Some Binuclear Hydrides of Platinum

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Reaction of $[PtCl_2(dppm)]$ (dppm = $Ph_2PCH_2PPh_2$) with $Na[BH_4]$ gives the binuclear cation $[Pt_2H_2(\mu\text{-}H)\text{-}(\mu\text{-}dppm)_2]^+$ isolated both as its chloride and hexafluorophosphate salts. Reaction of this complex cation with CCl_4 or hydrogen chloride affords the related $[Pt_2(\mu\text{-}Cl)H_2(\mu\text{-}dppm)_2]^+$ and $[Pt_2Cl_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$. The latter cation is also formed by protonation of the Pt–Pt bond in the platinum(I) complex $[Pt_2Cl_2(\mu\text{-}dppm)_2]$. The ^1H and ^{31}P n.m.r. spectra of these complexes are reported. Study of the hydride resonances is shown to be an excellent method of distinguishing between terminal and bridging hydride. The Pt–Cl and Pt–H vibrational bands are in agreement with the proposed structures of these complexes, but vibrational bands due to bridging hydride groups could not be observed.

REDUCTION of $[PtCl_2(dppm)]$ [dppm = bis(diphenylphosphino)methane] with sodium tetrahydroborate followed by treatment with hydrochloric acid in boiling benzene was previously shown to give the platinum(I) complex $[Pt_2Cl_2(\mu\text{-}dppm)_2]$ (1).[1,2] Complex (1) was characterized by detailed spectroscopic studies and the proposed structure was more recently confirmed by an X-ray structure determination.[3] A hydridoplatinum complex was obtained as an intermediate in the synthesis of (1). This hydride has now been characterized as (2a), a binuclear electron-deficient complex containing both terminal and bridging hydrido-groups, and details of this complex and of some other related hydridoplatinum complexes are now reported. A preliminary account of this work has already been published.[4]

RESULTS AND DISCUSSION

Preparation of the Complexes.—The preparative routes to the hydridoplatinum complexes are outlined in the Scheme. Analytical data and melting points are given in Table 1.

The trihydridodiplatinum complex (2a) may be prepared by reaction of either $[PtCl_2(dppm)]$ or (1) with $Na[BH_4]$ in methanol. The unsolvated complex (2a) is obtained on recrystallization from dichloromethane–isooctane, but, from methanol, a solvate containing both

methanol and water of crystallization is formed. Complex (2a) is readily converted into the hexafluorophosphate salt (2b) by reaction with $[NH_4][PF_6]$ in methanol.

Complex (2b) reacts with carbon tetrachloride in chlorinated solvents to give first the chlorodihydridodiplatinum complex (3b) and then the dichlorohydridodiplatinum complex (4b). Complex (3b) is prepared more readily by reaction of (2b) in dichloromethane solution with concentrated hydrochloric acid. In this reaction a gas, presumably hydrogen, is evolved. Complex (2a) undergoes similar reactions with CCl_4 as shown in the Scheme. The products (3a) and (4a) have been characterized by their n.m.r. spectra but have not been isolated since they are considerably less stable than the corresponding hexafluorophosphate salts. The rate of reaction of (2a) or (2b) with carbon tetrachloride is not reproducible, suggesting that the rate may be affected by impurities in the solvents or reagents, or possibly that a free-radical mechanism operates. When using such reactions preparatively it is therefore necessary to monitor the course of the reactions by periodically recording n.m.r. or i.r. (solution) spectra.

Complex (4a) is also formed by reaction of (1) with HCl, a reaction which involves protonation of the Pt–Pt bond of (1). This reaction is reversible and (4a) in

[1] M. P. Brown, R. J. Puddephatt, and M. Rashidi, *Inorg. Chim. Acta*, 1976, **19**, L33.

[2] M. P. Brown, R. J. Puddephatt, M. Rashidi, and K. R. Seddon, *J.C.S. Dalton*, 1977, 951.

[3] M. P. Brown, R. J. Puddephatt, M. Rashidi, Lj. Manojlović-Muir, K. W. Muir, T. Solomun, and K. R. Seddon, *Inorg. Chim. Acta*, 1977, L33.

[4] M. P. Brown, R. J. Puddephatt, M. Rashidi, and K. R. Seddon, *Inorg. Chim. Acta*, 1977, L27.

dichloromethane decomposes to (1) and hydrogen chloride. The hexafluorophosphate salt (4b) is, however, very much more stable in solution.

The hydridoplatinum complexes (2a), (2b), (3b), and (4b) are stable at room temperature in the solid state.

tetrachloroethane, but are only sparingly soluble in other common organic solvents.

Characterization of Complexes (2)—(4) *by N.M.R. Spectroscopy.*—The chief problems in characterization are in establishing whether the dppm ligands are
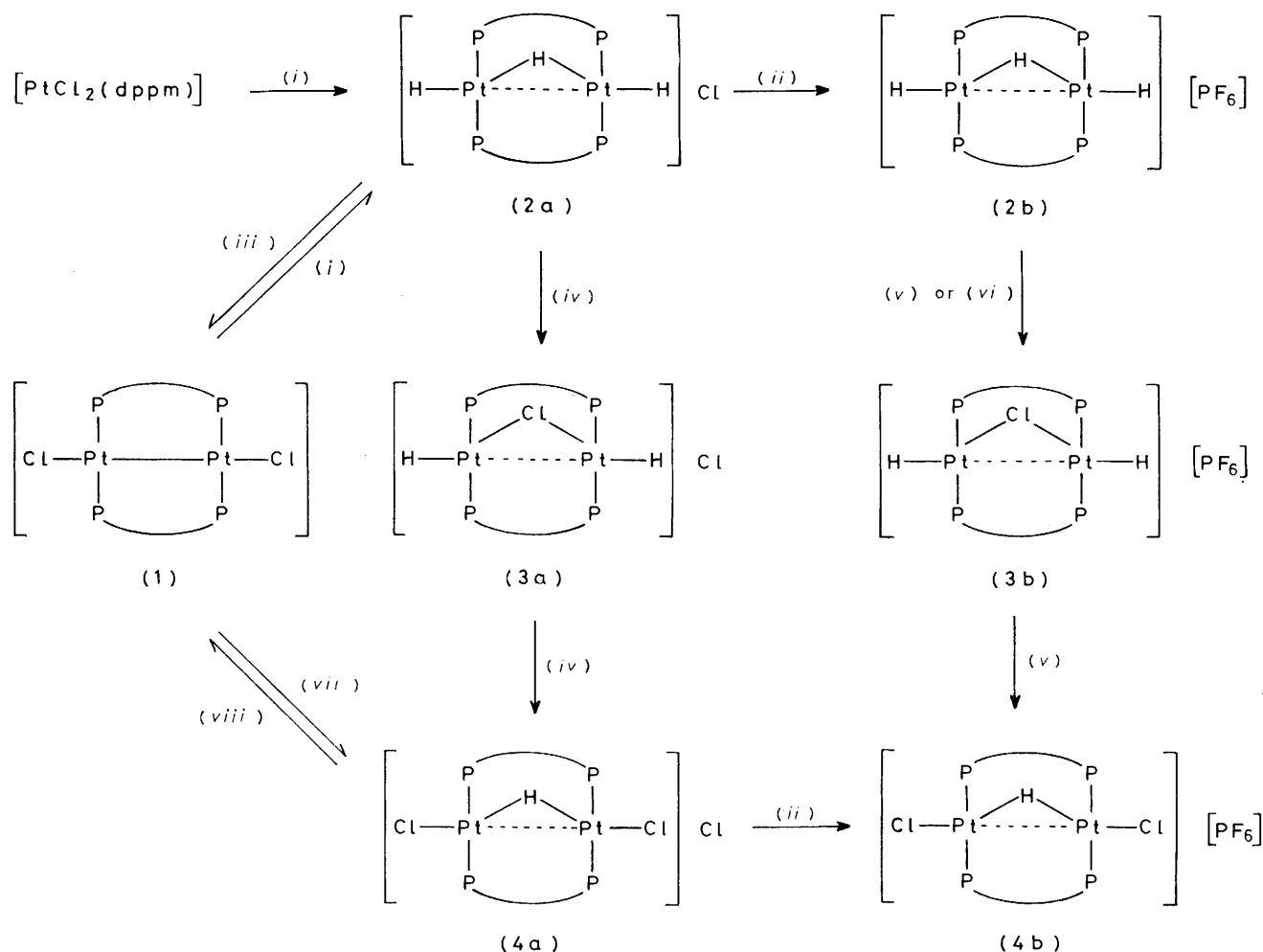
Scheme   Bridging $Ph_2PCH_2PPh_2$ (dppm) groups are denoted by P–P.   (*i*) $Na[BH_4]$–MeOH;   (*ii*) $[PF_6]^-$—MeOH;   (*iii*) $HCl–C_6H_6$, 80 °C;   (*iv*) $CCl_4–C_2D_2Cl_4$, 65 °C;   (*v*) $CCl_4–CHCl_3$ or $C_2D_2Cl_4$, 65 °C;   (*vi*) $HCl–CH_2Cl_2$, 20 °C;   (*vii*) $HCl–CHCl_3$;   (*viii*) CH_2Cl_2, –HCl

TABLE 1

Analytical data and melting points of the hydridoplatinum complexes

	Complex	M.p. $(\theta_c/°C)$ [a]	Analysis (%) [b]			
			C	H	Cl	F
(2a)	$[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]Cl$	210—214	50.1 (50.2)	4.0 (4.0)	3.3 (3.0)	
	$[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]Cl\cdot2MeOH\cdot2H_2O$	209—213	48.0 (48.4)	4.2 (4.4)	2.6 (2.8)	
(2b)	$[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2][PF_6]$	180—185	46.0 (45.9)	3.7 (3.6)		9.0 (8.7)
(3b)	$[Pt_2(\mu\text{-Cl})H_2(\mu\text{-dppm})_2][PF_6]$	148—154	44.6 (44.8)	3.6 (3.5)	2.9 (2.6)	8.3 (8.5)
(4b)	$[Pt_2Cl_2(\mu\text{-H})(\mu\text{-dppm})_2][PF_6]$	158—163	43.6 (43.6)	3.3 (3.3)	5.4 (5.2)	8.3 (8.3)

[a] All the complexes decomposed on melting.   [b] Calculated values are given in parentheses.

Most if not all of these hydrides appear to be photolyzed in daylight however. For example, colourless crystals of (2a) or (2b) rapidly become yellow in sunlight. The complexes are all soluble in the chlorinated solvents chloroform, dichloromethane, and particularly 1,1,2,2-

chelating to a single platinum atom or bridging between two platinum atoms, and whether the hydride ligands are terminal or bridging. The ¹H and ³¹P n.m.r. spectra are valuable in investigating both problems, and the relevant data are presented in Tables 2 and 3.

Criteria for distinguishing between chelating and bridging dppm ligands in platinum complexes have been discussed previously.[1,2] In the ^{1}H n.m.r. spectra the resonance due to the CH_2 protons of the dppm ligand is expected to give (approximately) a $1:4:1$ triplet for chelating dppm and a $1:8:18:8:1$ quintet for bridging dppm, due to coupling to ^{195}Pt ($I = \frac{1}{2}$, natural abundance 34%). The latter pattern (less the weak outer lines arising from molecules containing two ^{195}Pt atoms and which were usually not resolved) is observed in the region of the low-field ^{195}Pt satellites. The centre of the multiplet in each case is $\frac{1}{2}[^1J(PtP)]$ to low field of the centre of the overall ^{31}P n.m.r. spectrum, while the asterisked peak is due to the [AA'A''A'''XX'] spin system and is therefore $\frac{1}{2}[^1J(PtP) + {}^2J(PtP)]$ to low field of the centre of the ^{31}P spectrum. It is readily seen, therefore, that: in (2b), $^2J(PtP)$ is positive; in (3b), $^2J(PtP)$ is approximately zero; and in (4b), $^2J(PtP)$ is negative. For comparison, the value of $^2J(PtP)$ for (1) was -136 Hz.[2]

	CH$_2$ Groups		Terminal PtH				Bridging PtH	
Complex	$\delta(CH_2)$ p.p.m.	$^3J(PtCH_2)$ Hz	$\delta(H)$ p.p.m.	$^1J(PtH)$ Hz	$^2J(PtH)$ Hz	J' [b] Hz	$\delta(H)$ p.p.m.	$^1J(PtH)$ Hz
(2a)	4.70 [c]	34.8	−6.76	1 162	116		−5.85	540
(2b)	4.63	34.2	−6.86	1 138	103	1 260 (1 241)	−5.86	540
(3a)			−12.35 [d]	1 174	268	1 438 (1 442)		
(3b)	4.37	38.4	−12.00	1 174	305	1 476 (1 479)		
(4b)	4.32 [e]	45.0					−16.60 [f]	810

[a] Solvent $C_2D_2Cl_4$. [b] $J' = {}^1J(PtH) + {}^2J(PtH)$. Calculated values are given in parentheses. [c] $^2J(PH)$ 4.2 Hz at 65 °C. [d] $^2J(PH) + {}^3J(PH)$ 11.7 Hz. [e] $^2J(PH)$ 3.9 Hz, solvent CD_2Cl_2. [f] Quintet, $^2J(PH)$ 7.5 Hz.

Complex	$\delta(P)$ p.p.m.	$^1J(PtP)$ Hz	$^2J(PtP)$ Hz	$^3J(PP)$ [b] Hz	$^3J(PP)$ [b] Hz	N' [c] Hz
(2a)	18.04	2 769	16.6	56.0	18.2	2 785 (2 785)
(2b)	17.89	2 770	16.3	56.4	18.4	2 787 (2 786)
(3a)	13.24	2 665	6.8 [d]	52.9	15.5	2 672
(3b)	12.89	2 605	0 [d]	54.6	16.8	2 605
(4b)	6.60 [e]	2 317	−40.4	52.0	21.2	2 277 (2 276)

[a] In $C_2H_2Cl_4$ with trimethyl phosphate as reference. [b] $J(AA')$ and $J(AA''')$ of the AA'A''A'''X spin system. [c] $N' = {}^1J(PtP) + {}^2J(PtP)$; calculated values are given in parentheses. [d] Calculated from N' and $^1J(PtP)$; too small to measure directly. [e] Solvent CD_2Cl_2.

for all the hydrido-complexes, thus confirming that bridging dppm ligands are present.

The general form of the ^{31}P n.m.r. spectra of the hydrides is very similar to that previously reported for $[Pt_2Cl_2(\mu\text{-dppm})_2]$ (1), and, using the same arguments presented then, this supports the presence of the Pt_2-(μ-dppm)$_2$ unit in the hydrido-complexes.[2] The spectra contain a singlet due to molecules containing no ^{195}Pt atom, and second-order spectra arising from the [A-A'A''A'''X] and [AA'A''A'''XX'] spin systems from molecules containing one and two ^{195}Pt atoms respectively. The latter spin system gives rise to a doublet with separation $^1J(PtP) + {}^2J(PtP)$. Thus, since ^1J-(PtP) is taken to be positive and its magnitude can be determined from the [AA'A''A'''X] spectrum, the sign of $^2J(PtP)$ can be determined.[2] Figure 1 shows the ^{31}P n.m.r. spectra of the complexes (2b), (3b), and (4b)

The ^{31}P n.m.r. spectra also show that all the phosphorus atoms in each molecule are chemically equivalent or, if this is not so, that a rapid fluxional process operates which makes the phosphorus atoms effectively equivalent on the n.m.r. time scale.

The distinction between bridging and terminal hydride groups can be made from the hydride resonances in the ^{1}H n.m.r. spectra. Thus a bridging hydride, $\overline{Pt\text{-}H\text{-}Pt}$, is expected to give a $1:8:18:8:1$ quintet with a peak separation of $\frac{1}{2}[^1J(PtH)]$ due to coupling to ^{195}Pt (as for other ligands bridging between platinum atoms[2,5,6]). This pattern is observed for the hydrido-platinum resonance in the spectrum of (4b) as shown in Figure 2. The weak outer peaks of the quintet are barely distinguishable from the noise and are not shown. We were unable to observe a platinum hydride resonance

[5] P. L. Goggin, R. J. Goodfellow, and F. J. S. Reed, *J. Chem. Soc. (A)*, 1971, 2031.

[6] M. P. Brown, R. J. Puddephatt, and C. E. E. Upton, *J.C.S. Dalton*, 1976, 2490.

for complex (4a), possibly owing to the broadening effects of a fluxional process. Stone and his co-workers [7] have been able to observe a bridging hydride resonance for complexes such as $[Pt_2(\mu\text{-}H)_2(SiEt_3)_2\{P(C_6H_{11})_3\}_2]$ and have obtained evidence that the hydride ligands undergo a fluxional process at room temperature.

For the complexes which contain the unit H–Pt–Pt–H a central peak with satellites arising from coupling
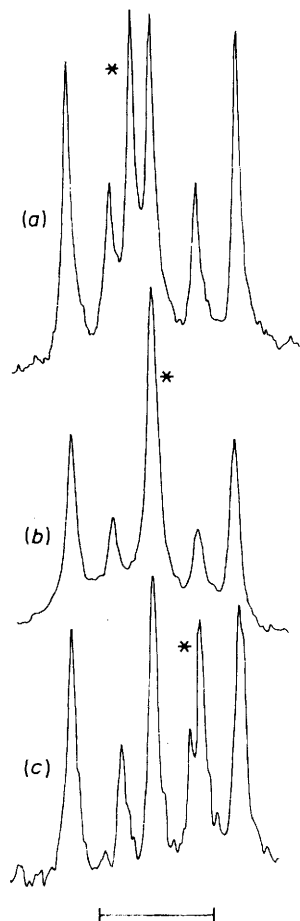
FIGURE 1 Phosphorus-31 n.m.r. spectra (36.4 MHz) in the region of the low-field ^{195}Pt satellites for complex (2b) (a), (3b) (b), and (4) (c). Field strength increases from left to right and the bar represents 50 Hz. The asterisked peak is due to the [AA′A″A‴X′] spin systems [in (b) this peak overlaps the central peak of the other low-field satellites]

to ^{195}Pt is expected. Considering only molecules containing one or no ^{195}Pt atoms, a five-line spectrum with relative intensity $1:1:4:1:1$ is expected, the separation between the outer satellites giving $^1J(PtH)$ and between the inner satellites giving $^2J(PtH)$. In molecules (11.4% of the total) containing two ^{195}Pt atoms the two hydrogen atoms and two ^{195}Pt atoms will give rise to a second-order AA′XX′ spectrum,[8] and this

[7] (a) M. Green, J. A. K. Howard, J. Proud, J. L. Spencer, F. G. A. Stone, and C. A. Tsipis, *J.C.S. Chem. Comm.*, 1976, 671; (b) M. Ciriano, M. Green, J. A. K. Howard, M. Murray, J. L. Spencer, F. G. A. Stone, and C. A. Tsipis, *J.C.S. Dalton*, in the press.

spectrum, which may take one of several possible forms, will contain a doublet with peaks separated by
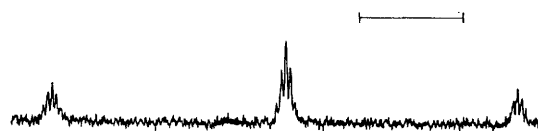
FIGURE 2 The ^1H n.m.r. spectrum (90 MHz) of complex (4b) in the Pt–H–Pt region. The three central peaks of the $1:8:18:8:1$ quintet are shown. Field strength increases from left to right and the bar represents 2 p.p.m.

$^1J(PtH) + {}^2J(PtH)$. Figure 3 shows the spectrum of complex (3b) in the hydridoplatinum region, and this clearly indicates the presence of the H–Pt–Pt–H skeleton. In particular, the lines due to the AA′XX′ spin system are separated by $|^1J(PtH)| + |^2J(PtH)|$ (Table 2), indicating that $^1J(PtH)$ and $^2J(PtH)$ have the same sign. Taking $^1J(PtH)$ to be positive, $^2J(PtH)$ is also positive in this complex.[9]

The trihydridodiplatinum complexes (2) contain both H–Pt–Pt–H and Pt–H–Pt units and the n.m.r. spectra at room temperature contain two reso⌐ ⌐nces in the hydride region with relative intensity *ca.* $2:1$, each with the ^{195}Pt satellites expected for the respective skeletons. Some overlapping of peaks occurs but, by recording n.m.r. spectra at both 60 and 90 MHz, all the expected satellites could be identified and the resulting coupling constants are given in Table 2. The hydride resonances for (2a) are sharp at -15 °C but broaden at higher temperatures and complete coalescence to a single broad peak occurs at 65 °C in $C_2D_2Cl_4$. This indicates
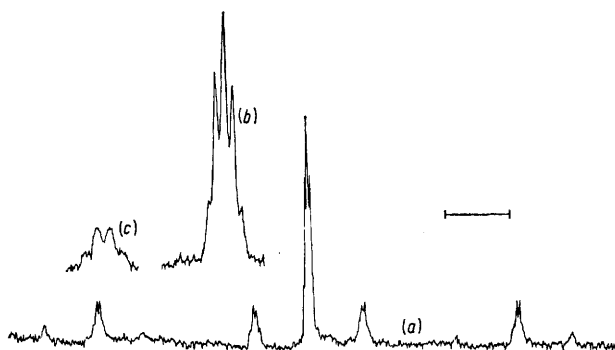
FIGURE 3 (a) The ^1H n.m.r. spectrum (90 MHz) of complex (3b) in the H–Pt–Pt–H region showing the central peak and three sets of ^{195}Pt satellites. The bar represents 2 p.p.m. The central peak (b) and the nearest low-field satellite (c) are shown on an expanded scale (bar represents 0.5 p.p.m.)

that exchange of terminal and bridging hydride groups occurs rapidly at 65 °C. No satellites due to coupling to ^{195}Pt could be observed in the high-temperature spectrum. This may indicate that the exchange process

[8] R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.
[9] D. W. W. Anderson, E. A. V. Ebsworth, and D. W. H. Rankin, *J.C.S. Dalton*, 1973, 854.

involves reversible dissociation from platinum of H^+, but it is also possible that the satellites are simply too broad to be observed. The broadening was not due to decomposition since the original spectrum is obtained on cooling the solution. Interestingly, the form of the CH_2 resonance of the dppm ligand in the ^1H n.m.r. spectrum of (2a) is also temperature dependent. At -15 °C the resonance is broad, but at 65 °C it is much sharper and coupling to ^{31}P is partially resolved. We suggest that the structure of the $[Pt_2H_3(dppm)_2]^+$ ion is as shown in Figure 4. At low temperature the two
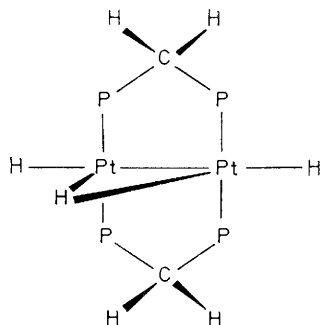

FIGURE 4 Proposed structure of $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ (2) (phenyl groups are omitted for clarity) showing the non-equivalence of the hydrogen atoms of the CH_2 groups

hydrogen atoms on each CH_2 group are non-equivalent (one is *cis* to the bridging hydride and the other *trans*) thus causing the broadening effect in the n.m.r., but at higher temperatures the fluxional process involving exchange of bridging and terminal hydrides creates an effective plane of symmetry containing the $Pt_2P_4C_2$ unit. Thus the hydrogen atoms of each CH_2 group become equivalent on the n.m.r. time scale and the resonance becomes sharper. If this interpretation is correct then the $\overline{Pt-H-Pt}$ bridge must be non-linear as shown. This form of hydride bridge is most common in transition-metal derivatives.

It could be argued that the criteria which have been applied to establish the existence of the bridging $\overline{Pt-H-Pt}$ unit would be equally consistent with the rapidly exchanging unit $HPt-Pt \rightleftharpoons Pt-PtH$. However, the assumption of structures containing such a unit cannot lead to a complete explanation of the spectroscopic data relating to either complexes (2) or (4). For example, in the case of (2) such a structure would need to contain three terminal hydride groups, only one of which exchanges rapidly between platinum centres. In the case of (4) a terminal hydride frequency would be expected in the i.r. spectrum whereas (see below) no such frequency is in fact observed.

Some of the hydridoplatinum peaks in the n.m.r. spectra show fine structure due to coupling with ^{31}P. For (4b) the bridging hydride resonance appears as a quintet due to coupling with four equivalent ^{31}P atoms, as expected for the proposed structure. The hydride resonances for (3) also show fine structure but the inter-

pretation is more difficult. Thus for molecules not containing ^{195}Pt the two hydrides and four phosphorus atoms give an $AA'X_2X'_2$ spin system and the sum of coupling constants $^2J(PH) + {}^3J(PH)$ can be obtained (Table 2). In molecules containing one ^{195}Pt atom the spin system is $AA'X_2X'_2M$ ($M = {}^{195}Pt$) and the form of the ^{195}Pt satellites is more complex than that of the central peak. We have been unable to interpret this fine structure in detail, since the spectra are not sufficiently well resolved.

Characterization by Vibrational Spectroscopy.—The dichlorohydridodiplatinum complex (4b) gave only one Pt–Cl stretching vibration in the i.r. spectrum at 326 cm^{-1} and one in the Raman spectrum at 343 cm^{-1} (Table 4). The non-coincidence of these bands suggests

TABLE 4

Infrared and Raman data (cm^{-1}) for the hydridoplatinum complexes [a]

Complex	ν(PtH) [b]		ν(PtCl)	
	I.r.	Raman	I.r.	Raman
(2a) [c]	2 137	2 143, 2 132 (sh)		
(2a) [d]	2 114, 2 096	2 112, 2 094		
(2b)	2 137	2 138		
(3b)	2 190	[e]	317	315
(4b)			326	343

[a] For powders (Raman) or Nujol mulls (i.r.). [b] Terminal hydridoplatinum bands. [c] Methanol solvate. [d] Unsolvated from CH_2Cl_2. [e] Too weak to be observed.

that the Pt_2Cl_2 unit is essentially linear. The frequencies are considerably higher than those for the platinum(I) complex (1) for which the corresponding bands are at 249 (i.r.) and 272 cm^{-1} (Raman).[2] Thus the Pt–Cl bonds are evidently strengthened on protonation of the Pt–Pt bond of (1).

The ratio of stretching frequencies for the bridging and terminal Pt–Cl bonds in $[Pt_2Cl_6]^{2-}$ is 0.92 : 1,[10] and a very similar value is obtained for the ratio of the stretching frequency of the bridging Pt–Cl band in complex (3b) to that of the terminal Pt–Cl band in (4b). Thus the frequencies are consistent with (3b) containing a bridging chloride as suggested.

For both complexes (2) and (3) the i.r. bands due to the terminal Pt–H stretching vibrations are strong. For (3b) this band is too weak to be observed in the Raman spectrum, while for (2b) the i.r. and Raman frequencies for ν_t(PtH) are coincident. Accidental degeneracy of the symmetric and asymmetric stretching frequencies of a linear HPtPtH unit in (2b) is possible but a non-linear HPtPtH unit cannot be excluded in this case. The unsolvated form of (2a) obtained from dichloromethane solvent gave two terminal PtH stretching bands in both the solid-state i.r. and Raman spectra, although the methanol solvate gave only one i.r. band. In solution, each gave a single ν_t(PtH) band. We are

[10] J. R. Ferraro, ' Low Frequency Vibrations of Inorganic and Co-ordination Compounds,' Plenum, New York, 1971; D. M. Adams, P. J. Chandler, and R. G. Churchill, *J. Chem. Soc. (A)*, 1967, 1272.

unable to offer a convincing explanation for this and the question of whether the HPtPtH unit in (2) is linear or not must await further investigation. Complexes (2) and (4) are thought to contain bridging $\overline{Pt-H-Pt}$ units but we have been unable to identify bands due to this group in either the i.r. or Raman spectra. The complex $[Pt_2(\mu\text{-}H)_2(SiEt_3)_2\{P(C_6H_{11})_3\}_2]$ exhibits $\nu(PtHPt)$ at 1 600 cm^{-1},[7] but our complexes give only a dppm ligand band in this region. Complex (4b) exhibits no identifiable Pt-H stretching vibration, consistent with the bridging hydride formulation, for which the bands due to $\nu(MHM)$ are often difficult to assign, but not with a structure containing a terminal hydride for which $\nu(PtH)$ is usually strong in the i.r. spectra.

In complex (1) the Pt-Pt stretching vibration gives rise to a strong band in the Raman spectrum at 150 cm^{-1},[2] but none of the hydride complexes gave a strong band in this region. This is probably due to the Pt-Pt interaction being much weaker in the complexes with bridging hydride or chloride ligands.

Bonding in the Complexes.—The cations in complexes (2) and (4) can be considered to be electron-deficient species. In each case the total electron count in the valence shell of both platinum atoms is 30, and each platinum can be considered to have 14 electrons plus a share of the two electrons in the three-centre $\overline{Pt-H-Pt}$ bond. In every case where a hydrogen atom bridges two transition-metal atoms the metal–metal distance is longer than it is when there is no bridging group.[11] Nevertheless metal–metal bonding is still expected and the bridge bond is perhaps best represented by the formulation $\overline{Pt--H--Pt}$.[11] The strongest evidence for a weaker Pt-Pt interaction in complexes (2) and (4) compared with the platinum(I) complex (1) is the absence of a strong band in the Raman spectrum due to the Pt-Pt stretching vibration. The extent of the predicted bond lengthening must await the results of X-ray structure determinations on the hydrido-complexes.

Complexes (3), which contain a bridging chloride acting as a three-electron ligand, are not electron deficient [each Pt atom has 16 electrons in its valence shell as in the usual mononuclear platinum(II) complexes]. It is predicted that Pt-Pt interaction will be weak or non-existent, therefore, and that the Pt-Pt distance will be longer than in the complexes containing bridging hydrides.[11]

It is interesting to consider the effect of the bridging hydride in complexes (2) and (4) on the strength of the terminal PtH and PtCl bonds respectively. It will be convenient to discuss this effect in terms of the *trans* influence of the bridging hydride ligand, although this concept is usually used in discussing bonding in regular square-planar platinum(II) complexes, and in complexes (2) and (4), it might be more realistic to consider the *trans* influence of the $Pt_2(\mu\text{-}H)$ unit. Values of both $\nu(PtH)$ and $^1J(PtH)$ for the terminal hydrides of (2), where the hydrides are *trans* to bridging hydride, are only slightly less than the respective values for (3), where the hydrides are *trans* to bridging chloride. This suggests that bridging hydride and bridging chloride in these complexes have similar *trans* influence. Comparison of these values of $^1J(PtH)$ and $\nu(PtH)$ with those for normal square-planar platinum(II) hydrides further suggests that the terminal hydrides in (2) are *trans* to a ligand of rather low *trans* influence.[12] For example, *trans*-$[PtCl(H)(PMePh_2)_2]$ has $\nu(PtH)$ at 2 220 cm^{-1} and $^1J(PtH)$ 1 260 Hz, whereas *trans*-$[PtH_2\{P(C_6H_{11})_3\}_2]$ has $\nu(PtH)$ at 1 712 cm^{-1} and $^1J(PtH)$ 792 Hz.[13,14] Thus the bridging hydride in complex (2) appears to have a much lower *trans* influence than a terminal hydride. This conclusion is confirmed by the high values of $\nu(PtCl)$ found for (4b), which again suggests that bridging hydride has a *trans* influence similar to that of chloride.[12] Thus it seems that the platinum orbitals involved in bonding to bridging hydride contain less s character than those used in bonding to terminal hydride, and this also explains the lower values of $^1J(PtH)$ associated with the bridging hydride. This coupling constant is also strongly affected by the *trans* ligand, being much lower when the bridging hydride is *trans* to terminal hydride in (2) than when *trans* to chloride in (4).

The formation of these cationic diplatinum complexes is remarkable, particularly when co-ordination of chloride ion in (2a) or (4a) would give complexes which would not be electron deficient. To a large extent, the formation of these complexes with bridging hydride or chloride ligands rather than the normal square-planar platinum(II) hydrides, which have been thoroughly studied in the past, must be due to the influence of the dppm ligands. Thus the $Pt_2(\mu\text{-dppm})_2$ skeleton is obviously favoured[2] and ensures that two platinum centres are held in close proximity, so that bridging by other ligands is then also possible. This effect might also be expected to lead to unusual chemical and perhaps catalytic activity of these hydrides, and these aspects are being pursued further.

EXPERIMENTAL

General techniques, details of spectroscopic methods, and the preparation of $[PtCl_2(dppm)]$ and $[Pt_2Cl_2(\mu\text{-dppm})_2]$ have been described previously.[2]

Bis-μ-bis(diphenylphosphino)methane-μ-hydrido-bis-[hydridoplatinum(II)] Chloride, $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]Cl$.— In a typical experiment, a solution of $Na[BH_4]$ (1g) in methanol (30 cm^3) was added slowly to a suspension of $[PtCl_2(dppm)]$ (2 g) in methanol (40 cm^3) under an atmosphere of nitrogen over a period of 1 h. The precipitate

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[13] B. L. Shaw and M. F. Uttley, *J.C.S. Chem. Comm.*, 1974, 918.
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was filtered off, washed with methanol, and dried *in vacuo* to give the impure trihydride (1.7 g) as a pinkish brown solid. Purification was carried out by one of the following ways.

(*a*) The impure product (1 g) was dissolved in CH_2Cl_2 (20 cm³). The solution was filtered and the volume of the filtrate was reduced to 10 cm³. Slow addition of iso-octane (4 cm³) precipitated a pale yellow solid (0.89 g). This procedure was repeated twice to give the pure *product* as white crystals (0.46 g). (*b*) The impure product (1 g) in methanol (80 cm³) was boiled for 5 min. The hot solution was filtered and set aside overnight. Colourless needles of the solvate, $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2]Cl\cdot2MeOH\cdot2H_2O$, were filtered off, washed with methanol (10 cm³), and dried *in vacuo*, yield 0.6 g.

$[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2][PF_6]$.—A suspension of impure $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2]Cl$ (1 g) in methanol (100 cm³) was boiled for 5 min. The hot solution was filtered into a flask containing $[NH_4][PF_6]$ in methanol (20 cm³ of 1.5% solution). The colourless crystals which formed were filtered off, washed with methanol, and dried *in vacuo*, yield 0.89 g.

*Bis-μ-bis(diphenylphosphino)methane-μ-chloro-bis[hydrido-platinum(*ii*)] Hexafluorophosphate*, $[Pt_2(\mu\text{-}Cl)H_2(\mu\text{-}dppm)_2]\text{-}$ $[PF_6]$. Several drops of concentrated hydrochloric acid were added to a solution of $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2][PF_6]$ (2.5 g) in dichloromethane (25 cm³). The solution effervesced slowly. After 1.5 h the solution i.r. spectrum indicated that no starting material remained. The volume of solution was reduced and iso-octane was added to precipitate the *product*, which was recrystallized from dichloromethane–benzene as colourless transparent needles, yield 1.92 g.

Alternatively, this complex could be prepared by heating

a solution of $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2][PF_6]$ (0.4 g) in $C_2H_2Cl_4$ (2 cm³) and CCl_4 (four drops) at 65 °C for 3 h. In this case the reaction was monitored by the ^{1}H n.m.r. spectrum. The *product* was obtained by precipitation with methanol (10 cm³), yield 0.05 g.

*Bis-μ-bis(diphenylphosphino)methane-μ-hydrido-bis[chloro-platinum(*ii*)] Hexafluorophosphate*, $[Pt_2Cl_2(\mu\text{-}H)(\mu\text{-}dppm)_2]\text{-}$ $[PF_6]$. (*a*) A solution of $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2][PF_6]$ (1.5 g) in deacidified $CHCl_3$ (15 cm³) and CCl_4 (0.5 cm³) was heated under reflux for 1.5 h under an atmosphere of nitrogen. The yellow crystals which formed on cooling were filtered off and washed with $CHCl_3$ (5 cm³). The *product* was purified by dissolving in CH_2Cl_2 (6 cm³) and reprecipitating by addition of methanol (3 cm³). The yellow needles which formed were filtered off, washed with methanol, and dried *in vacuo*, yield 0.55 g.

(*b*) Concentrated HCl (five drops) was added to a solution of $[Pt_2Cl_2(\mu\text{-}dppm)_2]$ (0.2 g) in $CHCl_3$ (6 cm³). After 10 min a solution of $[NH_4][PF_6]$ {0.2 cm³ of a solution containing $[NH_4][PF_6]$ (1 g) in methanol (8 cm³)} was added. After 5 min the solvent was evaporated. The residue was washed with water, dried *in vacuo*, and then recrystallized from dichloromethane–methanol to give yellow needles of the *product*.