

Oxidative Addition and Reductive Elimination Reactions of Hydridodiplatinum Complexes: Preparation, Properties, and X-Ray and Molecular Structure of Bis{ μ -[bis(diphenylphosphino)methane]-*P,P'*}-*f*-[bis(diphenylphosphino)methane]-*P*}- α -hydridodiplatinum(*Pt-Pt*) Hexafluorophosphate, $[\text{Pt}_2\text{H}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2][\text{PF}_6]$

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Summary The reaction of $[\text{Pt}_2\text{H}_2(\mu\text{-H})(\mu\text{-dppm})_2][\text{PF}_6]$ [dppm = bis(diphenylphosphino)methane] with dppm proceeds by reductive elimination of H_2 to give $[\text{Pt}_2\text{H}(\text{dppm})(\mu\text{-dppm})_2][\text{PF}_6]$, which has been shown by single-

crystal X-ray crystallography to contain both bridging and terminal dppm ligands and a Pt-Pt bond [2.770(2) Å] and which undergoes reversible oxidative addition of RSH (R = Me or PhCH₂) at the platinum(I) centres.

ALTHOUGH a number of novel binuclear platinum(II) hydrides¹ have recently been reported, there are no examples of binuclear platinum(I) hydrides in the literature. Other types of binuclear platinum(I) complexes are, however, known, for example $[\text{Pt}_2\text{Cl}_2(\mu\text{-dppm})_2]$ (**1**)^{2,3} [dppm = bis(diphenylphosphino)methane], $[\text{Pt}_2\text{Cl}(\text{CO})(\mu\text{-dppm})_2]^+$ (**2**)^{4,5} $[\text{Pt}_2\text{L}_2(\mu\text{-dppm})_2]^{2+6,7}$ [L = PR_3 , CO, or pyridine], and $[\text{Pt}_2\text{Cl}_4(\text{CO})_2]^{2-}$,⁸ which contain direct platinum-platinum bonds. We now report that the binuclear platinum(II) hydride $[\text{Pt}_2\text{H}_2(\mu\text{-H})(\mu\text{-dppm})_2][\text{PF}_6^-]$ (**3**)^{1a} reacts rapidly (in dichloromethane at 20 °C) with dppm (1:1 mole ratio), affording dihydrogen (1.0 mol) and a quantitative yield of a new hydride formulated, on the basis of elemental analysis and the stoichiometry of the reaction, as $[\text{Pt}_2\text{H}(\text{dppm})_3][\text{PF}_6^-]$ (**4**). Crystals of (**4**) suitable for an X-ray diffraction study were obtained from 1,2-dichloroethane-propan-1-ol (*ca.* 1:1 by volume).

Crystal data: (**4**), monoclinic, space group $P2_1/n$, $a = 13.702(2)$, $b = 14.255(2)$, $c = 39.556(6)$ Å, $\beta = 94.75(1)^\circ$, $Z = 4$. The intensities of X-ray reflections were measured on a CAD-4F diffractometer with Mo- K_α radiation. The structure was solved by the heavy-atom method and has been currently refined to $R = 0.072$, using 6049 reflections for which $I \geq 3\sigma(I)$.[†] The positions of hydrogen atoms have not been determined.

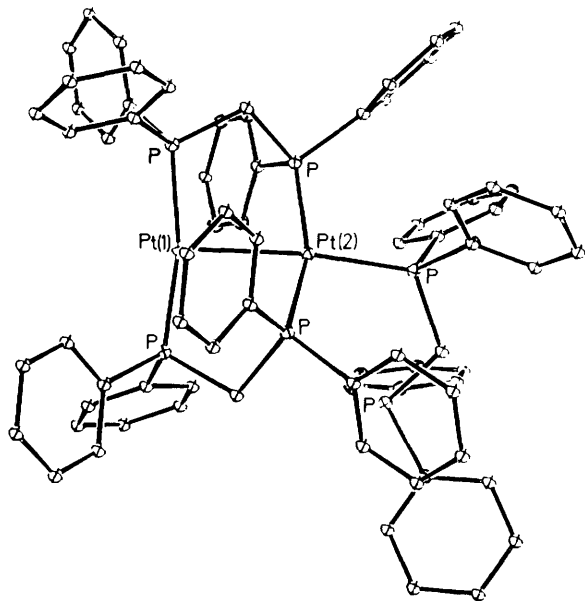
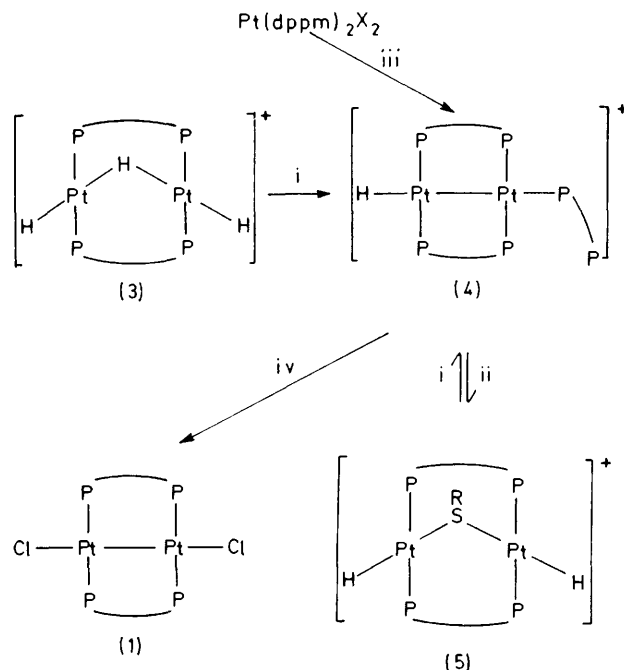


FIGURE. A view of the $[\text{Pt}_2\text{H}(\text{dppm})(\mu\text{-dppm})]^+$ ion. For clarity, all atoms are represented by thermal ellipsoids of arbitrary size.

The structure of the cation, shown in the Figure, is closely similar to those of (**1**)³ and (**2**).⁵ Its most interesting feature is that it displays two different modes of co-ordination of the dppm ligands. Two of these are bidentate, and they bridge the Pt-Pt bond to form a $\text{Pt}_2(\mu\text{-dppm})_2$ unit. The third ligand, however, is bonded to one metal

centre only, thus completing a considerably distorted square-planar environment around the Pt(2) atom. The geometry around Pt(1) is T-shaped, indicating a square-planar co-ordination with the 'vacant' site occupied by the hydrido ligand. Further support for this interpretation comes from the Pt-Pt distance of 2.770(2) Å, which is considerably longer than those of 2.651(1) and 2.620(1) Å found in (**1**) and (**2**), respectively. The weakening of the Pt-Pt bond in (**4**) is compatible with the high *trans*-influencing ability of the hydrido ligand. Thus the observation of a $\nu(\text{Pt-H})$ characteristic of a terminal hydrido ligand (*vide infra*) can now be readily understood. The Pt-P (*trans* to P) distances [2.248(9)—2.280(8) Å] are comparable with those observed in (**1**) and (**2**) [2.250(7)—2.308(5) Å]. The Pt-P (*trans* to Pt) distance [2.347(8) Å] is substantially longer, and may reflect the *trans*-influence of the Pt-Pt bond, and perhaps also the steric crowding around the Pt(2) atom.

Complex (**4**) is a pale yellow, air-stable solid. When recrystallised from propanone or 1,2-dichloroethane-propan-1-ol, it shows $\nu(\text{Pt-H})$ at *ca.* 2010 cm^{-1} in its i.r. spectrum; when recrystallised from dichloromethane or 1,2-dichloroethane, this band occurs at *ca.* 2040 cm^{-1} . Similar solvent-dependent behaviour for $\nu(\text{Pt-H})$ has been observed for (**3**).^{1a} ^1H and ^{31}P n.m.r. studies of complex (**4**) in solution indicate that it is fluxional upon the n.m.r. time scale and a detailed study of this dynamic behaviour is currently being undertaken. Complex (**4**) has also been prepared by the reduction of $\text{Pt}(\text{dppm})_2\text{X}_2$ (X = Cl, Br, I, or PF_6) by NaBH_4 in methanol (Scheme) and some of the reactions



SCHEME. $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm) groups are denoted by P—P; R = Me or PhCH_2 ; X = Cl, Br, I, or PF_6 . i, dppm; ii, RSH; iii, $\text{NaBH}_4\text{-MeOH}$ and PF_6^- ; iv, $\text{Pt}(\text{cod})\text{Cl}_2$ (cod = cyclo-octa-1,5-diene).

[†] The atomic co-ordinates for this work are available on request 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.

of (4) are also summarised. Complex (5; R = Me) has previously been characterized.^{6,9}

Binuclear complexes are of interest as models for catalysis and their oxidative addition and reductive elimination reactions are of significance in this respect. The formation of (4) by the dppm-induced elimination of H₂ from (3) and by a similar, but reversible, elimination of RSH from (5) are two novel examples of such reactions. Reductive elimination of H₂ or RSH normally proceeds (in mononuclear complexes) *via* an oxidation state change of two units but these reactions show that these molecules may be eliminated from platinum atoms undergoing an oxidation state change of only one unit when the complex is binuclear.

Our continuing studies indicate that (3) undergoes similar reactions with other two-electron donors (*e.g.* CO, PMe₂Ph, and PPh₃) and the possible relationship between (4) and [Pt₂(dppm)₃],¹⁰ is also being investigated in view of the reported catalytic activity of the latter.

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