

**Problems in the Assignment of Bonding Mode of Bridging Carbonyl Groups from the Carbonyl Stretching Frequency: the Molecular Structure of Bis- $\mu$ -[bis(diphenylarsino)methane]- $\mu$ -carbonyl-bis-[chloroplatinum(II)]**

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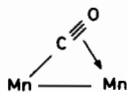
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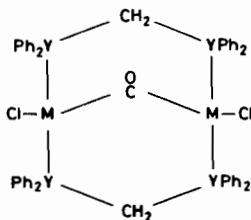
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The value of the carbonyl stretching frequency in metal compounds has long been used as a criterion of structure. Thus terminal carbonyls and bridging carbonyls typically absorb in the regions 1850–2125  $\text{cm}^{-1}$  and 1700–1850  $\text{cm}^{-1}$  respectively in neutral compounds [1]. Recently, the compound  $[\text{Mn}_2(\text{CO})_4(\mu\text{-CO})(\mu\text{-dppm})_2]$ , dppm = bis(diphenylphosphino)methane, was shown to have an unusually low  $\nu(\text{CO})$  at 1645  $\text{cm}^{-1}$  and this was shown to be due to the ( $\mu\text{-CO}$ ) group acting as a 4-electron ligand [2].



Another very low value for  $\nu(\text{CO})$  is found in  $[\text{Fe}_4(\text{CO})_{13}\text{H}]^-$ , which also contains a carbonyl acting as a 4-electron ligand [3].

Several compounds of structure (I) have recently been prepared and their carbonyl stretching frequencies are given below.



- Ia, M = Pd, Y = As,  $\nu(\text{CO})$  1720  $\text{cm}^{-1}$  [4]  
 Ib, M = Pt, Y = As,  $\nu(\text{CO})$  1635  $\text{cm}^{-1}$  [5, 6]  
 Ic, M = Pt, Y = P,  $\nu(\text{CO})$  1638  $\text{cm}^{-1}$  [5, 6]

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The low value of  $\nu(\text{CO})$  for Ia (similar to that found in ketones) has led to its being described as a metallo-ketone derivative [7], and a symmetric carbonyl bridge with a long Pd...Pd non-bonding distance has been confirmed by X-ray structural determination [4]. The even lower values of  $\nu(\text{CO})$  for (Ib) and (Ic) led to the prediction [5, 6] that these compounds have 4-electron bridging carbonyls, like those in  $[\text{Mn}_2(\text{CO})_4(\mu\text{-CO})(\mu\text{-dppm})_2]$  and  $[\text{Fe}(\text{CO})_{13}\text{H}]^-$ . This prediction is now shown to be incorrect by an X-ray structural determination on (Ib).

Crystals of (Ib) are tetragonal, space group  $P4_32_12$ , with four molecules in a unit cell of dimensions  $a = 15.157(4)$ ,  $c = 26.330(8)$  Å. The intensity data were measured with Mo- $K\alpha$  radiation on a CAD4 computer-controlled diffractometer. The structure was solved by the heavy atom method and refined to  $R = 0.068$  and  $R_w = 0.093$ , using some 1300 reflections with  $I \geq 3\sigma(I)$ .

The crystal structure of (Ib) is built of discrete binuclear molecules. The molecular structure, shown in Fig. 1, displays crystallographically imposed  $C_2$  symmetry, the diad axis coinciding with the C–O bond vector. A distorted square planar environment around each platinum atom is formed by chlorine, carbonyl-carbon and two mutually *trans* arsenic atoms. The Pt–As bond lengths are 2.400(5) and 2.397(5) Å.

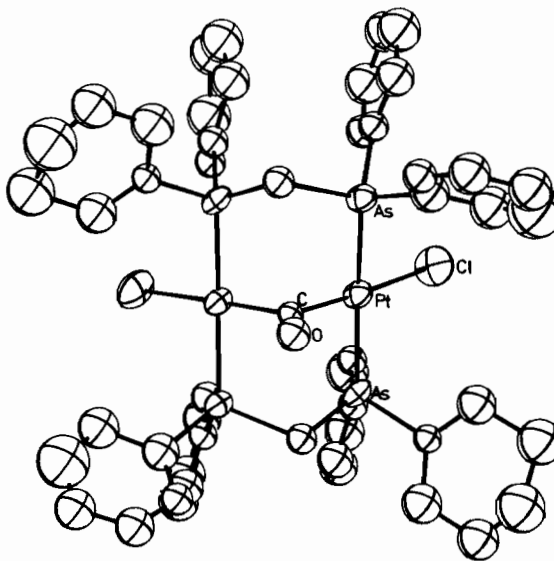


Fig. 1. A view of the molecular structure of  $[\{\text{PtCl}(\mu\text{-dpam})_2(\mu\text{-CO})\}]_2$ . Hydrogen atoms are omitted and unlabelled atoms are carbon.

The platinum atoms are bridged by the carbonyl group and two dpam ligands. The resulting Pt–Pt distance, of 3.162(4) Å, is too long to reflect signifi-

cant covalent metal-metal bonding. In  $[\{\text{PtCl}(\mu\text{-dppm})\}_2]$  [5] and  $[\{\text{Pt}(\mu\text{-dppm})\}_2\text{Cl}(\text{CO})]^+$  [8], where such bonding is thought to exist, the respective Pt-Pt distances are 2.652(2) and 2.620(1) Å. The latter two compounds contain linear Cl-Pt-Pt and Cl-Pt-Pt-CO units; in  $[\{\text{PtCl}(\mu\text{-dpam})\}_2(\mu\text{-CO})]$  however, the two Cl-Pt...Pt angles are 142°.

The most noteworthy structural feature is the geometry of the bridging carbonyl group. The  $\text{Pt}_2(\text{CO})$  fragment is planar and the Pt-C-Pt and Pt-C-O angles are 106(3) and 127(4)°, respectively. This suggests that the C atom may be regarded as being approximately  $\text{sp}^2$  hybridized and that it forms two  $\sigma$ -covalent (non-dative) bonds to the platinum atoms, which therefore should be considered as being in the formal oxidation state of two. Hence the compound may be formulated as a dimetallated ketone. Some support for this view comes from the Pt-C and Pt-Cl bond lengths (1.97(9) and 2.435(15) Å, respectively) which are comparable to those observed in linear  $\sigma\text{-C-Pt(II)-Cl}$  systems [9].

The overall molecular geometry is similar to that of the palladium analogue (Ia) in  $[\{\text{PdCl}(\mu\text{-dpam})\}_2(\mu\text{-CO})]\cdot 3\text{C}_6\text{H}_{14}$ , where the Pd-C-Pd and Pd-C-O angles are about 120° [4]. In complexes where CO bridges occur in conjunction with metal-metal bonding, the M-C-M angles are much smaller (less than 90°) [10]. The compounds (Ia) and (Ib), and probably also (Ic), for which a negligible Pt-Pt interaction has been predicted from n.m.r. studies [11], provide the only known examples of the carbonyl group bridging metal atoms which are not directly bonded to each other. Thus these compounds are exceptions to the generalization proposed by Cotton [12] that "bridging carbonyl groups never occur unless the bridged metal atoms are formally bonded to each other".

Since the structures of (Ia) and (Ib) are similar it is surprising that the values of  $\nu(\text{CO})$  are so different. We can offer no convincing explanation for this. Possibly back-bonding into the  $\pi^*$ -orbital of the carbonyl is sufficiently greater in (Ib) than in (Ia)

to account for the difference. The value of  $\nu(\text{CO})$  for (Ib) appears to be the lowest yet found for a  $\text{M}_2(\mu\text{-CO})$  bridge. Finally, these results show that it is not possible to distinguish between symmetrical 2-electron and unsymmetrical 4-electron CO bridging modes from  $\nu(\text{CO})$  frequencies.

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