p.m. with $^1J(^{195}Pt\text{-}^{31}P) = 3\,785$, $^2J(^{195}Pt\text{-}^{31}P) = 367$, and $^3J(^{31}P\text{-}^{31}P) = 51$ Hz.

Synthesis of $[Pt_3(\mu\text{-}SO_2)_3(PPh_3)_3]\cdot SO_2\cdot C_7H_8$.—$[Pt_3(\mu\text{-}CO)_3(PPh_3)_4]$ (0.2 g, 0.12 mmol) was dissolved in the minimum volume of toluene at 60 °C. SO_2 was bubbled through the solution for 20 min which became a lighter red colour and slowly deposited orange crystals of $[Pt_3(\mu\text{-}SO_2)_3(PPh_3)_3]\cdot SO_2\cdot C_7H_8$. The mixture was cooled, the orange crystals filtered off, washed with a little cold toluene and dried *in vacuo*. Yield 0.16 g (80%) (Found: C, 42.9; H, 3.0. $C_{61}H_{53}O_8P_3Pt_3S_4$ requires C, 42.6; H, 3.1%). I.r. (cm^{-1}): ν_{SO_2} (solvation) 1 325m, 1 140m; ν_{SO_2} (bridging) 1 275s, 1 260ms, 1 085vs. $^{31}P\text{-}\{^1H\}$ N.m.r. in CH_2Cl_2 solution with D_2O lock: $\delta(^{31}P)$ 57.1 p.p.m. with $^1J(^{195}Pt\text{-}^{31}P) = 4\,073$, $^2J(^{195}Pt\text{-}^{31}P) = 425$, and $^3J(^{31}P\text{-}^{31}P) = 51$ Hz.

Reaction of $[Pt_3(\mu\text{-}SO_2)_3(PPh_3)_3]$ *with* CO.—$[Pt_3(\mu\text{-}SO_2)_3(PPh_3)_3]$ (0.15 g, 0.096 mmol) was heated with toluene (50 cm^3) to 60 °C and CO bubbled through the mixture for 30 min to give a darker red solution. Reduction of the volume of the solution followed by addition of hexane gave $[Pt_5(CO)(\mu\text{-}CO)_5(PPh_3)_4]$ as a red-brown solid which was recrystallised from benzene–methanol. Yield 0.1 g (88%) (Found: C, 42.1; H, 2.9. $C_{78}H_{60}O_6P_4Pt_5$ requires C, 42.7; H, 2.7%). I.r. (cm^{-1}): ν_{CO} 2 005s, 1 902mw, 1 867s, 1 802vs, and 1 780vs (lit.,[18] 1 998vs, 1 899m, 1 858s, 1 812s, and 1 788vs).

Synthesis of $[Pt_3(\mu\text{-}SO_2)_3(PMe_2Ph)_3]$.—$[Pt_4(\mu\text{-}CO)_5(PMe_2Ph)_4]$ (0.20 g, 0.14 mmol) was dissolved in toluene at 60 °C. SO_2 was bubbled through the solution for 30 min. The solution became darker red and addition of hexane gave a red-brown

Table 5. Fractional atomic co-ordinates for $[Pt_5(CO)(\mu\text{-}CO)_2(\mu\text{-}SO_2)_3(PPh_3)_4]$

Atom	X/a	Y/b	Z/c
Pt(1)	0.253 43(7)	0.206 56(7)	0.177 15(5)
Pt(2)	0.063 66(7)	0.215 47(7)	0.138 82(5)
Pt(3)	0.125 46(7)	0.129 64(8)	0.256 66(5)
C(3)	0.101(2)	0.056(2)	0.326(1)
O(3)	0.090(2)	0.000(2)	0.370(1)
Pt(4)	0.222 55(7)	0.252 34(7)	0.302 24(5)
C(14)	0.162(2)	0.330(2)	0.230(1)
O(14)	0.097(2)	0.404(1)	0.210(1)
Pt(5)	0.335 11(7)	0.064 21(7)	0.270 02(5)
C(15)	0.325(2)	0.043(2)	0.181(1)
O(15)	0.336(2)	−0.008(1)	0.142(1)
S(45)	0.308 7(5)	0.122 5(5)	0.367 3(3)
O(451)	0.398(1)	0.131(1)	0.391 5(9)
O(452)	0.244(2)	0.085(1)	0.414(1)
S(21)	0.199 4(5)	0.229 7(5)	0.076 3(3)
O(211)	0.191(1)	0.324(1)	0.043 9(9)
O(212)	0.248(1)	0.148(1)	0.038 2(8)
P(2)	−0.056 4(5)	0.263 9(5)	0.068 1(2)
C(221)	−0.023(2)	0.323(2)	−0.006(1)
C(222)	−0.060(2)	0.420(2)	−0.020(1)
C(223)	−0.029(2)	0.462(2)	−0.078(1)
C(224)	0.033(2)	0.408(2)	−0.122(1)
C(225)	0.071(2)	0.304(2)	−0.109(1)
C(226)	0.044(2)	0.262(2)	−0.052(1)
C(211)	−0.097(2)	0.166(2)	0.041(1)
C(212)	−0.147(2)	0.185(2)	−0.013(1)
C(213)	−0.179(3)	0.109(3)	−0.030(2)
C(214)	−0.167(3)	0.023(3)	0.009(2)
C(215)	−0.112(3)	0.007(3)	0.063(2)
C(216)	−0.077(2)	0.081(2)	0.081(1)
C(231)	−0.171(2)	0.349(2)	0.102(1)
C(232)	−0.267(2)	0.363(2)	0.081(1)
C(233)	−0.354(3)	−0.432(3)	0.109(2)
C(234)	−0.343(3)	0.497(3)	0.148(2)
C(235)	−0.247(3)	0.486(3)	0.167(2)
C(236)	−0.162(2)	0.414(2)	0.143(1)
P(1)	0.389 6(5)	0.265 8(5)	0.146 1(3)
C(111)	0.503(2)	0.210(2)	0.191(1)
C(112)	0.599(2)	0.189(2)	0.158(1)
C(113)	0.683(3)	0.156(2)	0.193(2)
C(114)	0.674(3)	0.138(3)	0.259(2)
C(115)	0.576(2)	0.163(2)	0.291(1)
C(116)	0.492(2)	0.202(2)	0.254(1)
C(121)	0.354(2)	0.398(2)	0.154(1)
C(122)	0.404(2)	0.429(2)	0.200(1)
C(123)	0.374(3)	0.529(3)	0.203(2)
C(124)	0.298(3)	0.595(2)	0.166(2)
C(125)	0.251(3)	0.559(3)	0.129(2)
C(126)	0.278(2)	0.459(2)	0.122(1)
C(131)	0.444(2)	0.249(2)	0.065(1)
C(132)	0.472(2)	0.155(2)	0.044(1)
C(133)	0.530(2)	0.135(2)	−0.014(2)
C(134)	0.551(3)	0.209(3)	−0.054(2)
C(135)	0.520(3)	0.303(3)	−0.033(2)
C(136)	0.467(2)	0.324(2)	0.026(1)
P(5)	0.452 6(5)	−0.084 4(5)	0.289 1(3)
C(511)	0.541(2)	−0.122(2)	0.220(1)
C(512)	0.574(2)	−0.216(2)	0.203(1)
C(513)	0.639(3)	−0.242(3)	0.147(2)
C(514)	0.670(3)	−0.170(3)	0.112(2)
C(515)	0.641(3)	−0.077(3)	0.132(2)
C(516)	0.575(2)	−0.054(2)	0.184(1)
C(521)	0.394(2)	−0.180(2)	0.311(1)
C(522)	0.304(2)	−0.174(2)	0.293(2)
C(523)	0.257(3)	−0.245(3)	0.309(2)
C(524)	0.302(3)	−0.324(3)	0.349(2)
C(525)	0.396(3)	−0.332(3)	0.369(2)
C(526)	0.443(3)	−0.259(3)	0.352(2)
C(531)	0.536(2)	−0.099(2)	0.351(1)
C(532)	0.496(2)	−0.094(2)	0.415(1)
C(533)	0.559(3)	−0.110(2)	0.464(2)
C(534)	0.661(3)	−0.132(3)	0.449(2)
C(535)	0.703(3)	−0.142(3)	0.389(2)
C(536)	0.641(3)	−0.123(2)	0.337(2)
S(23)	−0.032 7(5)	0.188 4(6)	0.227 9(3)
O(231)	−0.086(2)	0.119(2)	0.228(1)
O(232)	−0.085(2)	0.272(2)	0.264(1)
P(4)	0.154 2(5)	0.361 7(5)	0.377 1(3)
C(411)	0.064(2)	0.473(2)	0.348(1)
C(412)	0.104(2)	0.534(2)	0.308(1)
C(413)	0.036(3)	0.624(3)	0.277(2)
C(414)	−0.064(3)	0.644(3)	0.293(2)
C(415)	−0.107(3)	0.585(3)	0.338(2)
C(416)	−0.039(3)	0.495(3)	0.364(2)
C(431)	0.234(2)	0.406(2)	0.418(1)
C(432)	0.192(2)	0.484(2)	0.457(2)
C(433)	0.250(3)	0.516(3)	0.491(2)
C(434)	0.352(3)	0.465(3)	0.491(2)
C(435)	0.398(3)	0.384(3)	0.457(2)
C(436)	0.339(3)	0.353(3)	0.417(2)
C(421)	0.081(2)	0.309(2)	0.438(1)
C(422)	0.085(2)	0.312(2)	0.503(1)
C(423)	0.029(3)	0.267(2)	0.548(2)
C(424)	−0.035(3)	0.225(3)	0.525(2)
C(425)	−0.040(3)	0.220(3)	0.464(2)
C(426)	0.013(2)	0.267(2)	0.415(2)
C(1)	0.974(4)	0.898(4)	0.256(3)
Cl(11)	0.858(1)	0.899(4)	0.230 1(7)
Cl(12)	1.066(1)	0.866(1)	0.190 9(8)
C(2)	0.765(6)	0.042(6)	0.473(4)
Cl(21)	0.838(1)	0.049(1)	0.401 1(9)
Cl(22)	0.731(2)	0.153(2)	0.508(1)
O(100)	0.7041	0.3165	0.3865
C(101)	0.6833	0.3802	0.3289
C(102)	0.7106	0.4698	0.3356
C(103)	0.5699	0.4085	0.3189

solid. This was recrystallised from dichloromethane–hexane to give $[Pt_3(\mu\text{-}SO_2)_3(PMe_2Ph)_3]$ as red crystals. Yield 0.12 g (71%) (Found: C, 25.0; H, 2.7. $C_{24}H_{33}O_6P_3Pt_3S_3$ requires C, 24.2; H, 2.8%). I.r. (cm^{-1}): ν_{SO_2} 1 252m, 1 246m, and 1 071vs. $^{31}P\text{-}\{^1H\}$ N.m.r. in CD_2Cl_2: $\delta(^{31}P)$ 18.0 p.p.m. with $^1J(^{195}Pt\text{–}^{31}P)$ = 3 974, $^2J(^{195}Pt\text{–}^{31}P)$ = 388, and $^3J(^{31}P\text{–}^{31}P)$ = 50 Hz.

Reaction of $[Pt_3(\mu\text{-}SO_2)_3(PMe_2Ph)_3]$ *with* CO.—$[Pt_3(\mu\text{-}SO_2)_3(PMe_2Ph)_3]$ (0.15 g, 0.13 mmol) was dissolved in toluene (40 cm^3) and warmed to 60 °C. CO was bubbled through the mixture for 30 min to give a red solution. Reduction of the volume of the solution followed by addition of hexane and standing gave $[Pt_5(CO)(\mu\text{-}CO)_5(PMe_2Ph)_4]$ as a red-brown microcrystalline solid. Yield 0.08 g (59%) (Found: C, 27.9; H, 2.8. $C_{38}H_{44}O_6P_4Pt_5$ requires C, 26.9; H, 2.6%). I.r. (cm^{-1}): ν_{CO} 1 992ms, 1 895w, 1 860ms, 1 798s, and 1 775vs.

Synthesis of $[Pt_5(CO)(\mu\text{-}CO)_2(\mu\text{-}SO_2)_3(PPh_3)_4]$.—$[Pt_5(CO)(\mu\text{-}CO)_5(PPh_3)_4]$ (0.3 g, 0.14 mmol) was dissolved in toluene (25 cm^3) at 60 °C and SO_2 bubbled through for 20 min. Addition of diethyl ether gave an orange solid. This was recrystallised from dichloromethane–diethyl ether to give red microcrystals of $[Pt_5(CO)(\mu\text{-}CO)_2(\mu\text{-}SO_2)_3(PPh_3)_4]$. Yield 0.21 g (67%) (Found: C, 39.9; H, 2.6. $C_{75}H_{60}O_9P_4Pt_5S_3$ requires C, 39.1; H, 2.6%). I.r. (cm^{-1}): ν_{CO} 2 050ms, 1 940 (sh), and 1 909s; ν_{SO_2} 1 240mw, 1 087vs, and 1 070vs.

Table 6. Metal–metal bond lengths (Å) in $[Pt_5(CO)_6(PPh_3)_4]$

Pt(1)–Pt(2)	2.726(1)	Pt(2)–Pt(3)	2.699(1)
Pt(1)–Pt(3)	2.804(1)	Pt(3)–Pt(4)	2.917(1)
Pt(1)–Pt(4)	2.760(1)	Pt(3)–Pt(5)	2.919(1)
Pt(1)–Pt(5)	2.737(1)	Pt(4)–Pt(5)	2.683(1)

Table 7. Crystal data, details of data collection, and structure analysis for $[Pt_5(CO)_3(SO_2)_3(PPh_3)_4]\cdot 2CH_2Cl_2\cdot Me_2CH(OH)$

Formula		$C_{80}H_{72}Cl_4O_{10}P_4Pt_5S_3$		
M		2 530.8		
Crystal system		Triclinic		
a/Å	13.991(6)		α/°	84.07(2)
b/Å	14.625(5)		β/°	83.34(3)
c/Å	21.285(4)		γ/°	70.76(4)
U/Å^3	4 074(3)			
Space group		$P\bar{1}$		
Z		2		
D_c/g cm^{-3}		2.06		
$F(000)$		2 396		
Linear absorption coefficient (cm^{-1})		93.4		
Data collection				
Mo-K_α radiation, λ/Å		0.710 69		
$\theta_{min.}$, $\theta_{max.}$/°		1.5, 22.5		
Total data		13 323		
Total unique data		10 756		
Observed data [$F^2 \geqslant 3\sigma(F^2)$]		7 033		
Merging R		0.0386		
Refinement		Large block-matrix least squares		
No. of parameters		487		
Weighting scheme, Chebyshev coefficients		30.09, 37.32, 10.19		
Final $R = \Sigma\Delta F/\Sigma F_o$		0.0594		
$R' = [\Sigma w\Delta F^2/\Sigma wF_o^2]$		0.0791		

Synthesis of $[Pt_5(CO)(\mu\text{-}CO)_5(AsPh_3)_4]$ *and its Reaction with* SO_2 *to give* $[Pt_5(CO)(\mu\text{-}CO)_2(\mu\text{-}SO_2)_3(AsPh_3)_4]$.—Red crystals of $[Pt_5(CO)(\mu\text{-}CO)_5(AsPh_3)_4]$ were obtained following the method reported by Chatt and Chini[23] for $[Pt_4(CO)_5(AsPh_3)_4]$ as follows. A solution of $K_2[PtCl_4]$ (1.03 g, 2.5 mmol) in water (5 cm^3) was added to a solution of $AsPh_3$ (1.53 g, 5 mmol) in warm ethanol (50 cm^3). The mixture was warmed on a water-bath for 1 h giving a white precipitate. Hydrazine hydrate (1 cm^3) was added. The suspension was boiled for 10 min giving a clear yellow solution which was filtered whilst hot. The filtrate was saturated with CO. Potassium hydroxide (1 g) in water (5 cm^3) was added after which a red-brown solid was obtained. The mixture was warmed at 50—60 °C under CO for 30 min, boiled for a short time and filtered whilst hot. The resulting red-brown residue was dissolved in benzene (20 cm^3) and methanol (15 cm^3) added. On standing, red crystals of $[Pt_5(CO)(\mu\text{-}CO)_5(AsPh_3)_4]\cdot C_6H_6$ were precipitated. Yield 0.35 g (29%) (Found: C, 41.4; H, 2.5. $C_{84}H_{66}As_4O_6Pt_5$ requires C, 41.2; H, 2.7%). I.r. (Nujol mull) (cm^{-1}): ν_{CO} 2 008vs, 1 905w, 1 867s, 1 802vs, and 1 792vs.

A sample of $[Pt_5(CO)(\mu\text{-}CO)_5(AsPh_3)_4]\cdot C_6H_6$ (0.2 g, 0.08 mmol) was dissolved in toluene (20 cm^3) and warmed to 60 °C. SO_2 was bubbled through the solution for 20 min during which time it became a lighter red colour. Addition of hexane yielded an orange solid which was recrystallised from benzene–methanol to give orange-red crystals of $[Pt_5(CO)(\mu\text{-}CO)_2(\mu\text{-}SO_2)_3(AsPh_3)_4]$. Yield 0.15 g (74%) (Found: C, 36.5; H, 2.6. $C_{75}H_{60}As_4O_9Pt_5S_3$ requires C, 36.4; H, 2.4%). I.r. (cm^{-1}): ν_{CO} 2 058s, 1 940 (sh), and 1 908s; ν_{SO_2} 1 241ms, 1 078vs, and 1 072vs.

Single-crystal X-Ray Crystallographic Structural Determination of $[Pt_5(CO)_3(SO_2)_3(PPh_3)_4]\cdot 2CH_2Cl_2\cdot Me_2CH(OH)$.—Crystals of $[Pt_5(CO)_3(SO_2)_3(PPh_3)_4]$ suitable for *X*-ray analysis were grown by the slow diffusion of diethyl ether into a dichloromethane–propan-2-ol solution of the platinum complex and a suitable crystal sealed in a 0.5-mm Lindemann capillary. Unit-cell parameters were initially determined from oscillation and Weissenberg photographs and later refined using 25 high-angle reflections automatically centred on an Enraf–Nonius CAD4 diffractometer. The crystal data and details of the structure refinement are summarised in Table 7. Intensity data were recorded on the CAD4 diffractometer using graphite-monochromated Mo-K_α radiation and an ω–2θ scan technique. During data collection the crystal showed no sign of decomposition. The data were corrected for Lorentz and polarisation effects and for absorption. The structure was solved *via* Patterson and electron density maps, refined by large blocked-matrix least-squares techniques, anisotropic thermal parameters being assigned to the non-carbon atoms. Hydrogen atoms were not refined, but positioned in idealised positions (C–H = 1.00 Å). The final cycle of refinement led to a conventional R factor of 0.059. In the structure factor calculations, neutral scattering factors were taken from ref. 25 and corrected for anomalous dispersion using Δf and $\Delta f''$ values from ref. 26. All the calculations were performed on the Oxford University ICL 2980 Computer using the CRYSTALS[27] suite of programs.

Acknowledgements

We thank the S.E.R.C. for financial support and Johnson Matthey for a generous loan of platinum metal salts.

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Received 17*th July* 1985; *Paper* 5/1216