μ-Sulphido-cyclo[bis(triphenylphosphine)platinum(II)carbonyltriphenylphosphine-platinum(II)]: Structures of a Complex Containing a Pt–Pt–S Three-membered Ring

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THE only known sulphidocarbonylplatinum complex, was prepared by Baird and Wilkinson,[1] and analysed as $Pt_2S(CO_2)(PPh_3)_3$. No satisfactory structure could be deduced chemically for this formula, and we have therefore carried out a single-crystal *X*-ray analysis. We find that the complex has in fact the formula $Pt_2S(CO)(PPh_3)_3$ and contains a single covalent Pt–Pt bond which forms with sulphur a three-membered ring.

μ-Sulphido-cyclo[bis(triphenylphosphine)platinum(II)carbonyltriphenylphosphineplatinum(II)] crystallises (Me_2CO–$CHCl_3$) as yellow plates (triclinic, $a = 10{\cdot}687$, $b = 25{\cdot}240$, $c = 9{\cdot}307$ Å, $\alpha = 95{\cdot}17$, $\beta = 104{\cdot}22$, $\gamma = 97{\cdot}67°$, $U = 2392{\cdot}3$ Å^3, $D_m = 1{\cdot}71$, $Z = 2$, $D_c = 1{\cdot}72$).

Three-dimensional *X*-ray data were collected on a Siemens four-circle automatic diffractometer. Using Cu-K_α radiation a total of 2898 independent reflections were measured

(to $\theta = 40°$), of which 678 were judged to be unobserved. The structure was solved by Patterson and Fourier methods. Disorder in one triphenylphosphine group (in ratio *ca.* 63 : 37) prevents an unambiguous assignment of the space group. Least-squares refinement in $P\bar{1}$, with 82 non-hydrogen atoms in the asymmetric unit, has now reached $R = 0{\cdot}069$. Refinement in $P1$ suggests that apart from the disorder the molecules conformessentially to $P\bar{1}$.

The complex exists in the crystal in two conformationally isomeric forms (Figure); the difference between the two isomers being mainly confined to one triphenylphosphine group in which the phenyl rings adopt two quite different conformations with respect to the rest of the molecule. This results in a slightly different orientation for each isomer of the adjacent carbonyl group. The conformation of each isomer is determined by the closest approach distance between an α-carbon of a phenyl ring and the carbonyl group (in each case 3·1—3·2 Å). Baird and Wilkinson noted that the i.r. spectrum of a Nujol mull contained two terminal carbonyl peaks (in ratio *ca.* 2 : 1) at 1989 and 1960 cm.$^{-1}$ which is consistent with the presence of one carbonyl group having slightly different environments in the two forms.

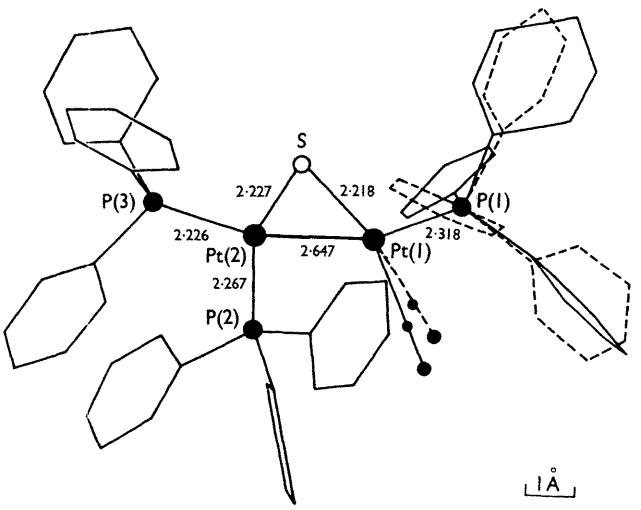

FIGURE. *The major and the lesser (dotted) isomer of* $Pt_2S(CO)(PPh_3)_3$ *viewed in* [001] *projection. Standard deviations are:* Pt–Pt, 0·002; Pt–S *and* Pt–P, 0·009 Å

The platinum atoms and their immediate neighbours are essentially planar, although the co-ordination about the metal atoms is far from square-planar (Table). Two platinum atoms and a sulphur form a triangle in which the Pt–Pt distance is 2·65 Å. This is the shortest such distance known (*cf.* 2·78 Å in the metal). We consider it to represent a single covalent Pt–Pt bond, in excellent agreement with the sum of Pauling's covalent radii (2·62 Å). Although compounds likely to contain covalent Pt–Pt bonds have been reported,[2] this is the first unequivocal structural evidence of such a bond. Distances in the range 2·85—3·4 Å are known,[3] but none shorter than that in the metal. In view of the acute Pt–Pt–S angles (*ca.* 53°), however, the possibility of a 'bent' bond of the type discussed by Dahl[4] should be considered. The only similar example of this type of ring is the Fe–Fe–S ring found in $Fe_2(CO)_8SO_2$.[5] The Pt–P distances are unexceptional but the Pt–S distances are slightly shorter than expected for a single covalent bond.

TABLE

Angle	σ
Pt(1)–Pt(2)–S	53·3 (0·3)°
S–Pt(2)–P(3)	106·8 (0·4)
P(3)–Pt(2)–P(2)	101·6 (0·4)
P(2)–Pt(2)–Pt(1)	98·2 (0·3)
Pt(2)–Pt(1)–S	53·6 (0·3)
S–Pt(1)–P(1)	104·5 (0·4)
P(1)–Pt(1)–O	97 (2)
O–Pt(1)–Pt(2)	105 (2)
Pt(1)–S–Pt(2)	73·1 (0·4)

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