

Donor–Acceptor Metal–Metal Bond in the Dinuclear Platinum(II) Complex $[\text{Pt}_2\text{Me}_3(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2][\text{PF}_6]$

By AILEEN A. FREW, LJUBICA MANOJLOVIĆ-MUIR,* and KENNETH W. MUIR
(*Chemistry Department, University of Glasgow, Glasgow G12 8QQ*)

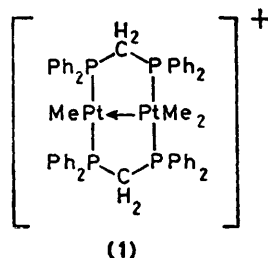
Summary An X-ray diffraction study of the title compound reveals that it contains a $\text{Pt}^{\text{II}} \rightarrow \text{Pt}^{\text{II}}$ donor–acceptor bond and confirms the other features of its novel structure previously deduced from n.m.r. evidence.

THE metal–metal bonding interaction in which one metal atom acts as a two-electron donor was first suggested by Hock and Mills in order to rationalise the molecular geometry of $[\text{Fe}_2(\text{CO})_6\{\text{C}_4\text{Me}_3(\text{OH})_2\}]$.¹ Evidence for such a bonding mode has since been found in other binuclear com-

plexes and in clusters.² In all of these compounds the donor and acceptor metal atoms share at least one atom of a bridging ligand, and the heteropolar $\text{M} \rightarrow \text{M}$ bond is thus only one component in a multi-centred interaction. The charge-equalising role of semi-bridging carbonyl ligands in preserving the electroneutrality principle in such species has been recognised by Cotton.^{2a}

Brown and coworkers³ have recently prepared a novel binuclear complex of platinum(II), $[\text{Pt}_2\text{Me}_3(\text{dppm})_2][\text{PF}_6]$, where $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$. From a detailed study of its

^1H - and ^{31}P -n.m.r. spectra they were able to deduce the geometrical arrangement of the ligands in the cationic structure in solution. This has led them to speculate on the possibility of donor-acceptor $\text{Pt} \rightarrow \text{Pt}$ bonding, for which no positive evidence could be obtained from n.m.r. measurements. We now report the results of an X-ray crystal structure analysis of this compound.



Crystals of $[\text{Pt}_2\text{Me}_3(\text{dppm})_2][\text{PF}_6]$ (1), sensitive to light and loss of solvent, were obtained by recrystallisation from a dichloromethane-*n*-hexane mixture. *Crystal data*: monoclinic, space group $P2_1/n$, $a = 10.220(4)$, $b = 25.522(6)$, $c = 23.832(3)$ Å, $\beta = 93.57(3)^\circ$. The crystal structure was solved by the heavy atom method and refined to $R = 0.081$, using 5467 diffractometric intensities with $I \geq 3\sigma(I)$. The asymmetric unit contains one cation, one anion, and three disordered CH_2Cl_2 solvent molecules.[†]

The solid state structure of the $[\text{Pt}_2\text{Me}_3(\text{dppm})_2]^+$ cation (1), shown in the Figure, is in conformity with that in solution as deduced³ from n.m.r. evidence. It, however, reveals a platinum-platinum separation of 2.769(1) Å, which falls within the range of the Pt-Pt bonding distances observed in other binuclear complexes and clusters.⁴ The Pt(1)-Pt(2) bond is bridged by two dppm ligands, which form two mutually *trans* Pt(2)-P bonds and two mutually *cis* Pt(1)-P bonds. The co-ordination around the Pt(2) centre is completed by a methyl group *trans* to the Pt(1)-Pt(2) bond and that around the Pt(1) centre by two methyl groups *cis* to one another. The environment of the Pt(2) atom displays a nearly ideal square planar geometry, the displacement of the Pt(2), Pt(1), P(1), P(3), and C(5) atoms from their mean plane not exceeding ± 0.04 Å. The arrangement of the P_2C_2 donor set around the Pt(1) atom is best viewed as square planar with slight tetrahedral distortions, the Pt(1), P(2), P(4), C(3), and C(4) atoms being coplanar to within ± 0.10 Å. The normal to this plane coincides to within 9° with the direction of the Pt(1)-Pt(2) bond. Thus, although the two metal centres show different co-ordination numbers and polyhedra, the details of the molecular geometry are such as to suggest that the filled $d(z^2)$ orbital of the Pt(1) atom interacts with a vacant orbital in the square plane of Pt(2) to form a donor-acceptor heteropolar $\text{Pt} \rightarrow \text{Pt}$ bond, in which the formal oxidation state of both metal ions is +2.

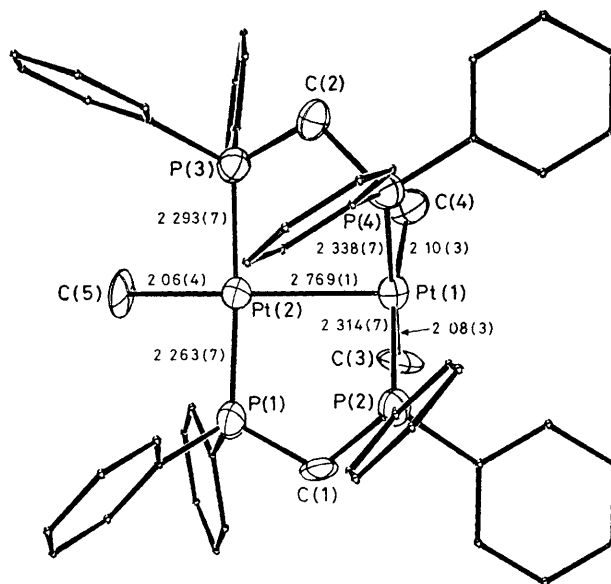


FIGURE. A view of the structure of the $[\text{Pt}_2\text{Me}_3(\mu\text{-dppm})_2]^+$ cation, showing selected bond lengths (Å). Selected bond angles are: Pt(2)-Pt(1)-P(2) 88.9(2), -P(4) 84.9(2), -C(3) 95.9(8), -C(4) 100.0(8), P(2)-Pt(1)-P(4) 107.9(2), -C(3) 83.0(7), -C(4) 166.4(8), P(4)-Pt(1)-C(3) 169.1(7), -C(4) 83.2(8), C(3)-Pt(1)-C(4) 85.9(11), Pt(1)-Pt(2)-P(1) 92.7(2), -P(3) 91.1(2), -C(5) 177.1(10), P(1)-Pt(2)-P(3) 176.2(2), -C(5) 87.7(10), and P(3)-Pt(2)-C(5) 88.5(10)°. The P(2)-Pt(1)-Pt(2)-P(1) and P(4)-Pt(1)-Pt(2)-P(3) torsion angles are, respectively, $-30.7(2)$ and $41.6(2)^\circ$.

The structure of the $[\text{Pt}_2\text{Me}_3(\mu\text{-dppm})_2]^+$ cation is without precedent in the chemistry of platinum. It does, however, bear a strong resemblance to the recently reported structure of $[\text{Rh}(\text{CO})\text{RhCl}_2\{(\text{PhO})_2\text{PN}(\text{Et})\text{P}(\text{OPh})_2\}_2]$, which has been considered as a mixed valence complex of rhodium(0) and rhodium(II), containing a homopolar Rh-Rh bond.⁵ An alternative interpretation, based on analogy with the cationic platinum complex, is to formulate it as a rhodium(I) species in which an electron pair is donated from the $d(z^2)$ orbital of a $[\text{RhCl}_2\text{P}_2]^-$ fragment into an acceptor orbital of an $[\text{Rh}(\text{CO})\text{P}_2]^+$ group. Thus, in conformity with the electro-neutrality principle, formation of the M \rightarrow M bond in both complexes tends to equalise charge of the two metal ions in the same oxidation state.

We thank Dr. M. P. Brown and Mrs. S. J. Cooper (University of Liverpool) for a sample of crystals and the University of Glasgow for a studentship (to A. A. F.).

(Received, 10th April 1980; Com. 376.)

[†] The atomic co-ordinates are available from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Requests should be accompanied by the full literature citation for this communication.

¹ A. A. Hock and O. S. Mills, *Acta Crystallogr.*, 1961, **14**, 139.

² (a) F. A. Cotton, 'Progress in Inorganic Chemistry,' Vol. 21, Wiley, New York, 1976; (b) G. R. John, B. F. G. Johnson, and J. Lewis, *J. Organomet. Chem.*, 1979, **181**, 143.

³ M. P. Brown, S. J. Cooper, R. J. Puddephatt, M. A. Thomson, and K. R. Seddon, *J. Chem. Soc., Chem. Commun.*, 1979, 1117.

⁴ M. P. Brown, J. R. Fisher, L. J. Manojlović-Muir, K. W. Muir, R. J. Puddephatt, M. A. Thomson, and K. R. Seddon, *J. Chem. Soc., Chem. Commun.*, 1979, 931; T. H. Tulip, T. Yamagata, T. Yoshida, R. D. Wilson, J. A. Ibers, and S. Otsuka, *Inorg. Chem.*, 1979, **18**, 2239; T. Yoshida, T. Yamagata, T. H. Tulip, J. A. Ibers, and S. Otsuka, *J. Am. Chem. Soc.*, 1978, **100**, 2063.

⁵ R. J. Haines, E. Meintjies, and M. Laing, *Inorg. Chim. Acta*, 1979, **36**, L403.