X-Ray Crystal and Molecular Structure of μ-Carbonylbis-μ-(bisdiphenylarsinomethane)-dichlorodipalladium(I); a Binuclear Compound of Palladium(I) without a Pd–Pd Bond

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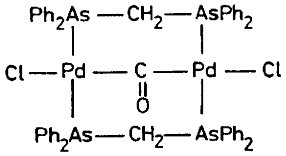
Summary The crystal structure of $[\text{Pd(dam)Cl}]_2\text{CO}$ (dam = $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2$) shows that the palladium atoms are not directly bonded or halogen bridged but that they are spin-paired *via* an unusual bridging carbonyl group.

THE interactions of dam[1] and dppm[2] (dam = $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2$, dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$) with the palladium(I) halogenocarbonyls, Pd(CO)X, have been reported to give $[\text{Pd(L–L)X}]_2$ (L–L = dam or dppm) but there were significant differences in their n.m.r. spectra suggesting that they had different structures. The dam complexes exhibited sharp AB quartets (4H, CH_2, $J_{\text{H–H}}$ 11·0 Hz, independent of halogen) showing that the dam ligands are equivalent but the two methylene protons are not. The resonance occured *ca.* 0·4 p.p.m. upfield of the free ligand which is most unusual. In contrast, the dppm complexes exhibited a sharp triplet (4H, CH_2, $J_{\text{P–H}}$ 4·2 Hz) for the iodide, a broad triplet (4H, CH_2, $J_{\text{P–H}}$ 4·8 Hz) for the bromide, and a triplet of quartets for the chloride (4H, CH_2, $J_{\text{P–H}}$ 6·1 and $J_{\text{H–H}}$ 2·8 Hz). All these resonances occurred *ca.* 1·4 p.p.m. downfield from the free ligand which is the usual position for the CH_2 resonance of co-ordinated dppm and dam. Further investigations have revealed that the dam complexes are in fact carbonyl complexes $[\text{Pd(dam)X}]_2\text{CO}$ with ν_{CO} 1720 cm^{-1}. We now report the crystal structure of $[\text{Pd(dam)Cl}]_2\text{CO}$ (**1**) which shows unique structural features.



(**1**)

Crystal data: $[\text{Pd(dam)Cl}]_2\text{CO}\cdot3\text{C}_6\text{H}_{14}$, $C_{69}H_{64}As_4Cl_2OPd_2$, tetragonal, space group $P4_1$ (C_4^2, No. 76), a = 22·0458(1), c = 14·4345(1) Å, U = 7015·4 Å^3, μ = 75.87 cm^{-1} for Cu-K_α radiation (λ = 1·5418 Å, Ni-filtered), Z = 4, D_c = 1·42, D_m = 1·42 g cm^{-3}.†

Crystals were obtained from a saturated solution of the complex in dichloromethane–n-hexane. Density measurements of the crystals showed that they contained three molecules of solvent per dimer unit and the crystals were unstable in the absence of solvent. The structure was solved by conventional heavy atom methods. Least-square refinement with the phenyl rings treated as rigid groups converged at R = 0·096 from 1698 independent reflections [$2\theta \leqslant 90°$ the limit of the observable data and $|F|^2 \geqslant 3\sigma(|F|^2)$] which were measured on a Siemens automatic diffractometer.

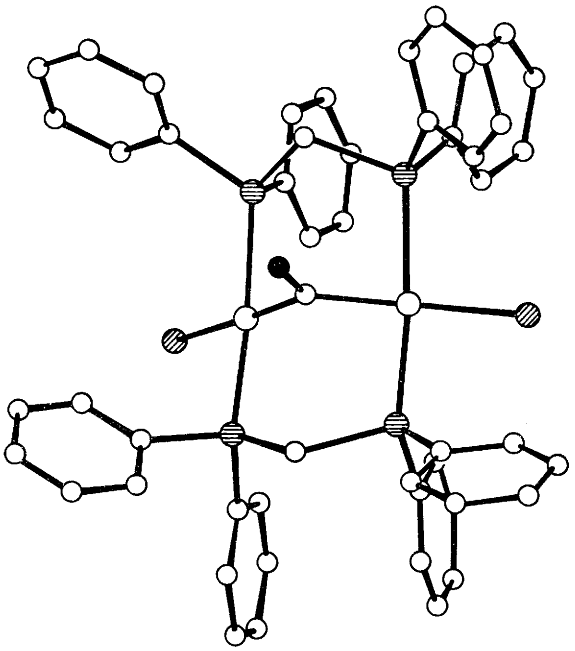

○,Pd; ⊜,As; ▨,Cl; ○,C; ●,O

FIGURE. The structure of $[\text{Pd(dam)Cl}]_2\text{CO}$.

The molecular structure is shown in the Figure. Each palladium atom has approximately square planar co-ordination with terminal chlorine atoms, two *trans* arsenic atoms from different dam groups, and the bridging carbonyl group common to both metal environments. The palladium distance [3·274(8) Å] is too long for a direct Pd–Pd bond {*cf.* $[\text{Pd(dppm)Br}]_2$ below}; since the compound is diamagnetic the spin-pairing of the metal atoms must occur *via* the carbonyl bridge. The carbonyl bridge is symmetrical within the experimental error [Pd–C, 1·84(5) and 1·95(6) Å] but the Pd–C–Pd angle is 119(3)° which is an extraordinary value since all other M–C–M angles at bridging carbonyls are < 88°.[3] The Pd–Cl [2·30(2) and 2·32(2) Å] and Pd–As [2·40—2·46(2) Å] appear normal and all distances and angles in the dam ligands are also normal. There is no twist about the Pd–Pd axis so that the Pd_2As_4 unit is planar. The solvent molecules occupy cylindrical holes along the screw axis parallel to the c-axis of the crystal. There appears to be gross random motion of these groups and their exact positions could not be determined, accounting for the limited nature of the observable diffraction data and the resultant somewhat high e.s.d.'s.

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† The atomic co-ordinates for this work 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.

The solvent included in the crystal was shown to be n-hexane by n.m.r. spectroscopy after dissolution of the crystals.

The crystal structure of $[Pd(dppm)Br]_2$ has already been reported;[4] the essential details are that there is a direct Pd–Pd bond of 2·699 Å which is rather long compared with other Pd^I complexes. In addition, there is a twist about the Pd–Pd bond effectively to decrease the bite of the dppm ligands. We saw this structure as a compromise between the conflicting requirements of strong metal–metal bonding and accommodation of the dppm ligands with minimum strain. Clearly, the larger bite of dam could not be accommodated in this way and this alternative structure is adopted. The structure is an exception to two well established dogmas of metal carbonyl chemistry, *viz*: (a) carbonyl bridges are always accompanied by metal–metal bonds[5] and (b) polymeric carbonyl halides invariably bridge through halogen and not through the carbonyl group.[6] In addition, the compound provides an unprecedented M–C–M angle of 120° and is the first dimeric Pd^I compound not to be directly metal–metal bonded.

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