Synthesis and Characterisation of $[Pt_2Me_3(Ph_2PCH_2PPh_2)_2][PF_6]$, a Binuclear Platinum(II) Methyl Complex of Novel Structure

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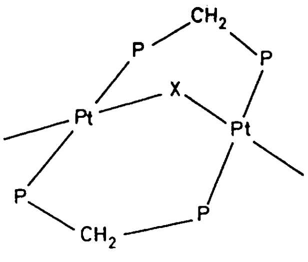
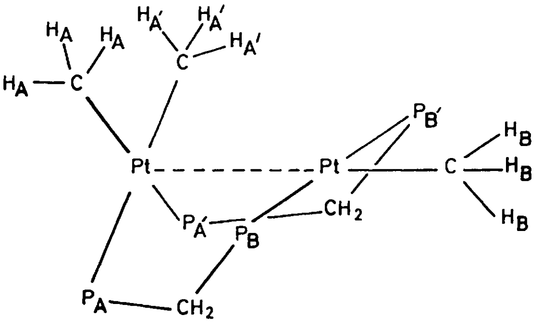
Summary The preparation and characterisation of $[Pt_2Me_3(dppm)_2]^+$, which has a unique structure involving a previously unpostulated conformation for a dppm bridged binuclear complex, are reported [dppm = bis(diphenylphosphino)methane].

The binuclear platinum(II) hydride $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$ [dppm = bis(diphenylphosphino)methane][1] has, like the related complexes $[Pt_2Cl_2(\mu\text{-}X)(\mu\text{-}dppm)_2]$[2–5] (X = S, CO, SO_2, and CH_2), an 'A-frame' structure,[6] (**1**), and thus possesses an electron-deficient Pt_2H bridge. We were interested in preparing the analogous trimethyl derivative to see if a similar electron-deficient Pt_2Me bridge would be formed. We report here the successful synthesis of the complex $[Pt_2Me_3(dppm)_2]^+$ (**2**), and show that this complex has a unique structure of a type not described by Benner and Balch[7] in their consideration of the structural types of dppm-bridged binuclear complexes. The structure adopted by this complex would indicate that Me is a poor bridging group for platinum, and that complexes containing a bridging Pt_2Me unit will be very difficult to synthesise.



(1)



(2)

Treatment of a mixture of *cis*-[PtMe$_2$(dppm)][8,9] and *cis*-[PtCl$_2$(dppm)] (3 : 1 molar ratio) in boiling methanol or propanone with KPF$_6$ readily gives yellow air-stable crystals of [Pt$_2$Me$_3$(dppm)$_2$][PF$_6$] (**2a**) (69% yield). Alternatively, the reaction of *cis*-[PtMe$_2$(dppm)] with perchloric acid (0·5 mol. equiv.) in cold propanone gives [Pt$_2$Me$_3$(dppm)$_2$][ClO$_4$] (**2b**) and methane (0·46 mol. equiv.). Compound (**2b**) is obtained in good yield, but is difficult to crystallise; (**2a**), however, may be readily recrystallised from dichloromethane or propanone, and gives satisfactory microanalysis. Its solutions decompose evolving methane and ethane, slowly in the dark and more rapidly in light. Although it has not yet been possible to obtain crystals suitable for an *X*-ray structural determination, the main structural features of (**2**) in solution have been deduced by a detailed study of its ^{1}H and ^{31}P n.m.r. spectra.†

Complete analysis of the complex ^{31}P{^{1}H} n.m.r. spectrum (40·5 MHz; CD$_3$COCD$_3$) of (**2**) gives the following data: $\delta(\mathrm{P_A})$, 27·13; $\delta(\mathrm{P_B})$, 23·66 p.p.m. [downfield from (MeO)$_3$PO]: $^{1}J(\mathrm{Pt_A{-}P_A})$, 1459; $^{1}J(\mathrm{Pt_B{-}P_B})$, 3009; $^{2}J(\mathrm{Pt_A{-}P_B})$, −15; $^{2}J(\mathrm{Pt_B{-}P_A})$, −15; $J(\mathrm{P_A{-}P_B})$, 45; $J(\mathrm{P_A{-}P_{B'}})$, 42; $^{1}J(\mathrm{Pt_A{-}Pt_B})$, 332 Hz [*n.b.* it was necessary to assume values of $^{2}J(\mathrm{P_A{-}P_{A'}}) = 50$ and $^{2}J(\mathrm{P_B{-}P_{B'}}) = 500$ Hz in the simulation]. This spectrum unambiguously establishes the bridging nature of both dppm groups, and reveals the presence of two pairs of equivalent phosphorus atoms. Moreover, the values of $^{1}J(\mathrm{Pt_A{-}P_A})$ and $^{2}J(\mathrm{P_A{-}P_{A'}})$ indicate[10] that P$_\mathrm{A}$ and P$_\mathrm{A'}$ are *cis* to one another, whilst the values of $^{1}J(\mathrm{Pt_B{-}P_B})$ and $^{2}J(\mathrm{P_B{-}P_{B'}})$ indicate[10] that P$_\mathrm{B}$ and P$_\mathrm{B'}$ are mutually *trans*. The value of $^{1}J(\mathrm{Pt_A{-}Pt_B})$ unfortunately allows little to be deduced about the nature of the Pt-Pt interaction,[11] but presumably indicates that the platinum atoms are in close proximity to one another.

The ^{1}H n.m.r. spectra (60, 100, and 200 MHz; CD$_2$Cl$_2$) of (**2a**) show, in addition to the resonances of the phenyl and P–CH$_2$–P groups (the latter centred at δ *ca.* 3·86), two overlapping resonances due to the methyl groups directly bonded to platinum. These are now considered separately.

(i) A terminal methyl resonance [$\delta(\mathrm{H_A})$ 0·85], of relative intensity 2 is coupled strongly to one Pt atom (Pt$_\mathrm{A}$), giving a 1 : 4 : 1 pattern [$^{2}J(\mathrm{Pt_A{-}H_A})$ 60 Hz], and shows fine structure due to ^{31}P coupling, similar in form and magnitude to that observed for *cis*-[PtMe$_2$(dppm)].[8] This latter coupling is second-order, confirming that the P$_2$PtMe$_2$ configuration around Pt$_\mathrm{A}$ is *cis*.

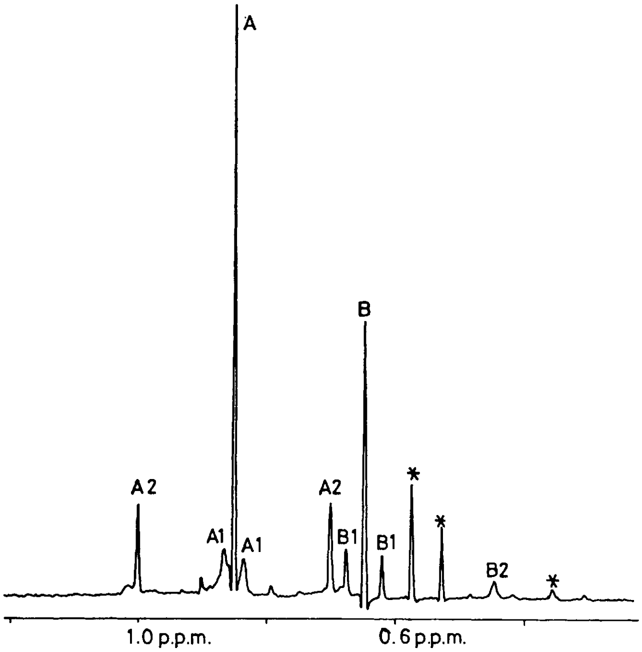


FIGURE. The ^{1}H{^{31}P} resolution-enhanced n.m.r. spectrum (200 MHz) of [Pt$_2$Me$_3$(dppm)$_2$]$^{+}$ in the Pt–Me region, showing the H$_\mathrm{A}$ (A) and H$_\mathrm{B}$ (B) resonances and their inner (1) and outer (2) ^{195}Pt satellites. Impurity peaks are denoted by asterisks. The low field (B2) peak is obscured by the main (A) peak at 200 MHz.

(ii) A terminal methyl resonance [$\delta(\mathrm{H_B})$ 0·65], of relative intensity 1 is coupled strongly to one Pt atom (Pt$_\mathrm{B}$), giving a 1 : 4 : 1 pattern [$^{2}J(\mathrm{Pt_B{-}H_B})$ 80·5 Hz], and to two equivalent P atoms [$^{3}J(\mathrm{P_B{-}H_B})$ 6·5 Hz]. These values are similar to those found in *trans*-[Pt(Me)Cl(PMe$_2$Ph)$_2$] and related complexes,[12] confirming the mutually *trans* configuration of P$_\mathrm{B}$ and P$_\mathrm{B'}$ deduced from the ^{31}P n.m.r. data. Moreover, additional coupling is superimposed on this latter 1 : 2 : 1 multiplet, and separate ^{195}Pt and ^{31}P decoupling experiments prove that it is due to long-range ^{195}Pt coupling [$^{3}J(\mathrm{Pt_A{-}H_B})$ 11 Hz]. The ^{1}H{^{31}P} spectrum in this region is shown in the Figure. The possibility of weaker long-range Pt$_\mathrm{B}$–H$_\mathrm{A}$ coupling (6 Hz) is also indicated, but is less convincing.

The above evidence strongly substantiates the structure proposed for (**2**), in which the co-ordination plane of Pt$_\mathrm{A}$ is approximately perpendicular to the Pt$_\mathrm{A}$–Pt$_\mathrm{B}$–Me$_\mathrm{B}$ axis.

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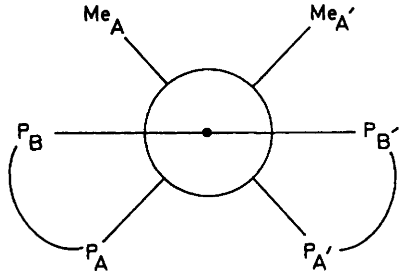
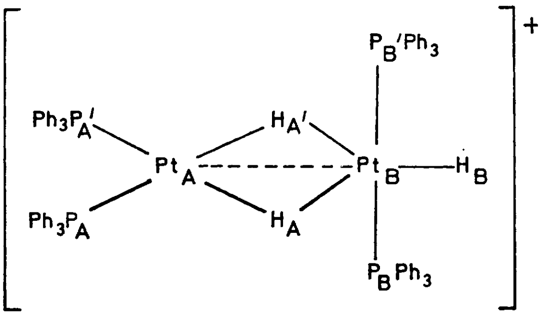
† *Added in proof*: Following the submission of this communication the crystal structure of the complex [Rh(CO)RhCl$_2${(PhO)$_2$PN(Et)P(OPh)$_2$}$_2$].CHCl$_3$ has been reported: R. J. Haines, E. Meintjies, and M. Laing, *Inorg. Chim. Acta*, 1979, **36**, L403. This complex possesses a structure essentially similar to that postulated for (**2**).



(2) Viewed from Me$_B$



(3)

Viewed from Me$_B$, along this axis, the structure is symmetrical. It is interesting to speculate as to whether the Pt$_A$–Pt$_B$ interaction may be regarded as a donor–acceptor bond. It is also interesting to compare the proposed structure for (**2**) with that for $[Pt_2H_3(Ph_3P)_4]^+$ (**3**).[13] If H$_A$ and H$_{A'}$ were not capable of bonding to Pt$_B$ [*i.e.* if the H$_A$–Pt$_B$ and H$_{A'}$–Pt$_B$ bonds were broken in (**3**)], then the structures of (**2**) and (**3**) can be seen to be basically rather similar: rotation of the co-ordination plane of Pt$_A$ by 90° interconverts the basic structural features. The steric requirements of dppm make structure (**3**) impossible for (**2**).

In conclusion, it may be noted that although the work of James *et al.*[14] has indicated that considerable caution must be exercised in assigning the structure of complexes containing ditertiary phosphines from n.m.r. data, the wealth of both ^{1}H and ^{31}P n.m.r. parameters in the case of (**2**) is such as to give confidence in the structural features as deduced above.

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