

Bis- μ -[bis(diphenylphosphino)methane]-bis(chloro-platinum)(Pt-Pt): Its Molecular Structure and the Reversible Addition of Carbon Monoxide to the Pt-Pt Bond

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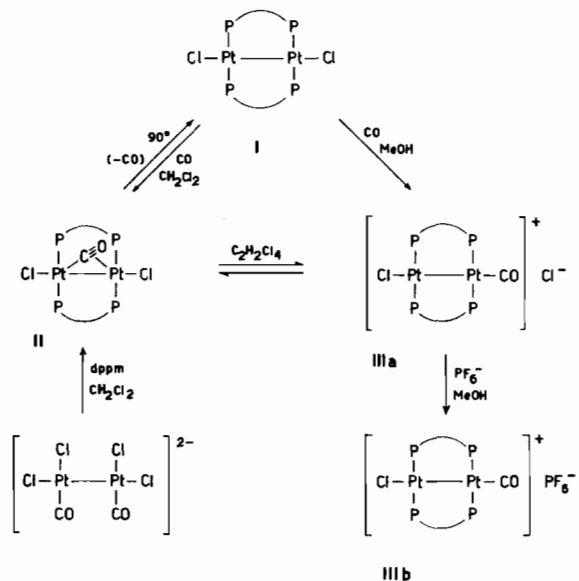
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The dimeric platinum(I) bis(diphenylphosphino)methane (dppm) complex $[\text{Pt}_2\text{Cl}_2(\text{dppm})_2]$ was originally assigned a chloride-bridged structure [1], but recent spectroscopic evidence strongly indicated the dppm-bridged structure (I) [2]. The latter struc-



Scheme. The $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm) bridging groups are denoted by P^-P .

ture is now proved correct by an X-ray crystal structure analysis. The compound was prepared in the way described earlier [2] and the crystals used in the structure analysis were obtained by slow evaporation of a solution in 1,2-dichloroethane-*n*-propanol at room temperature.

Crystals of $[\text{Pt}_2\text{Cl}_2(\text{dppm})_2]$ are monoclinic, space group $P2_1/c$, $a = 13.592$, $b = 16.577$, $c = 21.438$ Å, $\beta = 105.63^\circ$ ($\lambda = 0.71069$ Å), $Z = 4$, $D_c = 1.756$

g cm^{-3} . The intensities of X-ray reflexions were measured on a Hilger and Watts four-circle diffractometer, using Mo- $\text{K}\alpha$ radiation. Currently R is 0.086 for 4340 reflexions with $I > 3\sigma(I)$.

The crystal structure is built of discrete binuclear $[\text{Pt}_2\text{Cl}_2(\text{dppm})_2]$ molecules (Fig. 1). The platinum atoms are in square-planar environments, the angles between mutually *cis* platinum-ligand bonds ranging from $85.1(1)$ to $94.5(2)^\circ$. The metal co-ordination planes are twisted about the Pt-Pt bond vector, giving a dihedral angle of 38.5° . It therefore appears that the configuration of the molecule is determined predominantly by a tendency to minimise the anti-bonding interaction between filled interaxial metal d orbitals [3, 4].

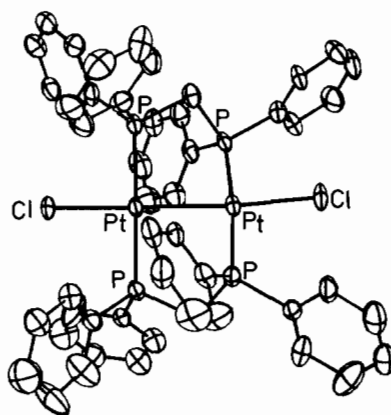


Fig. 1. A view of the molecular structure of $[\text{Pt}_2\text{Cl}_2(\text{dppm})_2]$. One carbon atom is obscured by a phenyl group, and hydrogen atoms are omitted for clarity.

The Pt-Pt bond length [2.652(2) Å] is practically the same as that [2.647(2) Å] found in the sulphide-bridged platinum(I) complex $[(\text{PPh}_3)_2\text{Pt}\cdot\text{S}\cdot\text{Pt}(\text{CO})(\text{PPh}_3)]$ [5], but is somewhat shorter than the recently reported Pd-Pd distance [2.699(5) Å] in the isomorphous and isostructural compound $[\text{Pd}_2\text{Br}_2(\text{dppm})_2]$ [6]. In the other few platinum(I) complexes examined crystallographically the Pt-Pt distances are 2.581-2.628(1) Å [7].

The Pt-P bond lengths [2.256(7)-2.290(7) Å] are in the range displayed by the Pd-P bond lengths [2.26(1)-2.32(1) Å] in $[\text{Pd}_2\text{Br}_2(\text{dppm})_2]$. The Pt-Cl distances [2.406(6) and 2.414(6) Å] are comparable with the Pt-Cl (*trans* to Pt) distances [2.382(10) and 2.426(9) Å] in the anionic platinum (I) complex $[\text{Pt}_2(\text{CO})_2\text{Cl}_4]^{2-}$, and may reflect a relatively high *trans*-influence of the Pt-Pt bond [4].

The above structure determination shows that the Pt-Pt bond of (I) is open to attack by small molecules, and we find that bubbling carbon monoxide through a solution of (I) in dichloromethane gives a

precipitate of the adduct $[\text{Pt}_2\text{Cl}_2(\text{dppm})_2(\text{CO})]$, (II), which can also be prepared by addition of dppm to the $[\text{Pt}_2\text{Cl}_4(\text{CO})_2]^{2-}$ anion (see the scheme). Heating (II) in the solid state to 90°C leads to loss of CO and (I) is obtained quantitatively, so that the CO addition is reversible. The CO stretching vibration of (II) is at 1638 cm^{-1} in the infrared spectrum. This indicates that the carbonyl is bridging between platinum atoms, and the remarkably low $\nu(\text{CO})$ further suggests the asymmetric bridging form



reported previously [8] only for $[\text{Mn}_2(\text{dppm})_2(\text{CO})_5]$. However, if this is the case, then rapid isomerization shown below must occur since the ^{31}P n.m.r. spectrum shows that all phosphorus atoms are effectively equivalent.



Further isomerization of (II) to the ionic terminal carbonyl complex (IIIa) occurs in solution. The complex (IIIa) is characterized by a typical terminal carbonyl stretching frequency of 2072 cm^{-1} . The equilibrium constant (II) \rightleftharpoons (IIIa) increases with solvent polarity and (IIIa) is the only species present in methanol solvent. The ionic nature of (IIIa) is confirmed by conversion to the more stable PF_6^- salt (IIIb) and the asymmetric nature of (III) is shown by analysis of the ^{31}P n.m.r. spectrum which is more complex than that of (I) and shows two distinct ^{31}P environments, corresponding to the phosphorus atoms adjacent to chloride or carbonyl respectively.

A complex $[\text{Pt}_2\text{Cl}_2(\text{dam})_2(\text{CO})]$ can be prepared by reaction of bis(diphenylarsino)methane (dam) with $[\text{Pt}_2\text{Cl}_4(\text{CO})_2]^{2-}$. The infrared spectrum shows $\nu(\text{CO})$ at 1635 cm^{-1} indicating a structure like that of

(II), but the arsine complex does not readily lose CO on heating nor does it isomerise readily to an ionic terminal carbonyl complex analogous to (III).

The easy reversible combination of carbon monoxide with (I) to give either a bridging or terminal carbonyl species, (II) or (III), makes this a useful model for the reversible adsorption of CO onto a metal surface where similar processes are thought to occur.

Acknowledgments

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