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X-Ray Crystal and Molecular Structure of μ-Carbonylbis-μ-(bisdiphenylarsinomethane)dichlorodipalladium(I); an Alternative Interpretation

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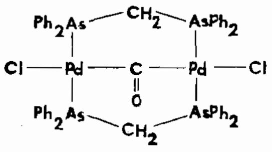
Colton *et al.* [1] have recently reported the X-ray crystal and molecular structure of the diamagnetic binuclear complex $[\{Pd(Ph_2AsCH_2AsPh_2)Cl\}_2CO]$, salient features of which include a non-bonding intramolecular Pd–Pd distance (3.274(8) Å), a Pd–C–Pd bond angle of 119° and a ν(CO) value of 1720 cm^{-1} – and have interpreted their data in terms of a binuclear carbonyl-bridged palladium(I) species.



The observed diamagnetic character was attributed to spin-pairing via the carbonyl bridge. These workers also noted that the structure is anomalous on several counts; the Pd–C–Pd bond angle is *ca.* 30 ° greater than those commonly found in bridging carbonyl structures, carbonyl halide complexes usually bridge through halide rather than carbonyl, and carbonyl bridges are always accompanied by metal–metal bonding interactions.

We suggest that the observed structure can be more realistically interpreted as an example of a dimetallated formaldehyde derivative, and that it involves a hitherto unrecognised keto bridge rather than a bridging carbonyl ligand. The revised formulation eliminates the inconsistencies referred to above. Thus the Pd–C–Pd bond angle (119°) and the value of ν(CO) are both fully consistent with the alternative keto structure, and the diamagnetism is entirely in keeping with the presence of square-planar coordinated palladium(II). Related complexes $[\{PdPh_2PCH_2PPh_2)X\}_2CO]$ and $[\{Pd(Ph_2PCH_2PPh_2)X\}_2CNR]$ (X = Cl, Br) are likewise best formulated as palladium(II) derivatives containing keto and ketimino bridges respectively [2].

We conclude from these observations that bridging CO ligands are capable of adopting *two distinct bonding modes;* one, commonly found in metal–metal bonded carbonyl structures, is characterised by a M–C–M bond angle of *ca.* 80–85° and a ν(CO) value of *ca.* 1850 cm^{-1} [3], whereas the other, found in the complexes under discussion, has a M–C–M bond angle of *ca.* 120° and a ν(CO) value of *ca.* 1700 cm^{-1}. The former situation is best discussed in terms of 3-centre molecular orbitals extending over the carbon and both metal atoms [3], analogous to the three-centre bonds in Al_2Me_6 or $(BeMe_2)_n$, in which the M–C–M angle is also anomalously small [4, 5]. The latter structure can be visualised in terms of two discrete metal–carbon σ-bonds, and is formally analogous to that found in organic ketones.

These models have previously been employed as alternatives to describe the bonding of bridging carbonyl ligands, with the multicentre approach now clearly preferred [3, 6]. However, the co-existence of the two forms as distinct bonding types applicable to metal–metal bonded and non metal–metal bonded bridging carbonyl situations respectively has not previously been recognised.

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