Crystal and Molecular Structure of Bis-μ-(bisdiphenylphosphinomethane)-dibromodipalladium(*Pd–Pd*), a Compound Containing Palladium(I)

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Summary The crystal structure of $[Pd(dppm)Br]_2$ (dppm = $Ph_2PCH_2PPh_2$) shows that the palladium(I) atoms are directly metal–metal bonded and adopt an idealised square-planar stereochemistry.

The preparation of the complexes $[Pd(dam)X]_2$ (dam = $Ph_2AsCH_2AsPh_2$; X = Cl, Br) and their establishment as compounds of palladium(I) was recently reported.[1] By the action of dppm ($Ph_2PCH_2PPh_2$) and the halogenocarbonyls Pd(CO)X we have now prepared similar complexes of the type $[Pd(dppm)X]_2$ and the crystal structure of one of these, $[Pd(dppm)Br]_2$, is reported here.

Crystal data: $C_{50}H_{44}Br_2P_4Pd_2$, $M = 1141$, monoclinic, space group $P2_1/c$; $a = 13{\cdot}661(4)$, $b = 16{\cdot}726(4)$, $c = 21{\cdot}442(6)$ Å, $\beta = 106{\cdot}00(4)°$ ($\lambda = 0{\cdot}7107$ Å for Mo-K_α); $U = 4710$ Å^3, $Z = 4$, $D_c = 1{\cdot}61$ g cm^{-3}, $\mu = 27{\cdot}18$ cm^{-1} for Mo-K_α.

Crystals were obtained from a dichloromethane–hexane solution and the structure was solved by conventional heavy atom methods. Least-squares refinement with phenyl rings treated as rigid groups converged at $R = 0{\cdot}078$ for 1495 independent reflections [$2\theta \leqslant 40°$ and $|F|^2 \geqslant 3\sigma(|F|^2)$] which were measured on a four-circle diffractometer with Mo-K_α radiation.

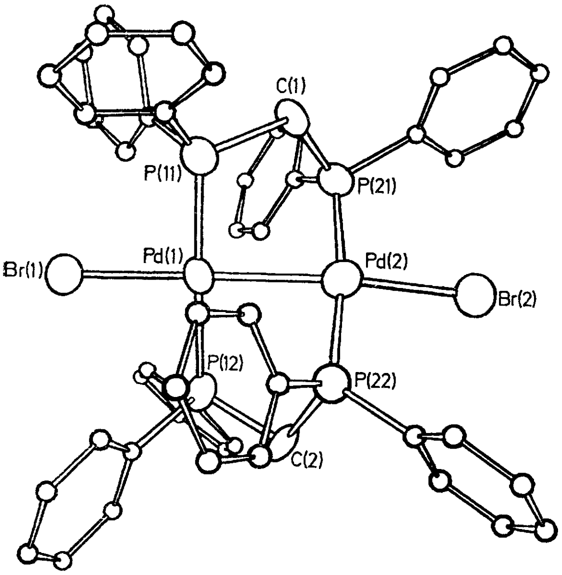

FIGURE. The molecule viewed approximately normal to the mean plane of the heavy atom skeleton. Bond distances in Å are: Pd(1)–Pd(2) 2·699(5); Pd(1)–Br(1) 2·527(6); Pd(2)–Br(2) 2·543(6); Pd(1)–P(11) 2·29(1); Pd(1)–P(12) 2·32(1); Pd(2)–P(21) 2·26(1); Pd(2)–P(22) 2·28(1). Bond angles are: P(11)–C(1)–P(21) 105(2)°; P(12)–C(2)–P(22) 103(2)°; angles subtended at the Pd atoms range from 84·9(3) to 96·4(3)°.

The molecular structure is illustrated in the Figure which is a view approximately normal to the mean plane of the heavy-atom skeleton of the molecule. It shows two bis(diphenylphosphino)methane ligands bridging a direct Pd–Pd bond of length 2·699 Å, part of an approximately linear Br–Pd–Pd–Br chain. Each P–Pd–P group is also approximately linear so that an idealised square-planar environment is completed for each palladium atom. There is a pronounced twist about the Pd–Pd bond with the result that the angle between the mean planes P(11)–Pd(1)–P(12)–Pd(2) and P(21)–Pd(2)–P(22)–Pd(1) is 39°.

Compounds of palladium(I) are rare and all except one of the crystal structures previously reported for this oxidation state involve delocalised aromatic systems bridging two palladium(I) atoms.[2] The Pd–Pd distances in these compounds are in the range 2·58—2·686 Å, and in the unbridged compound[3] which contains square-planar palladium(I) the Pd–Pd distance is 2·531 Å, all significantly less than in the present compound. One other relevant structure is that of $[\text{Pt}_2(\text{CO})_2\text{Cl}_4]^{2-}$ (ref. 4) which contains square-planar Pt^{I} with a metal–metal bond of 2·584 Å, again significantly shorter than the Pd–Pd bond in the present compound. Thus it appears that the Pd–Pd bond in this compound is unusually long.

We see the detailed conformation of $[\text{Pd(dppm)Br}]_2$ as resulting from the conflicting requirements of strong metal–metal bonding, minimisation of interactions between filled interaxial *d* orbitals (requiring a twist about the Pd–Pd bond),[4,5] and the accommodation of a bridging dppm ligand with minimum strain.

(*Received*, 1*st March* 1976; *Com.* 203.)

[1] R. Colton, R. H. Farthing, and M. J. McCormick, *Austral. J. Chem.*, 1973, **26**, 2607.

[2] G. Allegra, A. Immirzi, and L. Porri, *J. Amer. Chem. Soc.*, 1965, **87**, 1394; G. Allegra, G. Tettamanti Casagrande, A. Immirzi, L. Porri, and G. Vitulli, *ibid.*, 1970, **92**, 289; H. Werner, D. Tune, G. Parker, C. Kruger, and D. J. Brauer, *Angew. Chem. Internat. Edn.*, 1975, **14**, 185; A. Ducruix, H. Felkin, C. Pascard, and G. K. Turner, *J.C.S. Chem. Comm.*, 1975, 615; E. Ban, Pei-Tak Cheng, T. Jack, S. C. Nyburg, and J. Powell, *ibid.*, 1973, 368; Y. Kobayashi, Y. Iitaka, and H. Yamazaki, *Acta Cryst.* (*B*), 1972, **28**, 899.

[3] D. J. Doonan, A. L. Balch, S. Z. Goldberg, R. Eisenberg, and J. S. Miller, *J. Amer. Chem. Soc.*, 1975, **97**, 1961.

[4] A. Modinos and P. Woodward, *J.C.S. Dalton*, 1975, 1516.

[5] P. L. Goggin and R. J. Goodfellow, *J.C.S. Dalton*, 1973, 2355.