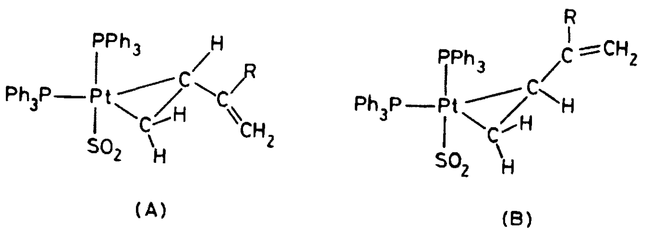
Reactions of Zero-valent Platinum–Sulphur Dioxide Complexes with Dienes; Isolation and *X*-Ray Crystal Structure of a Novel, μ-Phenyl, μ-Phosphido-, μ-Sulphur Dioxide Triangulo-triplatinum Cluster

By DAVID G. EVANS, GLYN R. HUGHES, and D. MICHAEL P. MINGOS*
(*Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford* OX1 3QR)

and JEAN-MARIE BASSETT* and ALAN J. WELCH
(*Department of Chemistry, The City University, London* EC1V OHB)

Summary The complex $Pt(SO_2)_2(PPh_3)_2$ reacts with butadiene and isoprene to give the complexes $Pt(1,2\text{-}\eta\text{-}C_4H_5R)(SO_2)(PPh_3)_2$ (R = H or Me) which, on refluxing in benzene, afford high yields of the *triangulo*-cluster compound $Pt_3(\mu\text{-}Ph)(\mu\text{-}PPh_2)(\mu\text{-}SO_2)(PPh_3)_3$, characterised by a single crystal *X*-ray diffraction study.

CONSIDERABLE interest has been shown recently in the co-ordination chemistry of sulphur dioxide, but the reactions of transition metal complexes of this ligand have received less attention.[1] We report herein the reactions of $Pt(SO_2)_2(PPh_3)_2$ with dienes, which are pertinent in view of a recent report of the catalysis of the reactions of SO_2 with dienes by platinum-metal complexes.[2]



(A) (B)

(1)
a; R = H
b; R = Me

The compounds $Pt(1,2\text{-}\eta\text{-}C_4H_5R)(SO_2)(PPh_3)_2{\cdot}2SO_2$ (**1a**) and (**1b**)† have been synthesised either by passing SO_2 through a solution of $Pt(1,2\text{-}\eta\text{-}C_4H_5R)(PPh_3)_2$[3] in toluene at low temperature (−10 °C) or by adding the diene to $Pt(SO_2)_2(PPh_3)_2$[4] in toluene which had been saturated with SO_2. In the absence of excess of SO_2 the corresponding complexes with a molecule of toluene of crystallisation, $Pt(1,2\text{-}\eta\text{-}C_4H_5R)(SO_2)(PPh_3)_2.C_7H_8$, are formed. The compounds (**1**) are pale-yellow, crystalline solids whose i.r. spectra show bands at *ca.* 1330 and *ca.* 1140 cm^{-1} (SO_2 of crystallisation) and *ca.* 1190 and *ca.* 1040 cm^{-1} (which can be assigned to an η^1-pyramidal co-ordinated SO_2 ligand)[1]. In addition, the compounds show a weak band at *ca.* 1620 cm^{-1} attributable to an unco-ordinated C=C unit. ^{1}H N.m.r. studies at room temperature have indicated that the complexes are essentially dissociated in solution according to equation (1) and it is only at −60 °C that resonances are

$$Pt(1,2\text{-}\eta\text{-}C_4H_5R)(SO_2)(PPh_3)_2 \rightleftharpoons Pt(SO_2)(PPh_3)_2 + C_4H_5R \quad (1)$$

observed which can be unambiguously attributed to a diene η^2-co-ordinated to platinum. A consequence of this dissociation is that the complexes (**1**) are air sensitive in solution and are readily oxidized to the sulphato-complex $Pt(SO_4)(PPh_3)_2$ by dioxygen.

The ^{31}P n.m.r. spectra of complexes (**1**) represent a superposition of two very similar ABX spin-systems arising from the presence of two inequivalent phosphorus atoms co-

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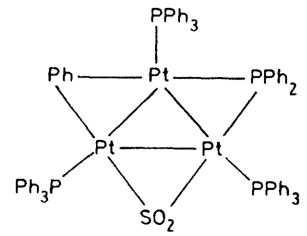
† Satisfactory chemical analyses have been obtained for all compounds described in this communication.

ordinated to ^{195}Pt {*e.g.* (**1a**) δ P_A 12·2, δ P_B 16·4, $^1J(\text{Pt–P}_A)$ 2982, $^1J(\text{Pt–P}_B)$ 2353, $^2J(\text{P}_A\text{–P}_B)$ 15; δ P_A 11·0, δ P_B 16·5, $^1J(\text{Pt–P}_A)$ 2981, $^1J(\text{Pt–P}_B)$ 2352, $^2J(\text{P}_A\text{–P}_B)$ 16}[‡] which is consistent with the presence of the rotamers (A) and (B).

No chemical or spectroscopic evidence has been found for a metallocycle resulting from insertion of SO_2 into the metal–diene π-system or for the formation of a 3-sulpholene system. Indeed, when suspensions of (**1**) in benzene were refluxed for 30 min, a deep-red solution was obtained; addition of methanol followed by cooling resulted in the separation of deep-red crystals of (**2**) in 55% yield. Compound (**2**) has been shown by a single crystal *X*-ray diffraction study to be the *triangulo*-triplatinum complex $Pt_3(\mu\text{-Ph})(\mu\text{-PPh}_2)(\mu\text{-SO}_2)(PPh_3)_3$, the first structurally characterised example of a platinum compound containing a bridging phenyl group.



(2)

Crystal data: $C_{72}H_{60}O_2P_4Pt_3S$, $M = 1698{\cdot}49$, triclinic, space group $P\bar{1}$ (from *E* statistics and successful refinement) $a = 14{\cdot}117(19)$, $b = 19{\cdot}551(8)$, $c = 12{\cdot}497(10)$ Å, $\alpha = 93{\cdot}69(5)$, $\beta = 105{\cdot}95(9)$, $\gamma = 103{\cdot}86(8)°$, $U = 3188{\cdot}2$ Å^3, $Z = 2$, $D_c = 1{\cdot}77$ g cm^{-3}, $F(000) = 1634$ electrons, graphite-monochromated Mo-K_α radiation ($\lambda = 0{\cdot}71069$ Å), μ-(Mo-$K_{\bar{\alpha}}$) = 64·7 cm^{-1}. Diffracted intensities were measured, to $\theta_{max} = 22°$, on a Hilger and Watts Y290 four-circle diffractometer. 7515 Reflections [$F \geq 2{\cdot}0\sigma(F)$] were used to solve (Patterson and difference-Fourier

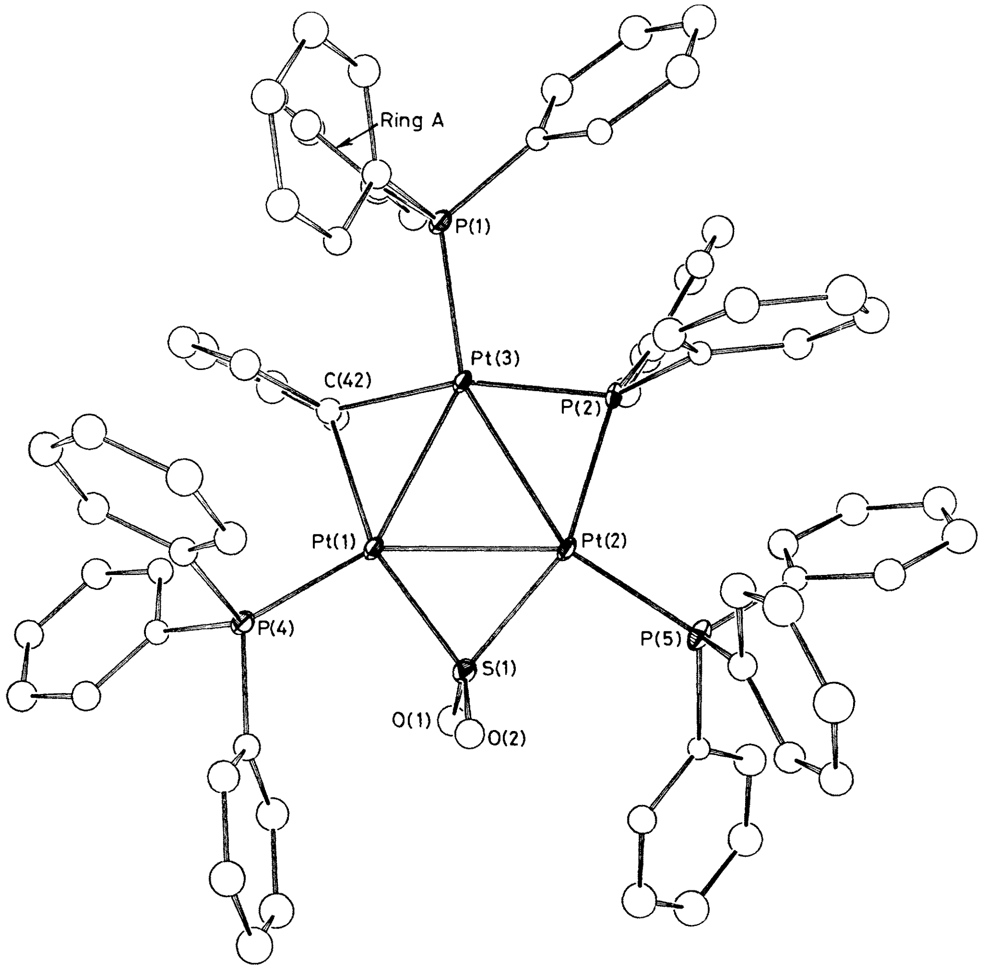


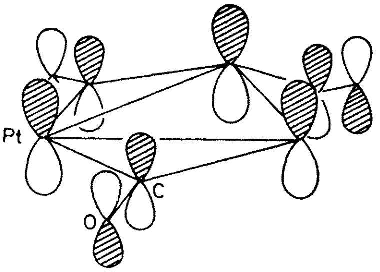
FIGURE. The molecular structure of compound (**2**), $Pt_3(\mu\text{-Ph})(\mu\text{-PPh}_2)(\mu\text{-SO}_2)(PPh_3)_3$. Important molecular parameters: Pt(1)-Pt(2) 2·7810(14), Pt(1)–Pt(3) 2·6958(12), Pt(2)–Pt(3) 2·8155(10), Pt(1)–S(1) 2·170(6), Pt(2)–S(1) 2·272(6), S(1)–O(1) 1·45(2), S(1)–O(2) 1·44(2), Pt(2)–P(2) 2·278(6), Pt(3)–P(2) 2·192(5), Pt(1)–C(42) 2·20(2), and Pt(3)–C(42) 2·12(2) Å.

[‡] Chemical shifts in p.p.m. relative to $P(OMe)_3O$, coupling constants in Hz.

syntheses) and refine (full-matrix least-squares) the structure to *R* 0·114.§

The molecular structure is illustrated in the Figure. Metal–metal distances fall within the range established for bridged platinum–platinum single bonds,[5,6] but additionally reflect the number of electrons contributed by each bridging ligand. Thus the bond lengths Pt(1)–Pt(3) 2·6958(12), Pt(1)–Pt(2) 2·7810(14), and Pt(2)–Pt(3) 2·8155(10) Å, correspond to the bridging ligands C_6H_5, SO_2, and PPh_2 which are, respectively, one-, two-, and three-electron donors. Furthermore, all the metal–metal links are asymmetrically bridged, the internal differences in Pt–ligand bond pairs being *ca.* 0·08—0·10 Å. From the phosphido- and sulphur dioxide bridges the shorter bonds are to the relatively electron-deficient atoms Pt(1) and Pt(3), whilst from the bridging phenyl group the difference in lengths is in the opposite sense to that expected by analogy. Although the asymmetry here is only marginally significant in terms of Pt–C distances, its origin may nevertheless be traced to an intramolecular quasi-graphitic interaction with the phenyl ring A of the $P(1)Ph_3$ ligand (the inter-ring dihedral angle is 14° and there are 3 inter-annular contacts of less than 3·5 Å). No other such intra- or inter-molecular-bonding contacts exist in the solid state structure of (**2**).

The total electron count in (**2**) is 42 electrons, so it is isoelectronic with $Pt_3(\mu\text{-}SO_2)_3(PPh_3)_3$,[6] but has two fewer valence-electrons than $[Pt_3(\mu\text{-}CO)_3(CO)_3]^{2-}$[7] and $Pt_3(\mu\text{-}CO)_3(PPh_3)_4$.[8] Extended Hückel molecular-orbital calculations on $[Pt_3(\mu\text{-}CO)_3(CO)_3]^{2-}$ and $Pt_3(\mu\text{-}SO_2)_3(CO)_3$[9] have suggested that the electronic properties of the bridging ligand can play an important role in influencing the total electronic count, since the stability of the highest-occupied molecular-orbital in $[Pt_3(\mu\text{-}CO)_3(CO)_3]^{2-}$ [see (C)], which has a_2'' symmetry, has a major contribution from the π^*-orbitals of the bridging carbonyl ligands. The corresponding molecular orbital in $Pt(\mu\text{-}SO_2)_3(CO)_3$ lies at *ca.* 1·20 eV higher energy since the bridging SO_2 ligand does not have a low lying, empty π^*-level perpendicular to the Pt_3 triangle and therefore the occupation of this molecular orbital is unfavourable.



(C)

a_2'' symmetry

Clearly, similar considerations apply to bridging Ph and PPh_2 ligands leading to the 42 valence-electron count in $Pt_3(\mu\text{-}Ph)(\mu\text{-}PPh_2)(\mu\text{-}SO_2)(PPh_3)_3$ and $Pt_3(\mu\text{-}SO_2)_3(PPh_3)_3$.

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§ 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.

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