

A Diplatinum(0) Complex with Three Bridging dppm Ligands. The X-Ray Structure Analysis of $[\text{Pt}_2(\mu\text{-dppm})_3]\cdot 2\text{C}_6\text{H}_6$ (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$)

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X-Ray diffraction study of the title compound has shown that $[\text{Pt}_2(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_3]$ adopts a 'manxane'-type (bicyclo[3.3.3]undecane-type) structure, with trigonal planar co-ordination of the platinum atoms and approximate C_{3h} molecular symmetry.

Binuclear transition metal complexes stabilised by bridging bis(diphenylphosphino)methane (dppm) ligands are currently extensively studied, the interest being centred on their reactions with small molecules, relevance to catalytic processes, and diverse structural properties. Many well characterised $\text{M}_2(\mu\text{-dppm})_2$ - and $\text{MM}'(\mu\text{-dppm})_2$ -complexes are now known, particularly numerous being those of Rh, Pd, and Pt. They display a range of different structural types and adopt various modes of metal-metal interaction, including σ -covalent and donor-acceptor bonding.¹⁻³

We now describe the first crystallographic characterisation of a binuclear complex in which the metal centres are bridged by three dppm ligands. So far only two complexes of this type have been reported: $[\text{Pd}_2(\text{dppm})_3]$ has been characterised analytically⁴ and $[\text{Pt}_2(\text{dppm})_3]$ both analytically and by multinuclear n.m.r. spectroscopy.⁵

Red crystals of $[\text{Pt}_2(\text{dppm})_3]\cdot 2\text{C}_6\text{H}_6$ were obtained from a benzene-propanol solution.⁵

Crystal data: $\text{C}_{75}\text{H}_{66}\text{P}_6\text{Pt}_2\cdot 2(\text{C}_6\text{H}_6)$, $M = 1699.6$, monoclinic, space group $I2$, $a = 22.539(4)$, $b = 16.878(2)$, $c = 20.641(2)$ Å, $\beta = 109.82(1)^\circ$, $U = 7387$ Å³, $Z = 4$, $D_{\text{calc}} = 1.53$ g cm⁻³ (Mo- K_α X-rays, $\lambda = 0.71069$ Å). Intensities of 4968 unique reflections, with $I \geq 3\sigma(I)$ and $\theta(\text{Mo-}K_\alpha) < 25^\circ$, were measured on a CAD-4F diffractometer. The structure was solved by the heavy atom method and refined by block-diagonal least-squares to the current R value of 0.040 ($R' = 0.053$).[†]

In the molecular structure of $[\text{Pt}_2(\text{dppm})_3]$, shown in Figure 1, the metal centres are held in close proximity by three bridging dppm ligands. Each platinum atom forms a trigonal planar array with three phosphorus donors to which it is bonded, and the two PtP_3 planes are parallel to one another (dihedral angle 0.5°). All three dppm ligands show essentially the same conformation and the molecular structure approximates to C_{3h} symmetry, the three-fold axis coinciding with the Pt-Pt vector. Such molecular symmetry is compatible with the n.m.r. spectrum of the compound in solution.⁵

It is interesting to note that the distortions of the PtP_3 fragments from ideal trigonal planar geometry are closely similar to those observed in the mononuclear d¹⁰ complex $[\text{Pt}(\text{PPh}_3)_3]$.⁶ The Pt-P bond lengths, P-Pt-P bond angles, and displacements of the metal atoms from their local P_3 planes are, respectively, 2.232(4)–2.289(4) Å, 115.5(2)–122.9(2)°, and < 0.06 Å in $[\text{Pt}_2(\mu\text{-dppm})_3]$, and 2.25(1)–2.28(1) Å, 115–122°, and 0.1 Å in $[\text{Pt}(\text{PPh}_3)_3]$.

The Pt-Pt separation is relatively long [3.023(1) Å] and may be considered indicative of little, if any, bonding interaction. It lies outside the range of $\text{Pt}^0\text{-Pt}^0$ bonding distances

[†] The crystal structure contains molecules of $[\text{Pt}_2(\text{dppm})_3]$ and benzene separated by van der Waals distances.

The atomic co-ordinates for this structure are available 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.

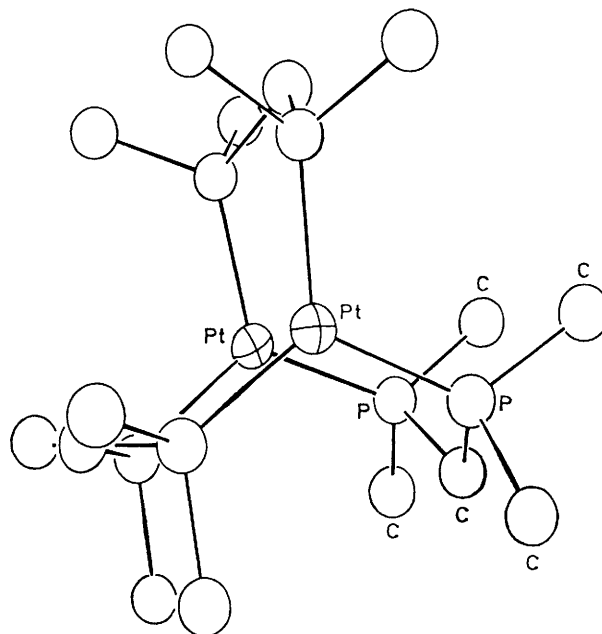
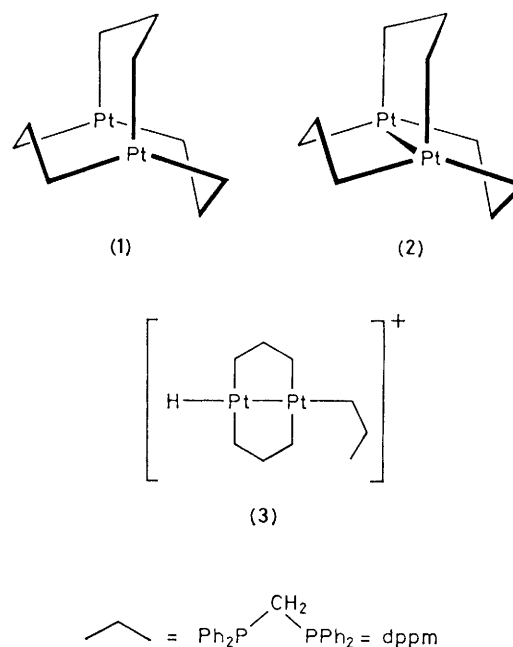


Figure 1. The molecular structure of $[\text{Pt}_2(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_3]$, with all but *ipso*-carbon atoms of the phenyl groups omitted for clarity.

usually found in clusters [2.61—2.79 Å].^{3,7,8} Furthermore, it is 0.26 Å longer than the distended Pt—Pt single bond [2.765(1) Å] in the d¹⁰–d¹⁰ dimer [Pt₂(Bu₂P[CH₂]₃PBu₂)₂], where a closer approach of the metal atoms is thought to be precluded by steric interactions of the two ligands.⁷

In view of the observed molecular geometry, [Pt₂(μ-dppm)₃] can be formulated as a 'manxane'-type⁹ complex (**1**), in which each platinum atom attains a 16-electron configuration; a propellane-like structure (**2**), suggested previously,⁵ would require the presence of a fully developed Pt–Pt bond.

In analogy with the chemistry of [Pt(PPh₃)₃], [Pt₂(μ-dppm)₃] reacts with a range of small molecules and can be easily protonated to yield [Pt₂H(η¹-dppm)(μ-dppm)₂]⁺ (**3**).^{5,10,11} It is now apparent that this oxidative-addition reaction occurs with breaking of a Pt–P bond in the parent compound and formation of a Pt¹–Pt¹ bond [2.769(1) Å]¹¹ in the product.

Crystallographic characterisation of [Pt₂(μ-dppm)₃] may be potentially useful in elucidation of the mechanisms of some environmentally important reactions. In 1978 Vaska and coworkers¹² described catalytic reductions of O₂ and NO by CO in the presence of a 'novel Pt⁰' dimer [Pt₂(dppm)₃], for which neither synthesis nor characterisation was reported. The red colour of their 'initial catalyst' in toluene solutions¹² and in the solid state¹³ may suggest, in the absence of further evidence, that it is the same compound as that obtained by Brown and coworkers⁵ and used in the diffraction study presented here.

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