

## Models for the Reaction of Hydrogen Sulphide with a Platinum(111) Surface: The Structure of the Cluster Cation $[\text{Pt}_3\text{H}(\mu_3\text{-S})(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_3]^+$

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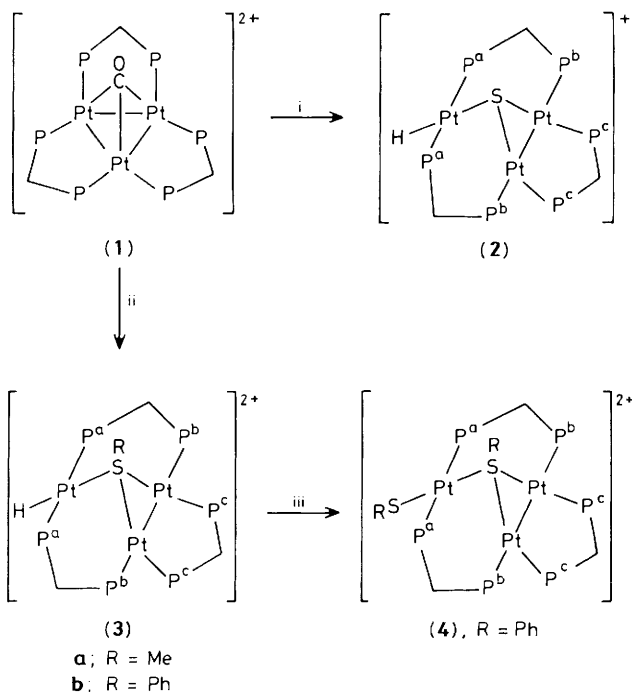
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The reactions of MeSH, PhSH, and H<sub>2</sub>S with the co-ordinatively unsaturated cluster  $[\text{Pt}_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$ , dppm = Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>, model important features of the poisoning of a Pt(111) surface by these reagents in giving the novel products  $[\text{Pt}_3\text{H}(\mu_3\text{-SMe})(\mu\text{-dppm})_3]^{2+}$ ,  $[\text{Pt}_3(\text{SPh})(\mu_3\text{-SPh})(\mu\text{-dppm})_3]^{2+}$ , and  $[\text{Pt}_3\text{H}(\mu_3\text{-S})(\mu\text{-dppm})_3]^+$ , which has been characterised by a single crystal X-ray determination.

The reaction of H<sub>2</sub>S with a platinum(111) surface gives hydrogen and a sulphide coat containing Pt<sub>3</sub>(μ<sub>3</sub>-S) units, and has been studied in detail because of the significance of poisoning of platinum catalysts by such reactions.<sup>1-3</sup> This article reports the reactions of H<sub>2</sub>S and RSH (R = Me or Ph) with the co-ordinatively unsaturated cluster cation<sup>4</sup>  $[\text{Pt}_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$  (1), dppm = Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>, to form Pt<sub>3</sub>(μ<sub>3</sub>-S) units, modelling the surface reaction. The major chemical results are shown in Scheme 1.

The reaction of H<sub>2</sub>S with (1) to give (2) involves oxidative addition of an S-H group to the cluster and loss of a proton from H<sub>2</sub>S. It is likely that an intermediate (3) with R = H is formed which then undergoes deprotonation, and this is supported by the observation that complexes (3) are stable products of reaction of (1) with RSH (R = Me or Ph) (Scheme 1). Excess of PhSH reacts with (3b) to give (4). The new complexes (2), (3), and (4) as the PF<sub>6</sub><sup>-</sup> salts are air-stable yellow solids, which were characterized by elemental analysis and <sup>1</sup>H, <sup>31</sup>P, and <sup>195</sup>Pt n.m.r. spectroscopy.<sup>†</sup>

The structure of (2), as the BPh<sub>4</sub><sup>-</sup> salt, was determined by X-ray crystallographic methods.<sup>‡</sup> The cation (Figure 1) contains a cluster of three platinum atoms, with bridging dppm ligands and a triply bridging sulphide ligand. The Pt(1)-Pt(3) distance of 2.597(4) Å is indicative of a single bond, whereas



Scheme 1. Reagents: i, H<sub>2</sub>S, -H<sup>+</sup>, -CO; ii, RSH, -CO; iii, PhSH, -H<sub>2</sub>.

<sup>†</sup> N.m.r. data in (CD<sub>3</sub>)<sub>2</sub>CO, refs. Me<sub>4</sub>Si (<sup>1</sup>H), (MeO)<sub>3</sub>PO (<sup>31</sup>P), and aqueous K<sub>2</sub>PtCl<sub>4</sub> (<sup>195</sup>Pt), multiplicities due to <sup>195</sup>Pt couplings not reported except for <sup>195</sup>Pt spectra: (2), δ (<sup>1</sup>H) -9.24 [t of t, 1H, <sup>1</sup>J(PtH) 1106, <sup>2</sup>J(PH) 13.5, <sup>4</sup>J(PH) 2.9 Hz, PtH]; δ (<sup>31</sup>P) 25.2 [t, 2P, <sup>1</sup>J(PtP<sup>a</sup>) 2992, <sup>2</sup>J(P<sup>a</sup>P<sup>b</sup>) 27 Hz, P<sup>a</sup>], 5.0 [t, 2P, <sup>1</sup>J(PtP<sup>b</sup>) 3110, <sup>2</sup>J(PtP<sup>b</sup>) 222, <sup>2</sup>J(P<sup>a</sup>P<sup>b</sup>) 27, <sup>3</sup>J(P<sup>b</sup>P<sup>b</sup>) 170 Hz, P<sup>b</sup>], and -12.7 [m, 2P, <sup>1</sup>J(PtP<sup>c</sup>) 3887 Hz, P<sup>c</sup>]; δ (<sup>195</sup>Pt) -3181 (t, Pt<sup>a</sup>) and -3172 p.p.m. (d of d, Pt<sup>b</sup>); i.r. (Nujol): ν(PtH) 2089 cm<sup>-1</sup>. (3a), δ (<sup>1</sup>H) -10.0 p.p.m. [t, 1H, <sup>1</sup>J(PtH) 1263, <sup>2</sup>J(PH) 11.8 Hz, PtH]; δ (<sup>31</sup>P) 28.6 [t, 2P, <sup>1</sup>J(PtP<sup>a</sup>) 2832, <sup>2</sup>J(P<sup>a</sup>P<sup>b</sup>) 20 Hz, P<sup>a</sup>], 2.1 [t, 2P, <sup>1</sup>J(PtP<sup>b</sup>) 3140, <sup>2</sup>J(PtP<sup>b</sup>) 140, <sup>2</sup>J(P<sup>b</sup>P<sup>a</sup>) 20, <sup>3</sup>J(P<sup>b</sup>P<sup>b</sup>) 160 Hz, P<sup>b</sup>], and -9.0 p.p.m. [s, 2P, <sup>1</sup>J(PtP<sup>c</sup>) 4158 Hz, P<sup>c</sup>]; δ (<sup>195</sup>Pt) -3387 (t, Pt<sup>a</sup>) and -3417 p.p.m. (d of d, Pt<sup>b</sup>); i.r. (Nujol): ν(PtH) 2146 cm<sup>-1</sup>. (4), δ (<sup>31</sup>P) 18.5 [s, 2P, <sup>1</sup>J(PtP<sup>a</sup>) 2558 Hz, P<sup>a</sup>], -6.4 [s, 2P, <sup>1</sup>J(PtP<sup>b</sup>) 3106, <sup>2</sup>J(PtP<sup>b</sup>) 147, <sup>3</sup>J(P<sup>b</sup>P<sup>b</sup>) 153 Hz, P<sup>b</sup>], and -7.7 p.p.m. [s, 2P, <sup>1</sup>J(PtP<sup>c</sup>) 4248 Hz, P<sup>c</sup>]; δ (<sup>195</sup>Pt) -3090 (t, Pt<sup>a</sup>) and -3388 p.p.m. (d of d, Pt<sup>b</sup>).

<sup>‡</sup> Crystal data for (2): C<sub>99</sub>H<sub>87</sub>BPt<sub>3</sub>S, M<sub>r</sub> = 2090.8, monoclinic, space group P2<sub>1</sub>/c, a = 11.338(1), b = 17.303(2), c = 42.957(3) Å, β = 90.30(1)°, U = 8428(2) Å<sup>3</sup>, Z = 4, D<sub>m</sub> = 1.65(1), D<sub>c</sub> = 1.648 Mg m<sup>-3</sup>, F(000) = 4104 electrons, λ(Cu-Kα) = 1.54184 Å, μ = 10.91 mm<sup>-1</sup>, T = 295 K. Intensity data were collected on an Enraf-Nonius CAD4F diffractometer by the θ-2θ technique using prefiltered Cu radiation. Full-matrix least-squares refinement on F [8258 unique observations with I > 3σ(I), 300 variables, p = 0.04, phenyl rings refined as rigid groups, C-C 1.392 Å, C-C-C 120°, H atom contributions included but not refined] converged at R = 0.0432, R<sub>w</sub> = 0.0426, goodness-of-fit = 2.54. The hydride ligand was located in a difference Fourier synthesis at 0.63(9) e Å<sup>-3</sup>, Pt-H, 2.00 Å. H-Pt-S, 178°, but not refined.

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, 1986.

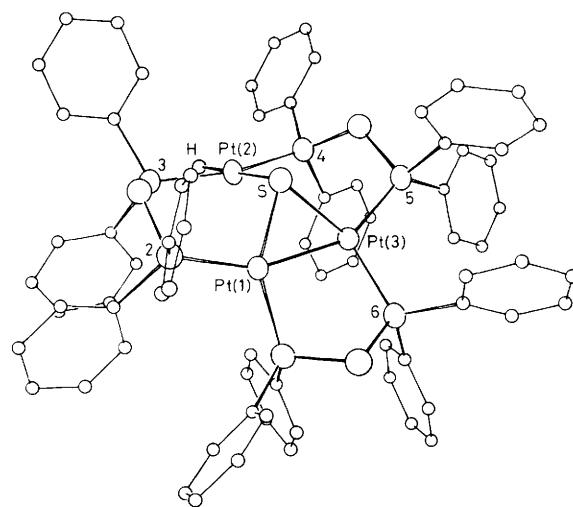


Figure 1. The structure of (2).

the Pt ··· Pt distances of 3.574(2) and 3.678(7) Å involving Pt(2) are clearly non-bonding. The co-ordination geometries at Pt(1) and Pt(3) are severely distorted square-planar [ $\angle$  S-Pt-P (S *trans* to P), 147.7(1) and 149.3(1)°, and P-Pt-Pt

(P *trans* to Pt), 155.7(1) and 151.8(1)° respectively]. That at Pt(2) is more regular, with a P–Pt–P angle of 168.0(1)°. The S–Pt(2) bond length (S *trans* to H) of 2.375(6) Å is significantly longer than those to Pt(1) and Pt(3) (S *trans* to P) of 2.294(5) and 2.311(3) Å, respectively, as might be expected from the greater *trans* influence of the hydride ligand.

The conversion of (1) into (2) models several features of analogous chemistry on the Pt(111) surface, including the easy displacement of CO by H<sub>2</sub>S and the formation of the Pt<sub>3</sub>(μ<sub>3</sub>-S) group.<sup>1–3</sup> The oxidative addition of the S–H bond probably also occurs in the surface reaction. The Pt–S bond lengths in (2) are only slightly longer than the Pt–S distance of 2.28(3) Å estimated for the Pt(111)–S structure from the vertical Pt–S layer spacing of 1.62 Å determined by low-energy electron diffraction, assuming that the Pt–Pt distances were not affected by sulphur adsorption.<sup>1</sup> If some lengthening of the Pt–Pt distances occurs as suggested by the cluster model (2), an even closer agreement in Pt–S bond lengths might be obtained. The cleavage of two Pt–Pt bonds on conversion of (1) into (2) can be rationalized in terms of the increase in cluster electron count from 42 to 46 electrons, and the much

greater ease of these reactions compared to reactions of H<sub>2</sub>S with clusters such as [Os<sub>3</sub>(CO)<sub>12</sub>]<sup>5</sup> is attributed to the co-ordinative unsaturation of (1).

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