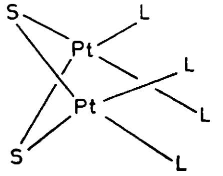
Heterometallic Complexes of Platinum with Bridging Sulphido-ligands: Crystal Structure of $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4\}_2Pd](BF_4)_2$

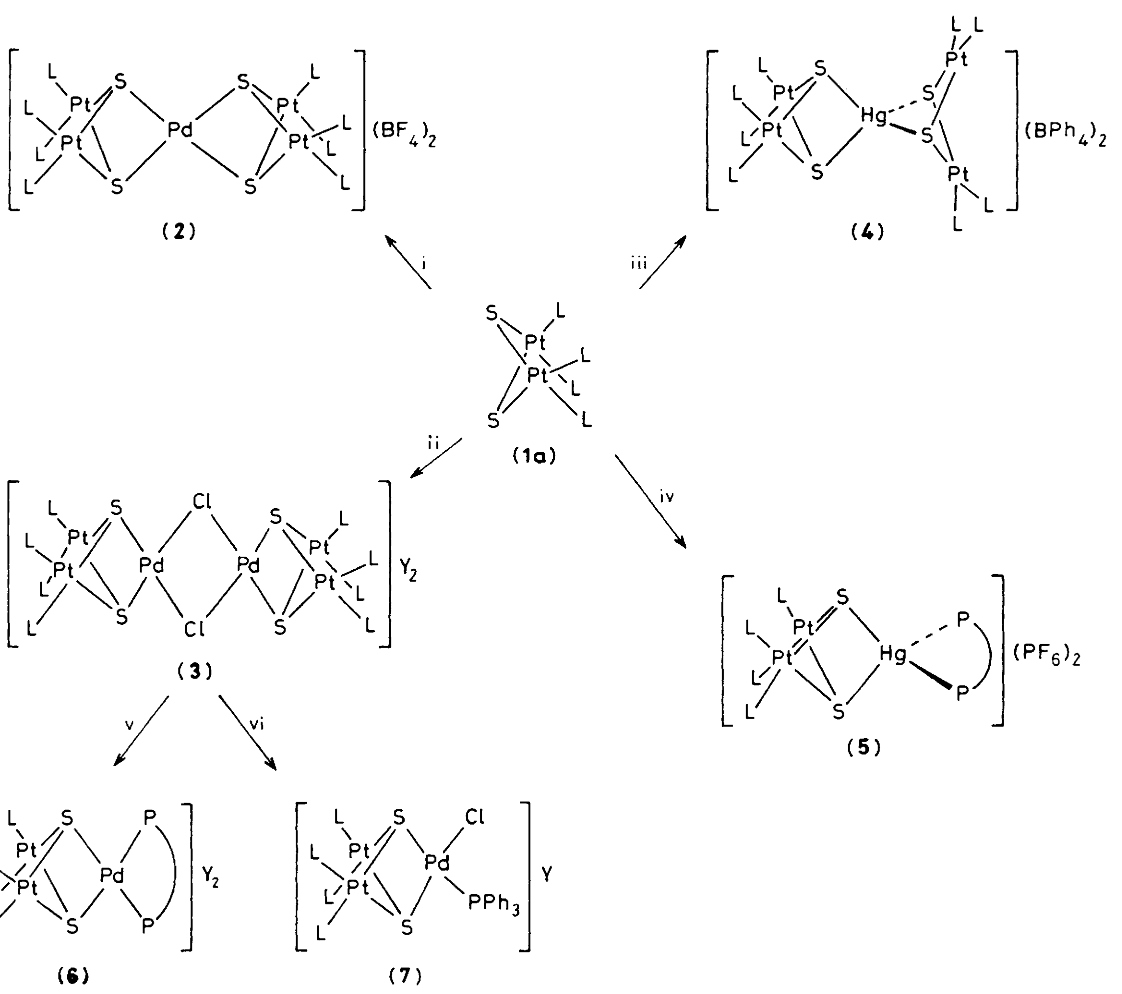
Clive E. Briant, T. S. Andy Hor, Nigel D. Howells, and D. Michael P. Mingos*
Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, U.K.

The complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ functions very effectively as a bidentate ligand towards other metal ions, *e.g.* Ni^{2+}, Pd^{2+}, Hg^{2+}, and Au^{+}, and therefore provides a good high yield route into heterometallic complexes containing 3, 5, and 6 metal atoms; the structure of one of these complexes, $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4\}_2Pd](BF_4)_2$, was determined by *X*-ray crystallography.



(1); a, L = PPh_3
b, L = $PPhMe_2$

Considerable interest has been shown recently in the synthesis of heterometallic complexes of the transition metals, because of their potential in catalytic processes requiring multiple metal sites.[1] Rational syntheses of compounds of this type have been developed by Vahrenkamp,[2] Shaw,[3] and Stone.[4] This paper describes the syntheses of some heterometallic complexes of platinum, which are of interest in this respect because some of them contain compact aggregates of up to six co-ordinatively unsaturated metal atoms. The complexes utilise the ligating properties of the sulphido-ligands in the binuclear complexes $[Pt_2(\mu\text{-}S)_2(PR_3)_4]$ (**1a,b**).[5] *X*-Ray crystallographic studies on (**1b**)[6] and a methylated derivative of (**1a**)[7] have established that this type of complex has a pair of hinged square-planes with a dihedral angle of approximately 125°. Thus (**1a**) and (**1b**) are sufficiently distorted from planarity to have viable cone angles as ligands and in addition have a sulphur–sulphur separation of approximately 3.00 Å, which is comparable to that found in bidentate thioether and phos-



Scheme 1. i, $[Pd(dmf)_4](BF_4)_2$ (dmf = dimethylformamide); tetrahydrofuran(THF); ii, $PdCl_2(PhCN)_2$, THF; MeOH, NH_4PF_6; iii, $HgCl_2(PPh_3)_2$, MeOH; $NaBPh_4$; iv, $HgCl_2$(dppe) [dppe = bis(diphenylphosphino)ethane], THF; NH_4PF_6, MeOH; v, dppe, MeOH; vi, PPh_3, MeOH. L = PPh_3 and Y = PF_6.

phine ligands and sulphido-complexes such as $[Fe_2(\mu\text{-}S)_2(CO)_6]^{2-}$ which are known to function as ligands.[8]

The donor properties of (**1a**) towards the metal ions Ni^{2+}, Pd^{2+}, Au^+, Hg^{2+}, and Ag^+ have been established, but the potential and versatility of (**1a**) as a ligand can be illustrated by the results which have been obtained for Pd^{2+} and Hg^{2+} and which are summarised in Scheme 1. All the compounds illustrated in Scheme 1 have been obtained in high yields (70—90%) as crystalline, air stable solids and characterised by $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ n.m.r. studies.† The co-ordination of two molecules of (**1a**) to Pd^{2+} and Hg^{2+} to form the square-planar (**2**) and tetrahedral (**4**) complexes was surprising and therefore (**2**) has also been characterised by a single crystal *X*-ray crystallographic analysis.

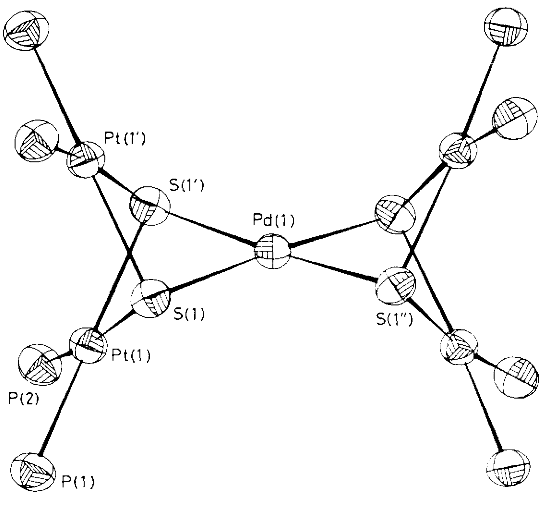


Figure 1. The molecular structure of the $[\{Pt_2(\mu\text{-}S)_2(PPh_3)_4\}_2Pd]^{2+}$ cation. For reasons of clarity the phenyl rings have been omitted. Important bond lengths include: Pd(1)–S(1) 2.348(2), Pt(1)–S(1) 2.344(3), Pt(1)–S(1′) 2.351(3), Pt(1)–P(1) 2.324(3), Pt(1)–P(2) 2.288(3) Å, and bond angles S(1)–Pd–S(1′) 76.4(1), S(1)–Pt–S(1′) 76.4(1), Pd(1)–S(1)–Pt(1) 86.4(1), Pd(1)–S(1)–Pt(1′) 86.3(1)°.

---

† Selected physical and spectroscopic data ($^{31}P\{^1H\}$ n.m.r. in CH_2Cl_2 and $^{195}Pt\{^1H\}$ n.m.r. in CD_2Cl_2) are as follows: (**2**), orange red; m.p. 195—197 °C; $^{31}P\{^1H\}$ n.m.r. (to high frequency of trimethyl phosphate), δ 17.13 p.p.m. [d, ^1J(PtP) 2771; ^3J(PtP) 23.5 Hz]. (**3**), Y = PF_6; orange; m.p. 290—293 °C; $^{31}P\{^1H\}$ n.m.r., δ 12.69 p.p.m. [^1J(PtP) 3180 Hz]. (**4**), yellow; m.p. 253—255 °C; $^{31}P\{^1H\}$ n.m.r., δ 13.01 p.p.m. [^1J(PtP) 3111 Hz]. (**5**), lemon yellow; m.p. 222—224 °C; $^{31}P\{^1H\}$ n.m.r., δ 13.49 p.p.m. [4P, $PtPPh_3$, ^1J(PtP) 3085 Hz], 1.64 [2P, $HgPPh_2$, ^1J (^{199}HgP) 1900 Hz]. (**6**), Y = BF_4; yellow; m.p. 330—334 °C; n.m.r.: $^{31}P\{^1H\}$, δ 9.98 [4P, $PtPPh_3$, ^1J(PtP) 3202 Hz], 39.05 p.p.m. [q, 2P, $PdPPh_2$, ^3J(PtP) 40 Hz, ^4J(PP) 4.1 Hz]; $^{195}Pt\{^1H\}$ (to high frequency of Na_2PtCl_6 in D_2O), δ −4266 p.p.m. [t, ^1J(PPt) 3207 Hz]. (**7**), Y = BPh_4; yellow; m.p. 144—147 °C; n.m.r.: $^{31}P\{^1H\}$, δ 12.36 [2P, PtP_APh_3, ^1J(PtP) 3136 Hz], 13.37 [2P, PtP_BPh_3, ^1J(PtP) 3212 Hz], 13.90 p.p.m. (1P, $PdPPh_3$); $^{195}Pt\{^1H\}$, δ −4280 p.p.m. [t, ^1J(PPt) 3169 Hz].

Crystal data: $C_{144}H_{120}B_2F_8P_8PdPt_4S_4$, M = 3 286.6, orthorhombic, space group *Pnnn* (No. 48), a = 18.389(5), b = 18.349(5), c = 19.007(6) Å, U = 6 413 Å^3, Z = 2, $F(000)$ = 3 216, D_c = 1.70 g cm^{-3}, Mo-K_α X-radiation (λ = 0.710 69 Å), μ(Mo-K_α) = 49.35 cm^{-1}. The structure was solved by heavy atom methods and refined by blocked matrix least-squares using the CRYSTALS programme package.[9] For 3 026 unique observed reflections [with $I \geqslant 3\sigma(I)$] measured on a CAD4 diffractometer in the range $2 \leqslant 2\theta \leqslant 50°$ the current R value is 0.038.‡ In common with many structures of this type the BF_4^- anions are disordered and have been approximated by a pair of tetrahedral ions with half occupancies.

The structure of the molecular cation of (**2**) which is illustrated in Figure 1 has crystallographically imposed D_2 symmetry. The geometry about the central palladium atom is very close to square-planar with the sulphur atoms lying ±0.088 Å from the best least-squares plane through the palladium and sulphur atoms. The five metal atoms define a 'bow-tie' arrangement, but the metal–metal distances are greater than 3.15 Å. Therefore, the bonding in the complex is satisfactorily described in terms of square-planar 16 electron palladium and platinum centres and no formal metal–metal bonds need be invoked. The complexes shown in Scheme 1, then, are described as aggregates rather than clusters.

The formation of the hexanuclear complex (**3**) which has also been characterised by X-ray techniques,[10] is significant because it demonstrates how the chemistries of such complexes could be developed by the facile cleavage of the Pd_2Cl_2 bridge by donor molecules. The oxidative-addition chemistries of complexes of the type (**2**), (**3**), (**6**), and (**7**) should also be of some interest.

The S.E.R.C. is thanked for financial support and Johnson-Matthey Ltd. for a loan of platinum metal salts.

Received, 16th June 1983; Com. 799

---

‡ Atomic co-ordinates 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.

References

1 D. A. Roberts and G. L. Geoffroy, 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Ch. 40, Pergamon Press, Oxford, 1982.
2 H. Vahrenkamp, *Philos. Trans. R. Soc., Ser. A*, 1982, **308**, 17.
3 P. G. Pringle and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1982, 81; 859; 861; 956; 1313.
4 F. G. A. Stone, *Philos. Trans. R. Soc., Ser. A*, 1982, **308**, 87.
5 J. Chatt and D. M. P. Mingos, *J. Chem. Soc. A*, 1970, 1243.
6 R. Mason, B. Law, and D. M. P. Mingos, unpublished results.
7 C. E. Briant, C. J. Gardner, T. S. A. Hor, N. D. Howells, and D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, to be submitted.
8 D. Seyferth, R. S. Henderson, and Li-Cheng Song, *Organometallics*, 1982, **1**, 125.
9 CRYSTALS User manual, J. R. Carruthers, Oxford University Computing Centre.
10 C. E. Briant, T. S. A. Hor, N. D. Howells, and D. M. P. Mingos, unpublished results.