Journal of Organometallic Chemistry, 304 (1986) 391–423
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

BIS-μ-[BIS(DIPHENYLPHOSPHINO)METHANE]DIHALODIPLATINUM-(*Pt–Pt*) AND ITS HYDRIDO 'A'-FRAME DERIVATIVES REVISITED *

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(Received October 21st, 1985)

Summary

Definitive ^1H, ^{31}P and ^{195}Pt NMR data are reported for the complexes $[PtX_2(dppm)]$ ($X = Cl$, Br or I; $dppm = Ph_2PCH_2PPh_2$), $[Pt_2X_2(\mu\text{-dppm})_2]$, $[Pt_2X_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$, $[Pt_2H_2Cl(\mu\text{-dppm})_2]^+$, $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$, $[Pt_2Cl_2(\mu\text{-Y})(\mu\text{-dppm})_2]$ ($Y = CH_2$, S or SO_2), $[Pt_2Me_2(\mu\text{-Cl})(\mu\text{-dppm})_2]^+$ and $[Pt_2Me_3(\mu\text{-dppm})_2]^+$. The complexes $[Pt_2X_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ ($X = Br$ or I) are reported for the first time, and evidence is presented that $[Pt_2H_2Cl(\mu\text{-dppm})_2]^+$ has a 'T'-frame structure (involving a donor–acceptor metal–metal bond) rather than an 'A'-frame structure. Early preparative routes to $[Pt_2X_2(\mu\text{-dppm})_2]$ ($X = Cl$, Br or I) were shown to give complexes contaminated with small amounts of $[Pt_2X_2(\mu\text{-H})(\mu\text{-dppm})_2]X$, and rapid intermolecular proton transfer between $[Pt_2X_2(\mu\text{-dppm})_2]$ and $[Pt_2X_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ was observed: for $X = Cl$, ΔG^* is 44.1 kJ mol^{-1}. The merits of ^{195}Pt NMR spectroscopy for studying platinum dimers are discussed, and a correlation between $^1J(PtPt)$ and $r(PtPt)$ was observed.

Since the original reports of the preparation of $[Pt_2Cl_2(\mu\text{-dppm})_2]$ ($dppm = Ph_2PCH_2PPh_2$) in 1972 [1], and its subsequent identification as a metal–metal bonded dimer, (**1**, $X = Cl$), in 1977 [2] (a conclusion later confirmed by an X-ray

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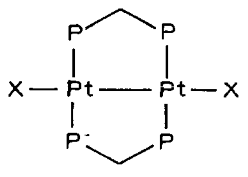
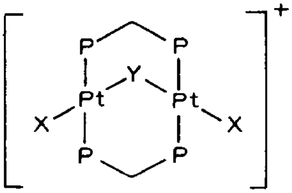
* Parts of this work have been presented as a Plenary lecture at the Golden Jubilee of the Indian National Science Academy, in an International Symposium entitled "New Vistas in Organometallic Chemistry" (Jaipur, March, 1984).

0022-328X/86/$03.50



(1: X = Cl, Br or I)

P⌒P = dppm



(2: X = Cl, Br or I, Y = H;
3: X = Y = H;
4: X = H, Y = Cl)

crystallographic study [3,4]), this complex has been used to prepare a wide range of platinum(I) and platinum(II) complexes containing the $\{Pt_2(\mu\text{-dppm})_2\}$ moiety, e.g. $[Pt_2Cl_2(\mu\text{-X})(\mu\text{-dppm})_2]$ {X = S, SO_2, CH_2 [5], CO [6], RNC (R = Me-4-C_6H_4) [7] or CS_2 [8]}, $[Pt_2L_2(\mu\text{-dppm})_2]^{2+}$ (L = PPh_3, PPh_2Me, $PPhMe_2$, py, NH_3, etc.) [9], $[Pt_2H(L)(\mu\text{-dppm})_2]^+$ (L = dppm, PPh_3, PPh_2Me, $PPhMe_2$ [10] or CO [11]), $[Pt_2R_3(\mu\text{-dppm})_2]^+$ (R = Me [12] or Et [13]), $[Pt_2Cl(CO)(\mu\text{-dppm})_2]^+$ [6], $[Pt_2(CO)_2(\mu\text{-dppm})_2]^{2+}$ [9,11], $[Pt_2ClX(\mu\text{-}CF_3C{=}CCF_3)(\mu\text{-dppm})_2]$ (X = Cl or H) [14], $[Pt_2H(L)(\mu\text{-}CF_3C{=}CCF_3)(\mu\text{-dppm})_2]^+$ (L = MeCN, PhCN or Me_2CO) [14], $[Pt_2X(CR'{=}CHR')(\mu\text{-}CR{=}CR)(\mu\text{-dppm})_2]$ (X = Cl, R = R' = CF_3 or CO_2Me; X = I, R = R' = CF_3; X = Cl, R = CF_3, R' = CO_2Me; X = Cl, R = CO_2Me, R' = CF_3) [14], $[Pt_2(SnCl_3)_2(\mu\text{-dppm})_2]$ [15], $[Pt_2Cl(SnCl_3)(\mu\text{-dppm})_2]$ [15], $[Pt_2H_2(\mu\text{-X})(\mu\text{-dppm})_2]^+$ (X = H, Cl [16] or SMe [5]), $[Pt_2Cl_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ [16], $[Pt_2R_2(\mu\text{-X})(\mu\text{-dppm})_2]^+$ (R = Me, X = H [17] or Cl [18]; R = Et, X = H [13]; R = C(O)Ph or Ph, X = Cl [19]), $[Pt_2Me(L)(\mu\text{-}CH_2)(\mu\text{-dppm})_2]^+$ (L = CO or $PPhMe_2$) [20], $[Pt_2(CH_2PPh_3)(X)(\mu\text{-}CH_2)(\mu\text{-dppm})_2]^+$ (X = Me or Cl) [20], $[Pt_2Cl_2(\mu\text{-}CS_2Me)(\mu\text{-dppm})_2]^+$ [8], $[Pt_2IX_2\{C(SMe)_2\}(\mu\text{-dppm})_2]^+$ (X = Cl or I) [8] and $[Pt_2Me_4(\mu\text{-dppm})_2]$ [21]. Several recent reports [14,22–25] indicate that some of these complexes may exhibit catalytic activity, and the 'A'-frame structures, **2**, **3** and **4** (and, incidentally, complexes of type **1**), have been the subject of extended Hückel molecular orbital calculations [26], which provide an interesting insight into the metal–metal bonding interactions in these systems. With this rapidly expanding range of complexes, a much greater understanding of the chemical and spectroscopic properties of the $\{Pt_2(\mu\text{-dppm})_2\}$ skeleton has been developed than was evident in the early publications. It is now timely, and indeed imperative (owing to their ubiquitous use as synthetic reagents), to reinvestigate the original reports of the preparations and properties of the complexes $[Pt_2X_2(\mu\text{-dppm})_2]$ (X = Cl, Br or I). In particular the following questions remain unresolved from the original reports [2]: (i) why do the complexes $[Pt_2Cl_2(\mu\text{-dppm})_2] \cdot 0.5CH_2Cl_2$ and $[Pt_2Cl_2(\mu\text{-dppm})_2] \cdot C_6H_6$ (apparently only differing by a molecule of solvation) show remarkably different physical properties?, (ii) why was no fine structure observed in the CH_2 signals in the ^1H NMR spectrum of $[Pt_2Cl_2(\mu\text{-dppm})_2]$ as described by Brown et al. [2], when it was clearly resolved in the earlier reports of Glockling and Pollock? [1], (iii) why was the profile of the high field satellites in the ^{31}P NMR spectrum of $[Pt_2Cl_2(\mu\text{-dppm})_2]$ broad, poorly resolved and temperature dependent?, (iv) why did $[Pt_2X_2(\mu\text{-dppm})_2]$ (X = Br or I) show signs of extensive decomposition in chlorinated hydrocarbons, when no similar reactivity has been found in related complexes prepared in later studies?, and (v) why do the NMR parameters for

$[Pt_2X_2(\mu\text{-dppm})_2]$ (X = Cl, Br or I) as reported by Brown et al. [2] differ significantly from those reported by Boag et al. [27] for the same complexes (albeit prepared by a different synthetic route)? We have now resolved all these problems, and report herein accurate ^1H, ^{31}P and ^{195}Pt NMR parameters for the complexes **1**. In the course of this work, we have also investigated the complexes $[Pt_2X_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ (X = Cl, Br or I) and $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ in the light of Hoffmann's theoretical treatment [26], and discovered evidence for a novel intermolecular proton transfer reaction between $[Pt_2Cl_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ and $[Pt_2Cl_2(\mu\text{-dppm})_2]$, corresponding to a reversible oxidative-addition to a metal–metal bond. Moreover, our reinvestigation of the complex originally described as $[Pt_2H_2(\mu\text{-Cl})(\mu\text{-dppm})_2]^+$ [16] has revealed that this description merely represents its time-averaged structure at ambient temperature, and that its true static low-temperature form is a novel example of a structure containing a donor–acceptor metal–metal bond: these observations reflect upon the mechanism recently proposed by Geoffroy and coworkers [28] for the photoinduced elimination of dihydrogen from this molecule, and the recently proposed mechanisms for 'A'-frame inversion for 'A'-frame complexes containing the $\{Pt_2(\mu\text{-dppm})_2\}$ skeleton [29].

Results and discussion

Synthetic routes to, and purity of, $[Pt_2X_2(\mu\text{-dppm})_2]$ (X = Cl, Br or I)

A low temperature (−90°C) ^{31}P NMR spectroscopic study (in CD_2Cl_2) of supposedly pure samples of $[Pt_2Cl_2(\mu\text{-dppm})_2]\cdot 0.5CH_2Cl_2$ prepared by the route described by Brown et al. [2], and indeed some original samples [30] of the compounds described in that paper, provided clear evidence for at least two, and sometimes three, platinum-containing species in solution. The predominant component (ca. 95%) of these mixtures gave a ^{31}P NMR spectrum which yielded chemical shift (δ) and coupling constant (J) data similar to, but not identical with, those observed in the room temperature spectrum (where only one platinum-containing species is apparently observed {see, for example, Fig. 2 of ref. 2}). Upon warming from −90°C to ambient temperatures, the distinctive pattern of peaks associated with the predominant species coalesces with a second set of peaks (having a similar pattern, but very different values of J and δ, and being present at a much lower concentration, ca. 5%). Coalescence occurred at ca. −45°C and above this temperature the spectrum reported in the original literature was obtained. The third component, which was present in a number of samples, was readily identified by its characteristic 1/4/1 triplet pattern and its $^1J(PtP)$ values as $[PtCl_2(dppm)]$ (vide infra). Indeed the signals due to $[PtCl_2(dppm)]$, even when initially absent in a rapidly quenched (to −90°C) freshly prepared solution, were found to increase in intensity as a function of time, suggesting that it was being formed by a reaction of one (but not necessarily both) of the other two platinum-containing species in solution (both of which exhibited the pattern due to the characteristic $AA'A''A'''X/AA'A''A'''XX'$ spin system of the $\{Pt_2(\mu\text{-dppm})_2\}$ skeleton [2,31]). Moreover, the similarity of the δ and J values of the minor component with those previously reported [16] for $[Pt_2Cl_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ suggested that this was the likely identity of this species, and hence the major component was assumed to be $[Pt_2Cl_2(\mu\text{-dppm})_2]$, implying that purities of only ca. 95% had been achieved by the described preparation [2].

A low temperature (ca. $-90°C$) ^{31}P NMR spectroscopic study of samples prepared in the manner described for the species $[Pt_2Cl_2(\mu\text{-dppm})_2] \cdot C_6H_6$ [2], and some original samples [30] of this complex, showed at least two components in solution. These had identical spectral parameters to those components observed for the dichloromethane solvate, but the relative proportions of these components was markedly different. The peaks assigned to $[Pt_2Cl_2(\mu\text{-dppm})_2]$ in the solution of the "benzene solvate" have significantly lower intensity than those due to the other dimeric species. Moreover, spectral features associated with $[PtCl_2(dppm)]$ in these solutions were always evident and increased with time to yield a significantly higher concentration of $[PtCl_2(dppm)]$ than had been observed in the solutions originating from the dichloromethane solvate. The peaks due to $[PtCl_2(dppm)]$ increased in intensity at a rate corresponding to a concomitant diminution of the signals due to $[Pt_2Cl_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$. These results clearly raised the question as to the nature of the experimental precursor to the solid product reported as "$[Pt_2Cl_2(\mu\text{-dppm})_2] \cdot C_6H_6$". The solid had been isolated (by the addition of 2,2,4-trimethylpentane) from a solution prepared by the action of concentrated hydrochloric acid upon a suspension of $[Pt_2Cl_2(\mu\text{-H})(\mu\text{-dppm})_2]Cl$ in benzene (see Scheme 1), and so the solution obtained prior to this final precipitation was examined at $-90°C$ by ^{31}P NMR spectroscopy. This revealed the presence of only one phosphorus-containing species, the spectral parameters of which clearly identified it as $[Pt_2Cl_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$. Furthermore, it is known [16] that $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]Cl$ will react with a mixture of chlorinated hydrocarbons to form, sequentially, $[Pt_2H_2Cl(\mu\text{-dppm})_2]Cl$ and then $[Pt_2Cl_2(\mu\text{-H})(\mu\text{-dppm})_2]Cl$, the rôle of the solvent being to act as a source of chloride ions. It is therefore, perhaps, not surprising that treatment of $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]Cl$ with hydrochloric acid should produce a similar product. Precipitation of $[Pt_2Cl_2(\mu\text{-H})(\mu\text{-dppm})_2]Cl$, at first sight, appears to have promoted partial dehydrochlorination of the product, to yield a mixture of $[Pt_2Cl_2(\mu\text{-H})(\mu\text{-dppm})_2]Cl$ and $[Pt_2Cl_2(\mu\text{-dppm})_2]$. This, however, is not the case. Experiments have shown that dehydrochlorination of the bridging hydrido complex occurs not at the precipitation stage, but upon the subsequent drying of the sample by continuous evacuation at room temperature. Prolonged evacuation results in a high level of conversion to neutral $[Pt_2Cl_2(\mu\text{-dppm})_2]$, and indeed it is this phenomenon which is responsible for the incorrect formulation of this product in the original report [2]. Thus, the synthetic route to $[Pt_2Cl_2(\mu\text{-dppm})_2]$ can now be rationalised. The final step, involving the treatment of the $[Pt_2Cl_2(\mu\text{-H})(\mu\text{-dppm})_2]Cl$ with dichloromethane, is a very convenient method of achieving complete dehydrochlorination, but it must be emphasised that the purity of the sample is best checked by ^{31}P NMR spectroscopy, as even the smallest traces of HCl can result in significant changes in the spectral parameters.

SCHEME 1. A summary of the standard preparation of $[Pt_2Cl_2(\mu\text{-dppm})_2]$, as reported in ref. 2.

A process which competes with the dehydrochlorination of $[Pt_2Cl_2(\mu\text{-}H)(\mu\text{-}dppm)_2]Cl$ (a reductive-elimination reaction) is the breakdown of its dimeric structure, induced by reaction with CH_2Cl_2, to form $[PtCl_2(dppm)]$; this process occurs even at −90°C (vide supra). It should be noted, however, that (contrary to the original report [2]) $[Pt_2Cl_2(\mu\text{-}dppm)_2]$ itself shows no reaction with dichloromethane under normal experimental conditions: the observed decomposition requires the presence of acid for its promotion (which occurs via the oxidative addition of H^+ to the metal–metal bond, to form $[Pt_2Cl_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$).

The reaction sequence illustrated in Scheme 1 gives low, irreproducible yields [32] of $[Pt_2Cl_2(\mu\text{-}dppm)_2]$, principally due to the difficulty with the $Na[BH_4]$ reduction step (preferential reaction of $[BH_4]^-$ with the solvent, methanol, occurring). It is well known [33] that for reductions involving $Na[BH_4]$ which require reaction times in excess of 30 min, the use of sterically hindered alcohols, especially propan-2-ol, often improves the yield of the desired product. However, when the reduction of $[PtCl_2(dppm)]$ was performed in propan-2-ol, the product isolated was not the expected $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2]Cl$, which shows a single ν(PtH) band in its IR spectrum at 2014 cm^{-1} [16], but a novel species which shows two bands in this region, at 2100 and 2120 cm^{-1}. This product, which was not further characterised, reacts vigorously with methanol to give the desired $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2]Cl$ (which was identified by both IR and ^{31}P NMR spectroscopy), but the overall yield was only slightly better than the original route. However, subsequently, a reliable synthetic route to $[Pt_2Cl_2(\mu\text{-}dppm)_2]$ has been developed [34] in a mixed methanol/ethanol solvent, which gives good yields of pure product.

The synthesis of samples of $[Pt_2X_2(\mu\text{-}dppm)_2]$ (X = Br or I) by the original route [2] was shown, by similar VT ^{31}P NMR studies to those described above, to produce grossly impure materials. The major component in each case was the protonated dimer $[Pt_2X_2(\mu\text{-}H)(\mu\text{-}dppm)_2]X$ (vide infra). A new route to $[Pt_2Br_2(\mu\text{-}dppm)_2]$ was thus devised: the original preparation [2] required 96 h, the new procedure (eq. 1) is complete in 3 h in ca. 95% yield. Moreover, the product showed no trace of any

$$[Pt_2Cl_2(\mu\text{-}dppm)_2] \xrightarrow[CH_2Cl_2]{Ag[PF_6]} \xrightarrow[CH_2Cl_2]{[NEt_4]Br} [Pt_2Br_2(\mu\text{-}dppm)_2] \qquad (1)$$

hydrido impurity. The original preparation of $[Pt_2I_2(\mu\text{-}dppm)_2]$ [2], by treatment of $[Pt_2Cl_2(\mu\text{-}dppm)_2]$ with NaI in propanone, will give satisfactory results if, and only if, the reaction mixture (especially the platinum complex) is free from acidic impurities. The complexes $[Pt_2X_2(\mu\text{-}dppm)_2]$ (X = Br or I) were quantitatively converted into $[Pt_2X_2(\mu\text{-}H)(\mu\text{-}dppm)_2]Y$ (X = Y = Br; X = I, Y = $[BF_4]$) by treatment of a solution in dichloromethane with a small amount of aqueous hydrobromic acid (49%) or tetrafluoroboric acid (40%) respectively. This is the first report of the cations $[Pt_2X_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$ (X = Br or I).

^1H, ^{31}P and ^{195}Pt NMR of $[PtX_2(dppm)]$ (X = Cl, Br or I)

The ^1H, ^{31}P and ^{195}Pt NMR parameters for the complexes $[PtX_2(dppm)]$ are detailed in Tables 1, 2 and 3, respectively. These data establish a base-line for the later discussion of the spectra of complexes **1**, **2**, **3** and **4**. The CH_2 resonances form a triplet {1/4/1, spacing of $\frac{1}{2}[^3J(PtH)]$} of triplets {1/2/1, spacing of $^2J(PH)$}, the P resonance is a triplet {1/4/1; spacing of $\frac{1}{2}[^1J(PtP)]$} and the Pt resonance is a

(Continued on p. 399)

TABLE 1

^{1}H NMR SPECTROSCOPIC DATA (δ in ppm, J in Hz)

Complex	Solvent	Field strength (MHz)	^{1}H NMR							
			PCH_2P				PtHPt			
			$\delta(CH_2)$ [a]	J'	$^2J(PH)$	$^3J(PtH)$	$\delta(H)$ [a]	$^1J(PtH)$	$^2J(PtH)$	$^2J(PH)$
$[PtCl_2(dppm)]$	CD_2Cl_2	300	4.48	–	11.1	69.0	–	–	–	–
	$CDCl_3$	300	4.45	–	11.0	70.0	–	–	–	–
$[PtBr_2(dppm)]$	CD_2Cl_2	300	4.53	–	11.0	71.0	–	–	–	–
	$CDCl_3$	300	4.49	–	10.8	71.0	–	–	–	–
$[PtI_2(dppm)]$	CD_2Cl_2	300	4.64	–	10.8	68.0	–	–	–	–
	$CDCl_3$	300	4.60	–	10.8	69.0	–	–	–	–
$[Pt_2Cl_2(\mu\text{-dppm})_2]$	CD_2Cl_2	300	4.41	[c]	[c]	55.3	–	–	–	–
$[Pt_2Cl_2(\mu\text{-dppm})_2]$ [b]	CD_2Cl_2	300	4.38	3.85	7.70	59.5	–	–	–	–
$[Pt_2Br_2(\mu\text{-dppm})_2]$	CD_2Cl_2	300	4.39	3.95	7.90	57.5	–	–	–	–
$[Pt_2I_2(\mu\text{-dppm})_2]$	CD_2Cl_2	300	4.50	4.05	8.10	58.5	–	–	–	–
$[Pt_2Cl_2(\mu\text{-H})(\mu\text{-dppm})_2]Cl$	CD_2Cl_2	90	4.49	[c]	[c]	44.0	−16.14	817.7	–	[c]

[Pt_2Cl_2(μ-H)(μ-dppm)$_2$][BF_4]	CD_2Cl_2	300	4.35	[c]	[c]	[c]	−16.52	812.3	–	6.5
	CD_2Cl_2	90	4.35	3.70	7.40	43.2	−16.62	808.2	–	[c]
	CD_2Cl_2	400	4.76 [d]	[c]	[c]	[c]	−16.45 [d]	814.0	–	[c]
			4.00 [d]	[c]	[c]	[c]				
[Pt_2Br_2(μ-H)(μ-dppm)$_2$]Br	CD_2Cl_2	300	4.53	[c]	[c]	[c]	−14.51	827.3	–	[c]
[Pt_2Br_2(μ-H)(μ-dppm)$_2$][BF_4]	CD_2Cl_2	300	4.52	[c]	[c]	40.0	−14.50	831.2	–	7.8
	CD_2Cl_2	90	4.49	4.04	8.08	41.3	−14.52	829.5	–	8.1
[Pt_2I_2(μ-H)(μ-dppm)$_2$][BF_4]	CD_2Cl_2	300	4.84	[c]	[c]	43.8	−11.03	837.8	–	7.5
	CD_2Cl_2	90	4.81	3.31	6.62	43.4	−11.04	835.0	–	7.4
[Pt_2H_2(μ-H)(μ-dppm)$_2$][PF_6]	CD_2Cl_2	300	4.66	[c]	[c]	32.4	−5.63	546.3	–	7.4
							−6.77 [e]	1150.7	115.0	11.9
	CD_2Cl_2	90	4.67	4.04	8.08	34.6	−5.70	544.0	–	[c]
							−6.73 [e]	1161.9	122.0	13.2
[Pt_2H_2Cl(μ-dppm)$_2$][PF_6]	CD_2Cl_2	400	4.43	[c]	[c]	[c]	−11.84 [e]	1178.0	310.0	[c]
	CD_2Cl_2	90	4.43	4.05	8.10	39.7	−11.84 [e]	1180.0	310.0	6.3
	CD_2Cl_2	400	5.06 [f,g]	[c]	[c]	[c]	−9.34 [e,f]	1360.0	212.0	[c]
			3.91 [f,g]	[c]	[c]	[c]	−13.77 [e,f]	962.4	418.0	[c]

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[a] Relative to tetramethylsilane; measured at ambient temperature, unless otherwise stated. [b] In the presence of 1,8-bis(dimethylamino)naphthalene. [c] Unresolved. [d] −30°C. [e] Terminal hydride. [f] −60°C. [g] See Fig. 3 of ref. 29 for the spectrum at −77°C which reveals δ(H) 5.09 ppm, ^2J(HH) 14, ^3J(PtH) ~ 60 Hz; δ(H) 3.93 ppm, ^2J(HH) 14, J' 5.5, ^2J(PH) 11 Hz.

TABLE 2. $^{31}P\{^1H\}$ NMR SPECTROSCOPIC DATA (δ in ppm, J in Hz)

Complex	Solvent	T(°C)	^{31}P NMR					
			δ(P) [a]	^1J(PtP)	^2J(PtP)	^3J(PP)	^3J(PP)	^1J(PtPt)
$[PtCl_2(dppm)]$	CD_2Cl_2	25	−66.4	3079	–	–	–	–
$[PtBr_2(dppm)]$	CD_2Cl_2	25	−67.5	3030	–	–	–	–
$[PtI_2(dppm)]$	CD_2Cl_2	25	−72.9	2878	–	–	–	–
$[Pt_2Cl_2(\mu\text{-dppm})_2]$	CD_2Cl_2	25	2.6	2945	−134.7	63.0	25.9	8146
	CD_2Cl_2	−86	3.8	2927	−136.7	62.8	25.0	8232
$[Pt_2Br_2(\mu\text{-dppm})_2]$	CD_2Cl_2	25	1.1	2914	−134.2	61.1	24.4	8865
	CD_2Cl_2	−84	0.6	2891	−134.3	61.0	24.4	8987
$[Pt_2I_2(\mu\text{-dppm})_2]$	CD_2Cl_2	25	−4.3	2878	−125.0	58.4	24.7	9009
	CD_2Cl_2	−84	−4.2	2852	−124.5	58.6	24.4	9109
$[Pt_2Cl_2(\mu\text{-H})(\mu\text{-dppm})_2]Cl$	CD_2Cl_2	−84	8.4	2319	−36.6	51.2	22.0	4838
$[Pt_2Br_2(\mu\text{-H})(\mu\text{-dppm})_2]Br$	CD_2Cl_2	−90	6.4	2341	−36.6	51.2	22.0	5443
$[Pt_2I_2(\mu\text{-H})(\mu\text{-dppm})_2][BF_4]$	CD_2Cl_2	−84	3.2	2283	−26.9	46.3	19.0	3886
$[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]Cl$	CD_2Cl_2	−86	18.4	2761	−14.6	56.2	19.5	521
$[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2][PF_6]$	CD_2Cl_2	25	17.7	2766	17.8	56.6	17.9	553
$[Pt_2H_2Cl(\mu\text{-dppm})_2][PF_6]$	CD_2Cl_2	25	12.6	2611	3.0	53.6	17.9	[c]
	CD_2Cl_2	−85	15.5 [d]	2756	−35.0	39.0	34.5	} [f]
			9.6 [e]	2404	−35.0	39.0	34.5	
$[Pt_2Me_2(\mu\text{-Cl})(\mu\text{-dppm})_2][PF_6]$	CD_2Cl_2	25	10.4	3028	35.4	30.5	3.0	453
	CD_2Cl_2	−70	11.6	3013	36.7	30.0	3.0	445
$[Pt_2Cl_2(\mu\text{-CH}_2)(\mu\text{-dppm})_2]$	$C_2D_2Cl_4$	25	11.4	3384	73.2	26.0	3.3	864
$[Pt_2Cl_2(\mu\text{-S})(\mu\text{-dppm})_2]$	$C_2D_2Cl_4$	25	1.8	2877	10.0 [g]	14.0 [g]	11.0 [g]	192
$[Pt_2Cl_2(\mu\text{-SO}_2)(\mu\text{-dppm})_2]$	CD_2Cl_2	25	18.1	3617	275	44.1	0	147

[a] Relative to trimethylphosphate in D_2O; solvent corrected. [b] See Appendix for details of calculations. [c] $\chi_i(1)$ lines not observed. [d] Corresponds to P_B and $P_{B'}$ in **8**. [e] Correponds to P_A and $P_{A'}$ in **8**. [f] Not calculable from spectrum. [g] Obtained from simulation; see text.

TABLE 3

$^{195}Pt\{^1H\}$ NMR SPECTROSCOPIC DATA (δ in ppm, J in Hz)

Complex	Solvent	T(°C)	^{195}Pt NMR			
			δ(Pt) [a]	^1J(PtP)	^2J(PtP)	^1J(PtPt) [b]
$[PtCl_2(dppm)]$	CD_2Cl_2	25	710	3079	–	–
$[PtBr_2(dppm)]$	CD_2Cl_2	25	422	3028	–	–
$[PtI_2(dppm)]$	CD_2Cl_2	25	−185	2881	–	–
$[Pt_2Cl_2(\mu\text{-dppm})_2]$	CD_2Cl_2	25		2950	−133.5	8145
	CD_2Cl_2	−70	−421	2926	−136.8	8197
$[Pt_2Br_2(\mu\text{-dppm})_2]$	CD_2Cl_2	25	−566	2917	−132.0	8805
$[Pt_2I_2(\mu\text{-dppm})_2]$	$C_2D_2Cl_4$	25	−772	2874	−124.6	9007
$[Pt_2Cl_2(\mu\text{-H})(\mu\text{-dppm})_2]Cl$	CD_2Cl_2	−84	−134	2320	[c]	[d]
$[Pt_2Br_2(\mu\text{-H})(\mu\text{-dppm})_2]Br$	CD_2Cl_2	−90	−376	2346	[c]	5585
$[Pt_2I_2(\mu\text{-H})(\mu\text{-dppm})_2][BF_4]$	CD_2Cl_2	−84	−844	2280	[c]	3827
$[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]Cl$	CD_2Cl_2	−86	−609	2748	[c]	501
$[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2][PF_6]$	$C_2D_2Cl_4$	25	−596	2771	[c]	538
$[Pt_2H_2Cl(\mu\text{-dppm})_2][PF_6]$	CD_2Cl_2	25	−348	2606	[c]	1260
	CD_2Cl_2	−70	−525 [e]	2760	[c]	1320
			−199 [f]	2404	[c]	
$[Pt_2Me_2(\mu\text{-Cl})(\mu\text{-dppm})_2][PF_6]$	CD_2Cl_2	25	−17	3032	36.6	452
$[Pt_2Me_3(\mu\text{-dppm})_2][PF_6]$	$(CD_3)_2CO$	25	347	1466	22.0	2745
			136	2991	22.0	
$[Pt_2Cl_2(\mu\text{-CH}_2)(\mu\text{-dppm})_2]$	$C_2D_2Cl_4$	25	146	3383	73.4	858
$[Pt_2Cl_2(\mu\text{-S})(\mu\text{-dppm})_2]$	$C_2D_2Cl_4$	25	276	2884	[c]	201
$[Pt_2Cl_2(\mu\text{-SO}_2)(\mu\text{-dppm})_2]$	$C_2D_2Cl_4$	25	652	3551	271.3	< 540

[a] Relative to a frequency of 21.4 MHz on an NMR machine where TMS resonates at exactly 100.00 MHz. [b] See Appendix for details of calculation. [c] Unresolved. [d] Signal-to-noise obscured χ_i-lines. [e] Corresponds to Pt_y in **8**. [f] Corresponds to Pt_x in **8**.

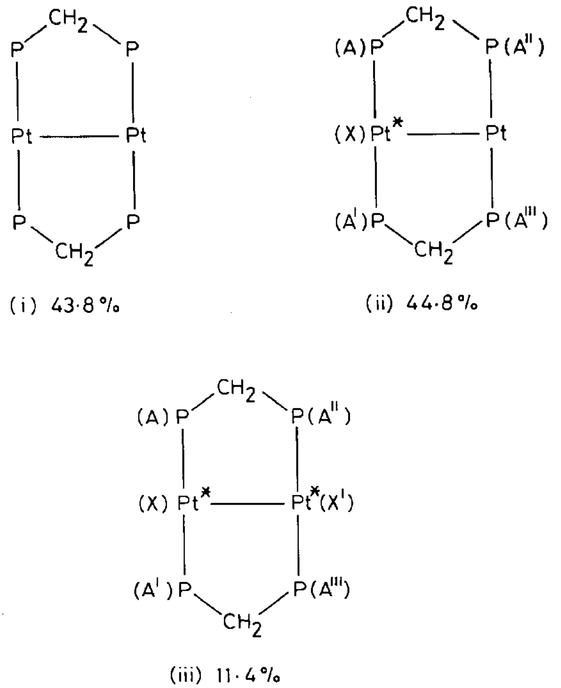
triplet {1/2/1; spacing of ^1J(PtP)}, characteristic of the simple A_2X spin system.

As has been found for several series of complexes [35–37], δ(Pt) for $[PtX_2(dppm)]$ follows the expected *trans*-influence series trend for X (the order of *trans* influence is Cl < Br < I), the values of δ(Pt) decreasing in the order Cl > Br > I; the magnitudes of ^1J(PtP) follow the same trend.

*^1H, ^{31}P and ^{195}Pt NMR spectra of **1**, **2**, **3** and **4***

(a) $[Pt_2X_2(\mu\text{-dppm})_2]$

The isotopomer distribution for the $\{Pt_2(\mu\text{-dppm})_2\}$ skeleton is illustrated in Fig. 1 [2]. The ^1H NMR spectra of the CH_2 protons in **1** are expected to consist of five peaks of relative intensity 1/7.8/17.3/7.8/1, exhibiting a separation of $\frac{1}{2}[^3J(PtH)]$. Each line of this multiplet should be further split into a quintet of separation $\frac{1}{2}[^2J(PH)+{}^4J(PH)]$, defined as the apparent coupling constant (J'), due to virtual coupling with the neighbouring phosphorus atoms {n.b. if it is assumed that $^4J(PH) \sim 0$ Hz, then $^2J(PH) = 2J'$}. This is indeed the case for **1** (X = Br or I), and the parameters are given in Table 1. For **1** (X = Cl), however, no splitting corresponding to ^2J(PH) was observed. This situation was also found by Brown et al. [2], but Glockling [1] had observed a value of ^2J(PH) of 3.8 Hz for this complex {which, in reality, is J' and not ^2J(PH)}, which had been prepared by him in an aprotic medium. Upon the addition of 1,8-bis(dimethylamino)naphthalene ("proton



(i) 43·8%

(ii) 44·8%

(iii) 11·4%

Fig. 1. The natural abundance of ^{195}Pt-containing species for the $\{Pt_2(\mu\text{-dppm})_2\}$ skeleton (Pt* = ^{195}Pt).

sponge") to a solution of **1** (X = Cl) in CD_2Cl_2, the spectrum became well resolved (see Fig. 2), giving a value of J' of 3.85 Hz. The effect of the proton sponge can only be to remove any vestigial traces of H^+ from the solution, the presence of which must have been causing loss of fine structure by virtue of a rapid exchange reaction (see later). However, the ^{31}P NMR spectrum of **1** (X = Cl) at −90°C indicated that the amount of $[Pt_2Cl_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ which could have been present must have been < 0.1%, as no detectable levels of this species were observed. This emphasises the extreme sensitivity of $[Pt_2Cl_2(\mu\text{-dppm})_2]$ to even trace amounts of acid impurities.

For all three complexes **1**, the protons of the methylene group were magnetically equivalent despite the large dihedral angle (38.5°) [3,4], which Colton and coworkers had postulated would lead to magnetic non-equivalence [38]. These observations require that rapid flipping of the $\{Pt_2P_2C\}$ five-membered rings must be occurring in solution, and a similar conclusion was recently drawn for the palladium analogues of **1** [39], in contrast to earlier erroneous observations [38]. The data reported in Table 1 represent the only reliable values for the complexes **1** to have been published.

The analysis of the $^{31}P\{^1H\}$ spectra of **1** has been discussed in detail elsewhere [2,27]; to ensure that no impurities were present in the solutions of **1**, all ^{31}P data were accumulated at ca. −90°C. The spectral parameters $\{\delta(P), J(PtP)$ and $J(PP)\}$ are reported in Table 2 and were all in very good agreement with those reported by Goodfellow and coworkers [27] (n.b. their samples had been prepared from $[Pt_2X_4(CO)_2]^{2-}$ in an aprotic medium), but the values for **1** (X = Br or I) differed dramatically from those by Brown et al. [2]. These results confirm that the samples prepared in the earlier work [2] were severely contaminated with protonated impuri-

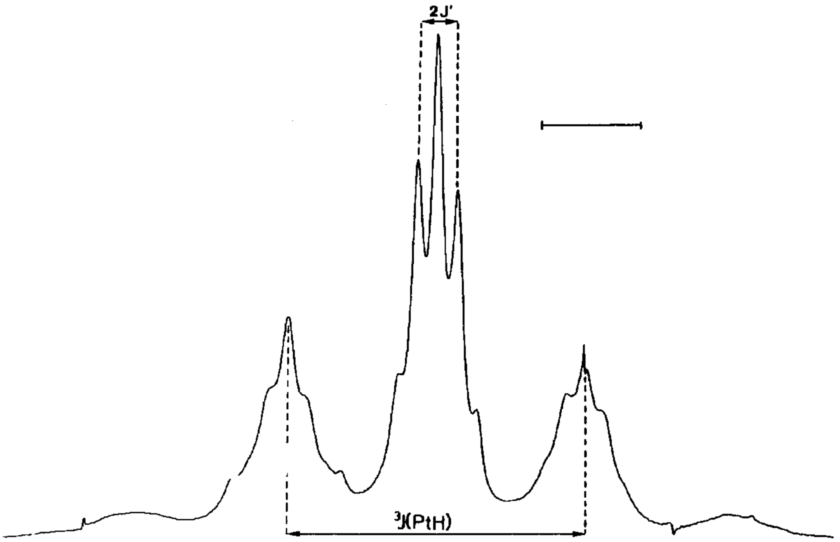


Fig. 2. The ^{1}H NMR (300 MHz) spectrum of $[Pt_2Cl_2(\mu\text{-dppm})_2]$ in CD_2Cl_2, in the presence of 1,8-bis(dimethylamino)naphthalene at ambient temperature. The bar represents 20 Hz.

ties. As for **1** (X = Cl), we find that **1** (X = Br or I) shows no reaction with CH_2Cl_2 in the absence of acidic impurities. Moreover, the ^{195}Pt satellites in the ^{31}P spectrum of pure $[Pt_2Cl_2(\mu\text{-dppm})_2]$ are symmetrical, well-resolved and of equal intensity, in marked contrast to those observed in earlier work [2]. The reason for the collapse of the low frequency satellite in the presence of $[Pt_2Cl_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ is discussed later.

The ^{31}P NMR spectra of **1** also revealed clear $\chi_i(1)$ and $\chi_i(2)$ lines from the $AA'A''A'''XX'$ isotopomers, which permitted the calculation of ^1J(PtPt) for these complexes (see Appendix (i)): a typical spectrum for **1** (X = I) and a computer simulation [40] are illustrated in Fig. 3. The significance of these data are discussed later in this paper. ^{31}P{^{1}H} spectra for samples of pure **1** recorded at −90°C and then at ambient probe temperature revealed a small, but significant, variation in both ^1J(PtP) and ^1J(PtPt). The values of ^1J(PtP) decreased by ca. 1% upon cooling, whereas ^1J(PtPt) increased (see Table 2) by a similar factor.

Although ^1J(PtPt) can readily be calculated from the ^{31}P{^{1}H} spectra of the complexes **1**, the weakness of the $\chi_i(1)$ features (see Fig. 3) in general means that observation of these signals is often difficult (either due to low solubilities or masking by stronger features). In contrast, the analogous features in the ^{195}Pt NMR spectra are relatively much stronger and, even in very complex spin systems (such as found in $[Pt_2(SnCl_3)_2(\mu\text{-dppm})_2]$ [15] and $[Pt_2(PMe_2Ph)_2(\mu\text{-dppm})_2]^{2+}$ [9]) yield unambiguous values of ^1J(PtPt) [41]. The analysis of these spectra is discussed in Appendix (i). The parameters obtained from the ^{195}Pt NMR spectra of **1** are detailed in Table 3, and a typical spectrum, for **1** (X = I), is illustrated in Fig. 4, along with a computer simulation [40]. The slight difference in the values of ^1J(PtPt) in Tables 2 and 3 is attributable to the differing digital resolution (see Appendix (ii)) of the spectrometers upon which the spectra were recorded. The trend in δ(Pt) with change of X is identical to that observed for the complexes $[PtX_2(dppm)]$, discussed above. The complexes **1** resonate at ca. 1000 ppm to lower frequency than $[PtX_2(dppm)]$,

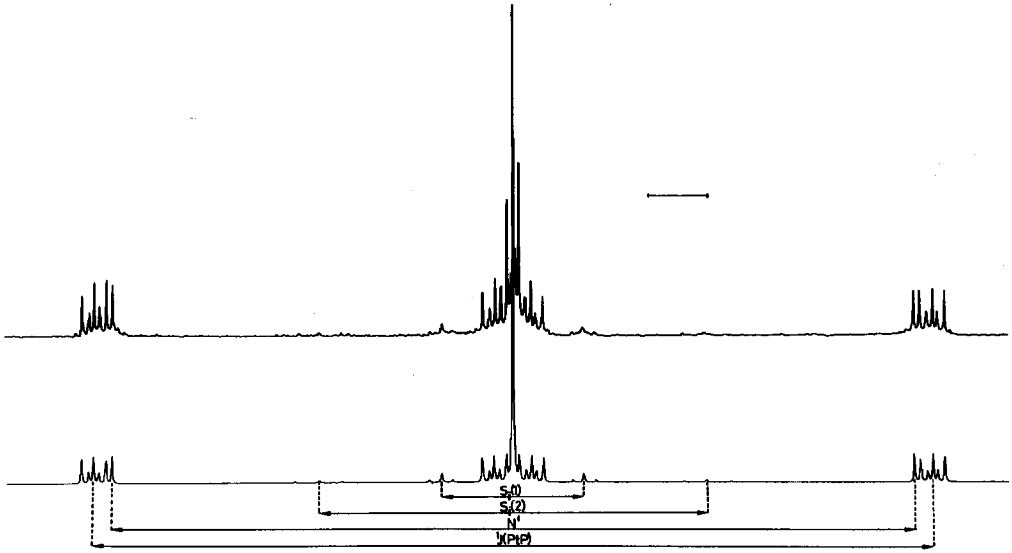
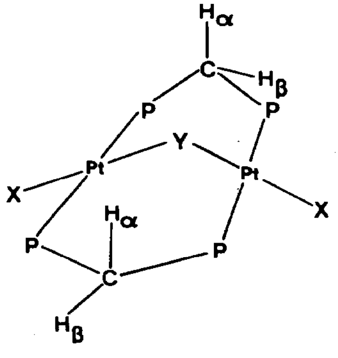


Fig. 3. The $^{31}P\{^1H\}$ NMR spectrum (upper trace) and computer simulation (lower trace) of $[Pt_2I_2(\mu\text{-}dppm)_2]$ in CD_2Cl_2 at −84°C. The bar represents 200 Hz.

suggesting that the presence of the Pt–Pt bond results in a build-up of electron density on the formally platinum(I) atoms {although, from an electronic standpoint, they are perhaps better considered as platinum(II)}. This is in accord with recent XPES data [42], in which the Pt $4f_{7/2}$ binding energy of $[Pt_2Cl_2(\mu\text{-}dppm)_2]$ (72.4 eV) was found to be 0.9 eV less than that of $[PtCl_2(dppm)]$, and 0.8 eV greater than $[Pt(PPh_3)_3]$ or $[Pt(PPh_3)_4]$, and both these observations, taken together, suggest that there is some value in retaining a description of the complexes **1** which formulates them as platinum(I) dimers.

(b) $[Pt_2X_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$ *(X = Cl, Br or I)*

The complexes $[Pt_2X_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$ possess the 'A'-frame structure **2** (X = Cl, Br or I), upon the combined evidence of the VT ^1H, ^{31}P and ^{195}Pt spectra presented in this section. This means that the α and β methylene protons, see **5**, should be non-equivalent for these complexes. However, examination of the 300 MHz ^1H NMR spectra of **2** at ambient probe temperatures revealed the presence of



(5)

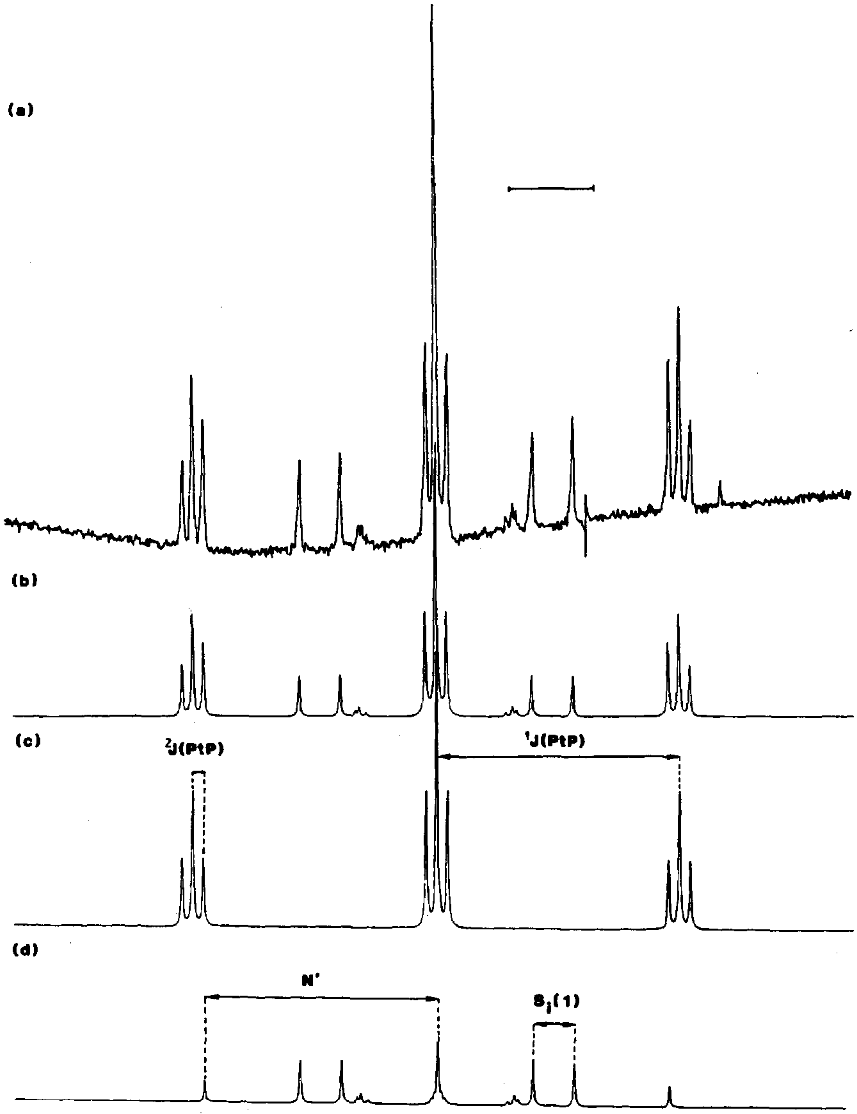


Fig. 4. (a) The ^{195}Pt NMR spectrum of $[Pt_2I_2(\mu\text{-dppm})_2]$ in $C_2D_2Cl_4$ at ambient temperature. The bar represents 1000 Hz. (b) The full computer simulation of (a). (c) The computer simulation of the $AA'A''A'''X$ component of (a). (d) The computer simulation of the $AA'A''A'''XX'$ component of (a).

only one broad CH_2 resonance, with no evidence for any fine structure, either from ^3J(PtH) or ^2J(PH) coupling. When the spectra were recorded under similar conditions, except at 90 MHz, only one signal was again seen, but on this occasion the ^3J(PtH) and J' coupling was fully resolved (see Fig. 5). As lowering the observation frequency is equivalent to raising the temperature, it was clear that a fluxional process occurs with a coalescence temperature close to room temperature. The VT ^{1}H NMR spectra of **2** ($X = Cl$) are presented in Fig. 6, and it is immediately clear that the fluxional process involves 'A'-frame inversion, which equivalences the α and β protons of structure **5** whilst retaining the presence of the bridging proton (n.b.

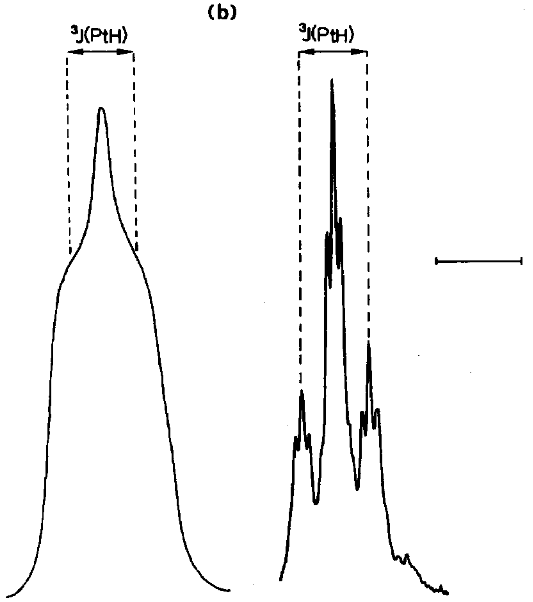


Fig. 5. The ^{1}H NMR spectra of $[Pt_2Br_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ in CD_2Cl_2 at ambient temperature at (a) 300 and (b) 90 MHz. The bar represents 50 Hz.

the hydridic region of the spectrum is temperature invariant between −50 and +30°C [43]). The mechanism of this inversion is discussed in detail, for all 'A'-frame complexes containing the $\{Pt_2(dppm)_2\}$ skeleton, elsewhere [29]. For **2** (X = Cl), T_c is +10°C at 400 MHz, corresponding to an approximate $\Delta G^{\neq}$ for the 'A'-frame inversion process of 53.95 kJ mol^{-1} [44].

Consideration of the values of $\delta(H)$ for the hydride bridge in **2** shows a correlation with the nature of X, the shift becoming increasingly less negative (i.e. less hydridic) with increasing *trans* influence of X (see Table 1); no such correlation exists for $\delta(CH_2)$.

The $^{31}P\{^1H\}$ spectra of **2** were recorded at < -70°C in the presence of an excess of acid, to avoid problems with possible dissociation (see later), and the parameters (obtained by routine analysis) are listed in Table 2, along with the calculated values (see Appendix (i)) of ^1J(PtPt). The spectral profile for the complexes **2** is similar to that for the complexes **1**, and this was also the case for their ^{195}Pt NMR spectra (see Table 3).

(c) $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$

The ^{31}P and ^{195}Pt NMR spectra of complex **3** merit more than passing consideration, but the ^{1}H spectra have been considered in detail recently [25,29], and will be discussed no further here (see Table 1). However, the low value of ^1J(PtPt) at ca. 530 Hz (cf. Tables 2 and 3) produces interesting perturbations to both the ^{31}P (see Fig. 7a) and ^{195}Pt (see Fig. 7c) spectra of **3**. In both spectra, $\chi_o(1)$ lines were observed (for the first time for complexes containing the $\{Pt_2(dppm)_2\}$ skeleton), which enabled direct measurement of ^1J(PtPt), as described in Appendix (i). The $\chi_i(1)$ and $\chi_o(1)$ lines are significantly more prominent in the ^{195}Pt spectrum than in the ^{31}P spectrum, in which they are barely discernible.

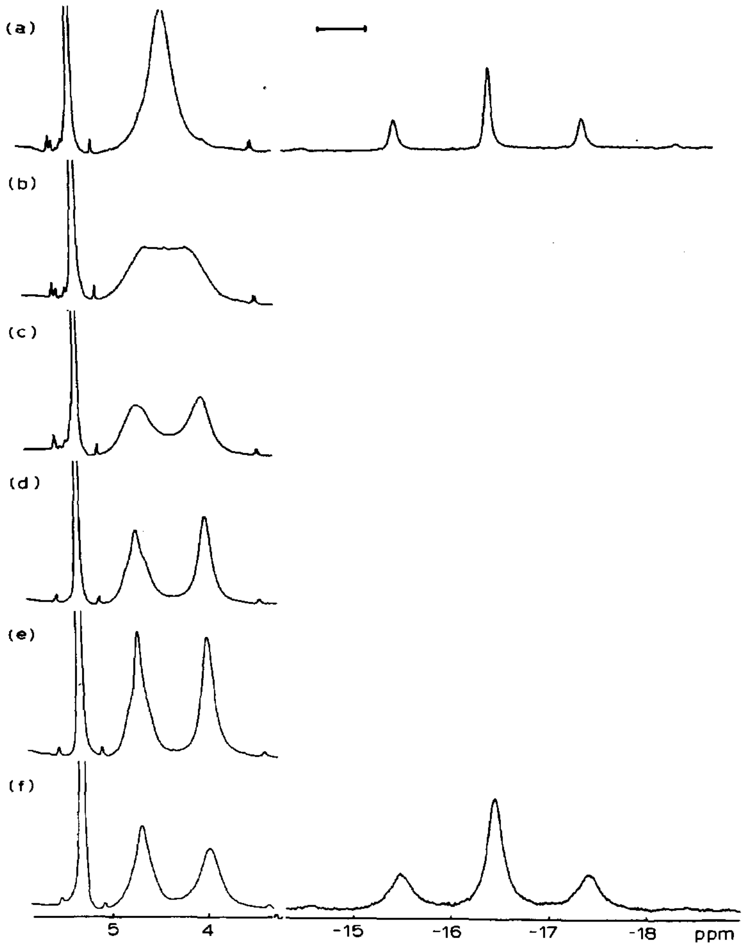
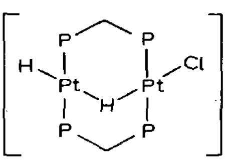


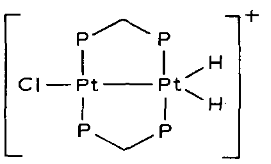
Fig. 6. The ^1H NMR (400 MHz) spectra of $[Pt_2Cl_2(\mu\text{-}H)(\mu\text{-dppm})_2]^+$ in CD_2Cl_2 at (a) +23, (b) +10, (c) 0, (d) −10, (e) −30, and (f) −50°C. The bar represents 200 Hz.

(d) “$[Pt_2H_2(\mu\text{-}Cl)(\mu\text{-dppm})_2]^+$”

$[Pt_2H_2(\mu\text{-}Cl)(\mu\text{-dppm})_2][PF_6]$ (**4**) was, on the basis of ambient temperature ^1H and ^{31}P NMR spectroscopy, originally assigned the anticipated ‘A’-frame structure [16]. However, the variable temperature ^1H (Fig. 8), ^{31}P (Fig. 9) and ^{195}Pt (Fig. 10) spectra of this complex unambiguously show that structure **4** only reflects the time-averaged structure, and that its low-temperature form contains two different platinum and hydrogen atoms and two different types of phosphorus atoms. Possible structures are **6**, **7** and **8**. Structure **7** can be immediately eliminated, as both protons are equivalent.



(6)



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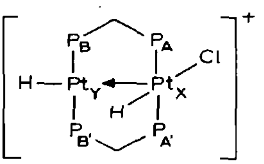
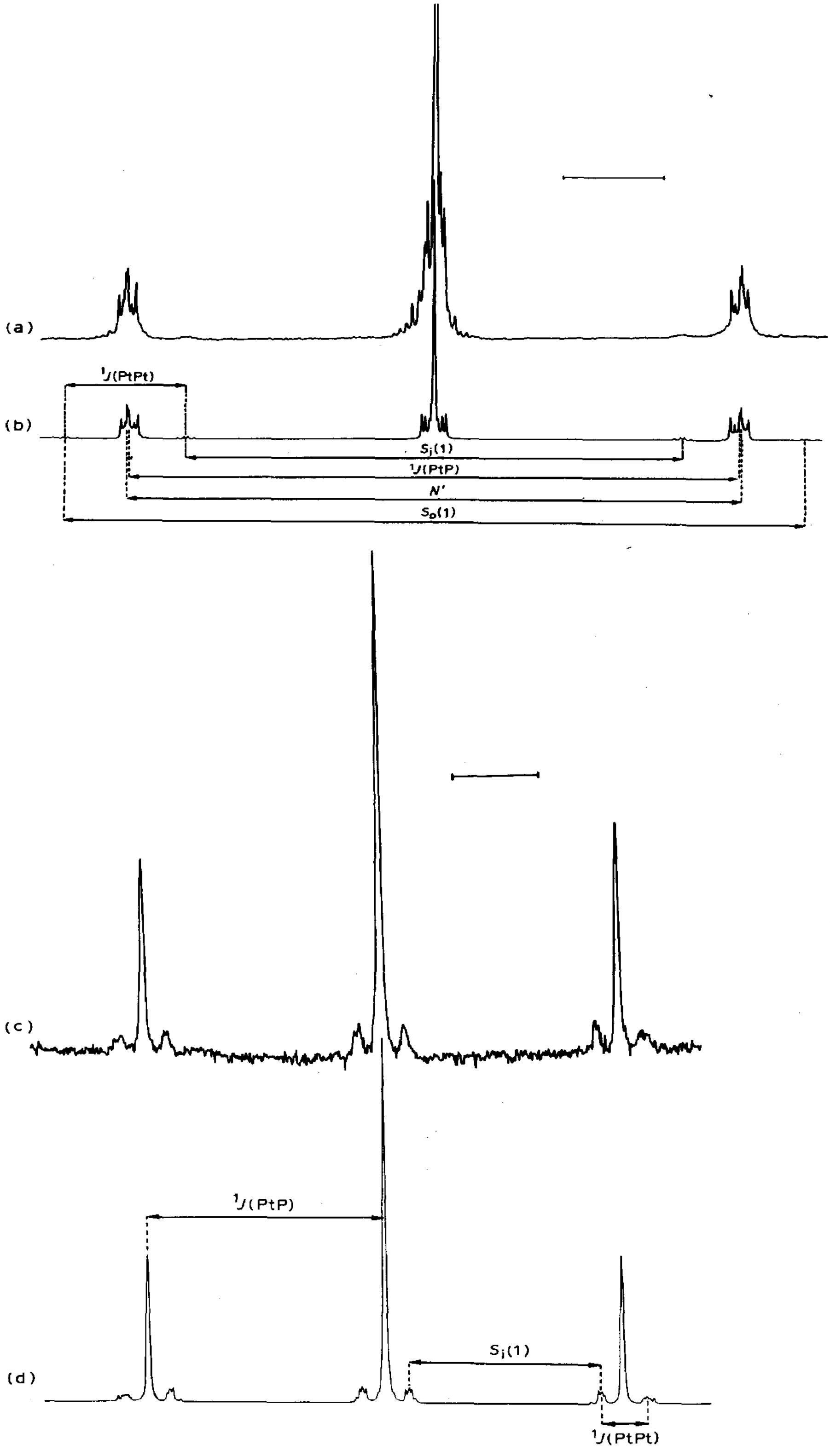


(8)


(a)
^1J(PtPt)
(b)
S_i(1)
^1J(PtP)
N'
S_o(1)
(c)
^1J(PtP)
S_i(1)
(d)
^1J(PtPt)

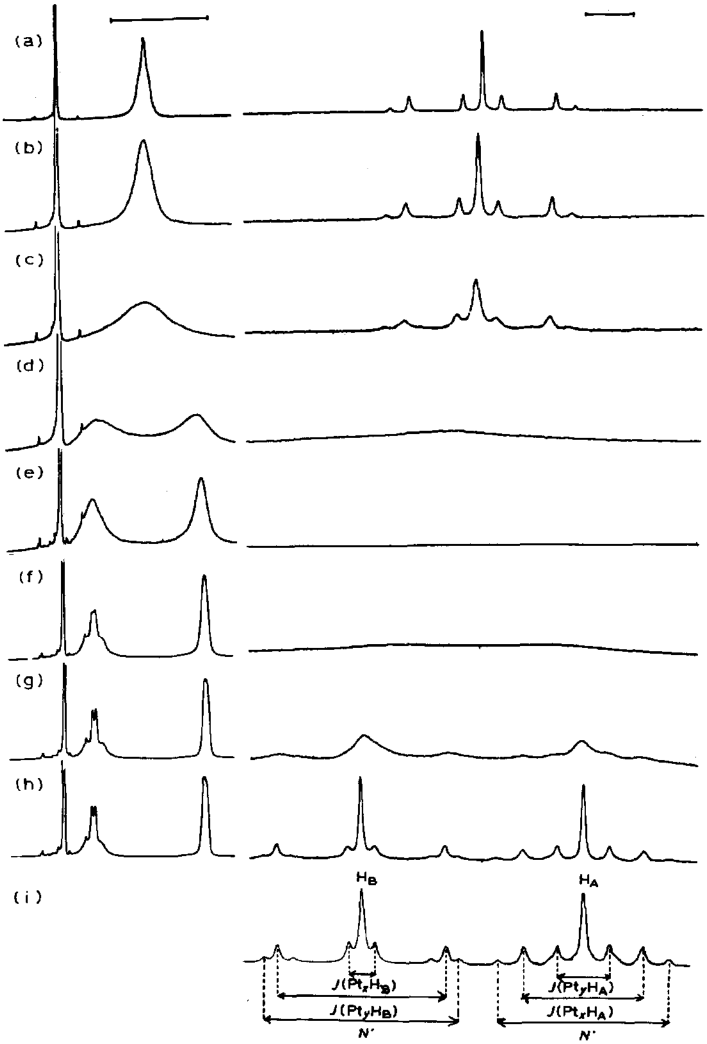
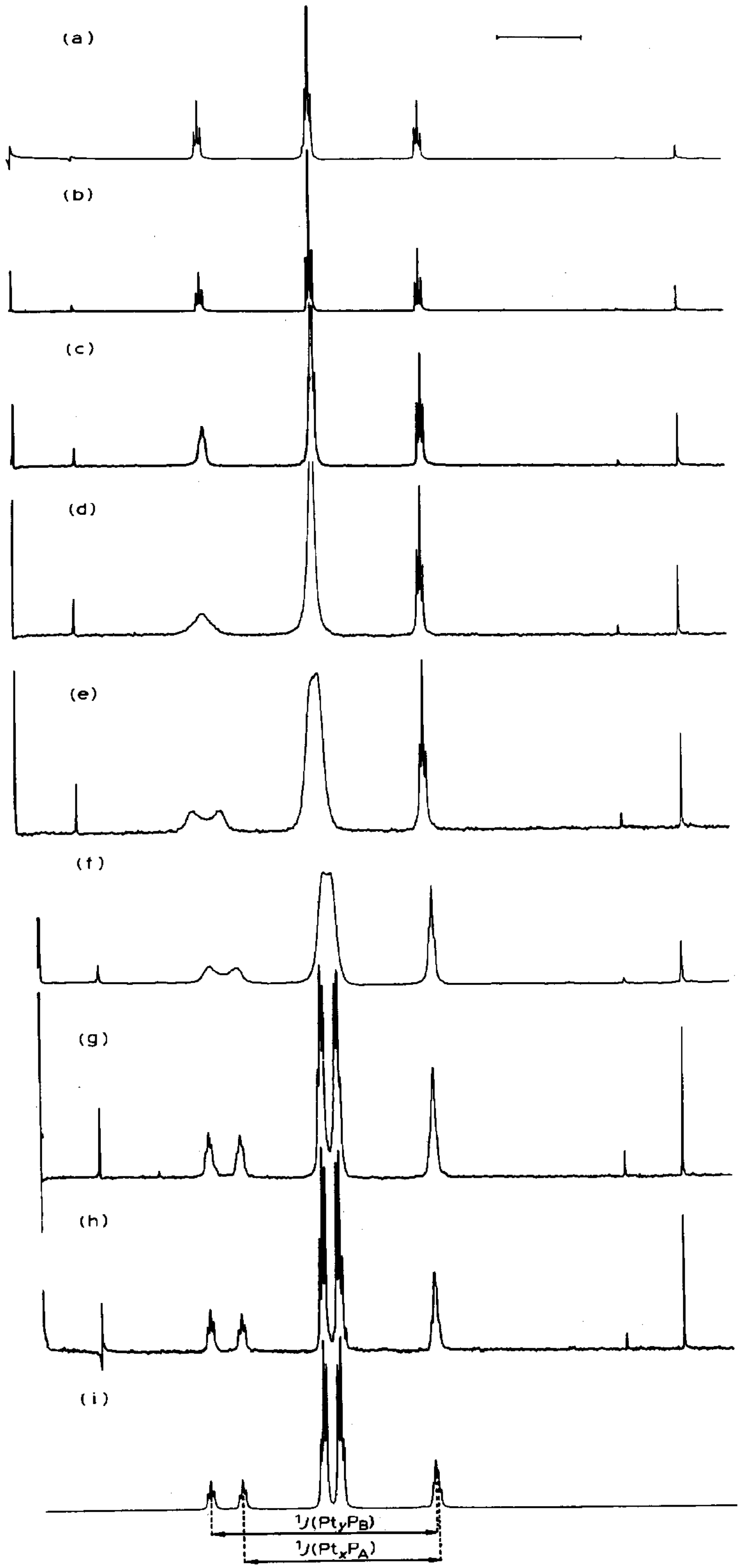


Fig. 8. The ^1H NMR (400 MHz) spectra of $[Pt_2H_2(\mu\text{-Cl})(\mu\text{-dppm})_2]^+$ in CD_2Cl_2 at (a) +23, (b) +5, (c) −5, (d) −15, (e) −25, (f) −35, (g) −45, and (h) −55°C. The bars represent 400 Hz. (i) represents the computer simulation of the hydride region of (h).

The low temperature ^1H spectrum (Fig. 8) shows that both hydrides are terminal, and so structure **6** can also be discounted. Structure **8** appears particularly attractive as (i) it is the *trans*-analogue of the crystallographically characterised *cis*-$[Pt_2Me_3(\mu\text{-dppm})_2]^+$ salt [12] and (ii) it lends itself to a facile intramolecular fluxional process (eq. 2). The detailed analyses of the ^1H, ^{31}P and ^{195}Pt spectra are also supportive of structure **8**, as will now be demonstrated. Structure **8** may be considered as a 'T'-frame structure [46].

Fig. 7. (a) The $^{31}P\{^1H\}$ NMR spectrum of $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ in CD_2Cl_2 at −86°C. The bar represents 450 Hz. (b) The full computer simulation of (a). (c) The ^{195}Pt NMR spectrum of $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ in CD_2Cl_2 at −86°C. The bar represents 1000 Hz. (d) The full computer simulation of (c).


(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
${}^1J(Pt_yP_B)$
${}^1J(Pt_xP_A)$

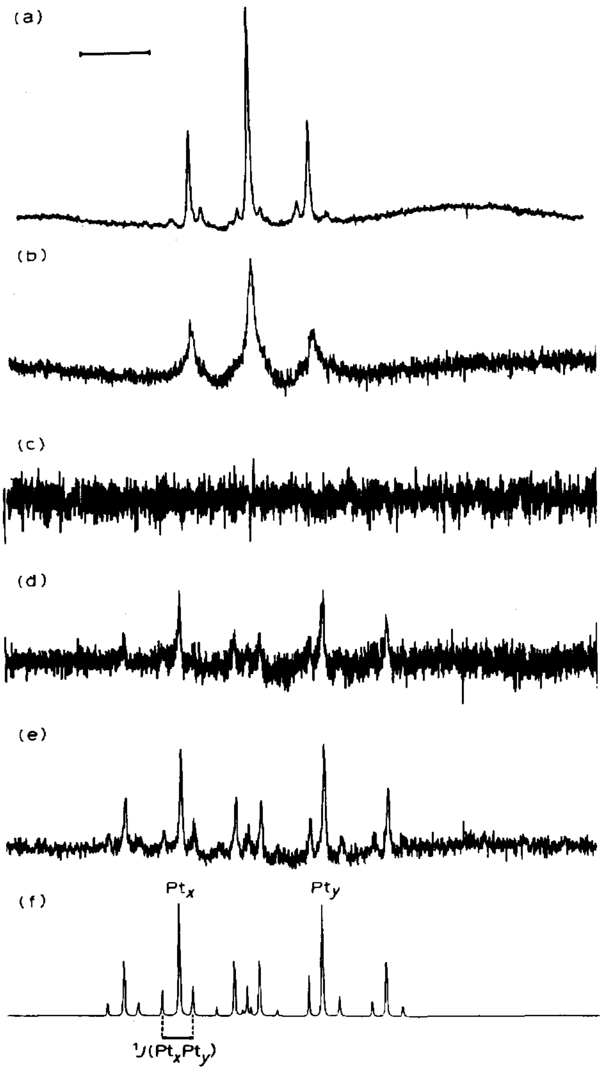
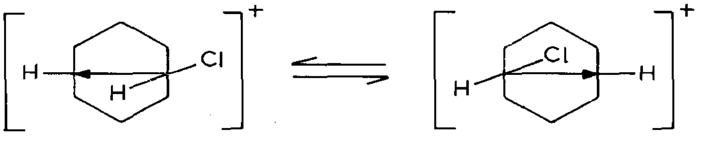


Fig. 10. The $^{195}Pt\{^1H\}$ (19.16 MHz) NMR spectra of $[Pt_2H_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2][PF_6]$ in CD_2Cl_2 at (a) +30, (b) −2, (c) −25, (d) −58, and (e) −70°C. The bar represents 3000 Hz. (f) represents the computer simulation of the hydride region of (e).



(2)

The low-temperature ^{31}P spectrum of $[Pt_2H_2Cl(\mu\text{-}dppm)_2]^+$ is characteristic of an *AA'BB'/AA'BB'X/AA'BB'Y/AA'BB'XY* spin system {cf. ref. 6} and its routine

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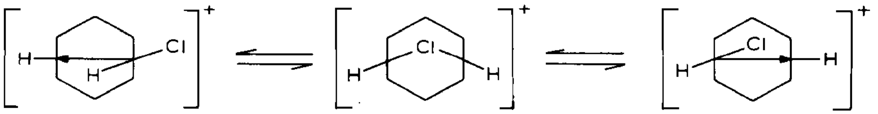
Fig. 9. The $^{31}P\{^1H\}$ NMR spectra of $[Pt_2H_2(\mu\text{-}Cl)(\mu\text{-}dppm)_2][PF_6]$ in CD_2Cl_2 at (a) +30, (b) −2, (c) −51, (d) −55, (e) −69, (f) −71, (g) −75, and (h) −85°C. The bar represents 1000 Hz. (i) represents the computer simulation of (h).

analysis yields the parameters detailed in Table 2, and confirmed by computer simulation: it does not yield a value for ^1J(PtPt). However, this can be measured directly from the low-temperature ^{195}Pt spectrum (Fig. 10), as indicated in the computer simulations (Fig. 10). Despite a chemical shift difference between Pt_x and Pt_y of 326 ppm, the ratio of $\delta(Pt_x-Pt_y)/J(Pt_xPt_y)$ is ca. 4.75, well within the range of second-order effects, and this accounts for the unsymmetrical intensity distribution in the signals of the *AA'BB'XY* isotopomer. The value of ^1J(PtPt) for **8** of 1320 Hz is higher than that measured from the ^{195}Pt spectrum of the time-averaged structure (1260 Hz); this lower value arises from the expected (see later) small contribution from the 'A'-frame isomer **4**, as shown in eq. 3. The ambient temperature ^{31}P spectrum of $[Pt_2H_2Cl(\mu\text{-dppm})_2]^+$ showed no discernable $\chi_i(1)$ lines; computer simulation using parameters determined from the ^{195}Pt NMR spectrum confirmed that although these signals carried a very low intensity, they should have been just detectable: the reason for the absence is not clear.



(3)

The ^{1}H NMR spectrum of $[Pt_2H_2Cl(\mu\text{-dppm})_2]^+$ at low temperature (Fig. 8) is readily assigned, and a consideration of the magnitude of the coupling constants ^2J(PtH) allows unambiguous identification of Pt_xH and Pt_yH signals (see Table 1). The hydride resonances (Fig. 8), the phosphorus resonances (Fig. 9) and the platinum resonances (Fig. 10) undergo a coalescence at various temperatures, but all correspond to the same fluxional process. Thus, for the hydride resonances, T_c −38°C and $\Delta\nu$ 1773 Hz (at 400 MHz) correspond to $\Delta G^{\neq}$ 40.9 kJ mol^{-1} [44]; for the phosphorus resonances, T_c −68°C and $\Delta\nu$ 205 Hz (at 36.27 MHz) correspond to $\Delta G^{\neq}$ is 39.2 kJ mol^{-1} [44]; for the platinum resonances, T_c −25°C and $\Delta\nu$ 6246 Hz (at 19.16 MHz) correspond to $\Delta G^{\neq}$ 40.7 kJ mol^{-1} [44]. Thus, for the fluxional process illustrated in eq. 2, given the limitations of the Eyring equation [44], $\Delta G^{\neq}$ is 40 ± 1 kJ mol^{-1}. This process thus occurs significantly faster than the "'A'-frame inversion" which equivalences the α and β protons of structure **8** {and, incidentally, structure **4**}, which is observed in the collapse of the two methylene resonances (observed at low temperature) to a broad singlet with T_c −16°C and $\Delta\nu$ 464 Hz (at 400 MHz), corresponding to $\Delta G^{\neq}$ 47.8 kJ mol^{-1}. The mechanism for this inversion is discussed elsewhere [29].

^{31}P and ^{195}Pt NMR spectra of related 'A'-frame complexes

The 'A'-frame complexes {of structure type **5**} $[Pt_2Me_2(\mu\text{-Cl})(\mu\text{-dppm})_2][PF_6]$ and $[Pt_2Cl_2(\mu\text{-Y})(\mu\text{-dppm})_2]$ ($Y = CH_2$, S or SO_2) were studied by ^{31}P and ^{195}Pt NMR spectroscopy (see Tables 2 and 3).

In view of the fluxional behaviour exhibited by $[Pt_2H_2Cl(\mu\text{-dppm})_2][PF_6]$, it was clearly of some interest to see if $[Pt_2Me_2(\mu\text{-Cl})(\mu\text{-dppm})_2][PF_6]$ showed a similar phenomenon. The low temperature (−70°C) ^{31}P NMR spectrum of this latter complex was essentially identical to its ambient temperature spectrum (apart from the normal slight variations of J with temperature), and showed no signs of broadening or coalescence phenomena. It was thus concluded that this species was,

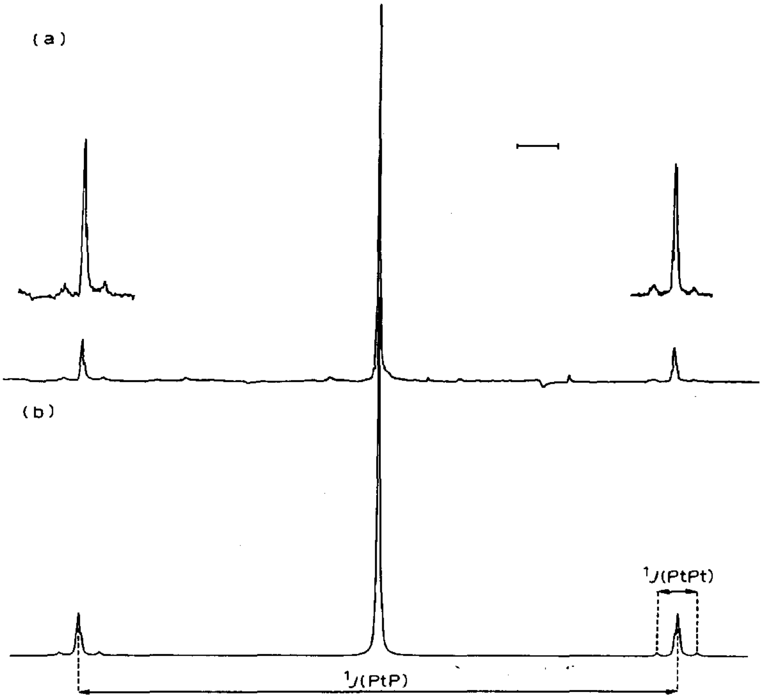


Fig. 11. (a) The $^{31}P\{^1H\}$ NMR spectrum of $[Pt_2Cl_2(\mu\text{-}S)(\mu\text{-}dppm)_2]$ in CD_2Cl_2 at −70°C. The bar represents 200 Hz. (b) The full computer simulation of (a).

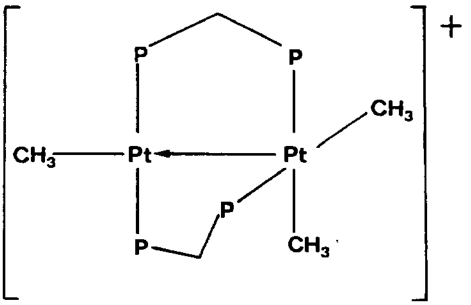
indeed, a genuine 'A'-frame complex, or that the barrier for fluxionality was extremely low. Moreover, the low value of ^1J(PtPt) of 450 Hz {cf. ^1J(PtPt) of 2745 Hz for $[Pt_2Me_3(\mu\text{-}dppm)_2][PF_6]$, vide infra} would suggest that the contributions of 'T'-frame structures of type **8** are so small as to be neglected, if an equilibrium similar to eq. 3 existed. Thus, overall, the complex is best described as a genuine 'A'-frame species.

The ^{31}P NMR spectra of $[Pt_2Cl_2(\mu\text{-}Y)(\mu\text{-}dppm)_2]$ ($Y = CH_2$, S or SO_2) were redetermined (cf. [5]), and the ^{195}Pt NMR spectra were measured for the first time. These spectra led to the first determinations of ^1J(PtPt) for these compounds. Unusually, in the case of $[Pt_2Cl_2(\mu\text{-}SO_2)(\mu\text{-}dppm)_2]$, an accurate value of ^1J(PtPt) could not be obtained from the ^{195}Pt NMR spectrum, as the χ_i and χ_o lines were obscured by the phosphorus satellites, and only an upper limit could be established. Fortunately, the ^{31}P spectrum of this complex showed well-defined $\chi_i(1)$ lines, from which ^1J(PtPt) was calculated (see Table 2).

In the case of $[Pt_2Cl_2(\mu\text{-}S)(\mu\text{-}dppm)_2]$, the platinum satellites observed in the ^{31}P NMR spectrum were very broad (which, in an earlier paper [5], led to the complex incorrectly being assumed to be fluxional at ambient temperatures). Resolution enhancement did not improve the definition, nor did cooling the sample to −70°C (Fig. 11). This demonstrated that no fluxional process was occurring, and that the signals were naturally broad. Judicious selection of ^2J(PtP) and ^3J(PP) allowed the observed spectrum to be computer simulated (Fig. 11), and these values are included in Table 2. The value of ^2J(PtP) thus evaluated was consistent with the observed profile of the ^{195}Pt NMR spectrum.

^{31}P and ^{195}Pt NMR spectra of $[Pt_2Me_3(\mu\text{-}dppm)_2]^+$

Having established that $[\mathrm{Pt_2H_2Cl}(\mu\text{-dppm})_2]^+$ possesses the 'T'-frame structure **8**, it was natural to compare it with $[\mathrm{Pt_2Me_3}(\mu\text{-dppm})_2]^+$ (**9**), which has been examined crystallographically [12] and the presence of the donor–acceptor metal–metal bond unambiguously established. The principal difference between **8** and **9** is that **8** contains mutally *trans* phosphine ligands on the donor metal, whereas **9** has mutually *cis* phosphine ligands. The literature value of ^1J(PtPt) for **9** of 332 Hz [12] (assigned from a best fit simulation of the ^{31}P NMR spectrum, which is rather complex) was significantly, and surprisingly, lower than that found for **8**. Given the uncertainties in establishing ^1J(PtPt) in this manner, the ^{195}Pt NMR spectrum of **9** was recorded (see Fig. 12), which unambiguously (by direct observa-



(9)

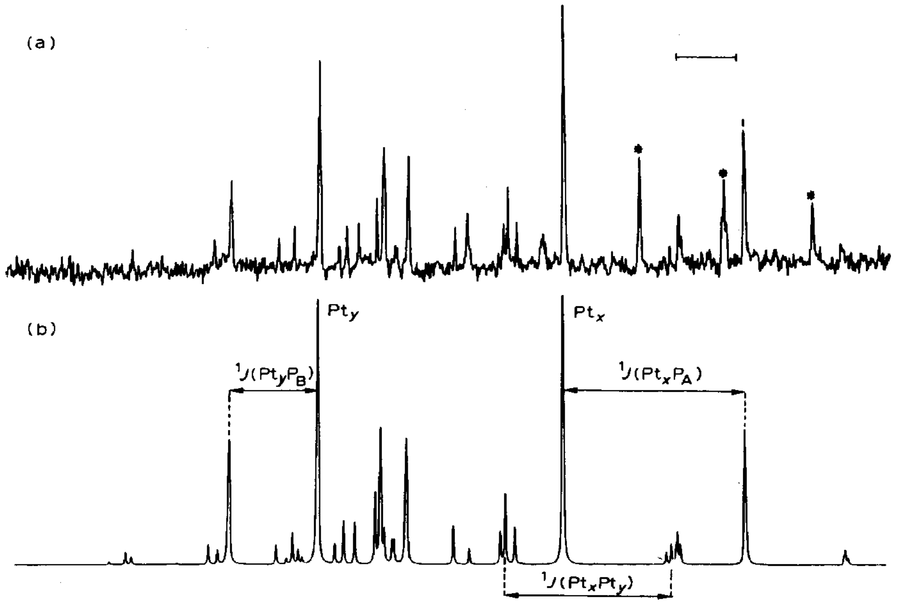


Fig. 12.(a) The ^{195}Pt NMR spectrum of $[\mathrm{Pt_2Me_3}(\mu\text{-dppm})_2][\mathrm{PF_6}]$ in $(\mathrm{CD_3})_2\mathrm{CO}$ at ambient temperature. The bar represents 1000 Hz, and the most intense impurity peaks are marked with an asterisk. (b) The full computer simulation of (a).

tion) yielded a value of ${}^1J$(PtPt) of 2745 Hz; this new value is now in accord with the value measured for **8** (see Table 3).

Significance of ${}^1J$(PtPt) values

Goodfellow and coworkers [27], in an extensive study of ${}^1J$(PtPt) in dimeric platinum complexes, concluded that "coupling constants vary wildly for compounds with apparently very similar structures and there is no obvious relationship with the nature of the link between the platinum atoms, especially with their separation". However, the structures examined were rather disparate, and it would be of interest to examine a series of structurally related species, in this case containing a common $\{Pt_2(\mu\text{-dppm})_2\}$ skeleton. Figure 13 shows a plot of r(PtPt) against ${}^1J$(PtPt), and it is clear that there is a relationship between these parameters.

For the complexes **1** (X = Cl, Br or I), the values of ${}^1J$(PtPt) follow the order I > Br > Cl, which (as suggested by Goodfellow and coworkers [27]) correlates with the order expected according to the *trans*-influence of the halide ions. However, for the cationic complexes $[Pt_2L_2(\mu\text{-dppm})_2]^{2+}$ (L = NH_3, py or CO) [9], the ${}^1J$(PtPt) values follow the order NH_3 > py > CO, which is the exact opposite of the order predicted by the *trans* influence of the ligands, and for the complexes **2** (X = Cl, Br or I), ${}^1J$(PtPt) follows the order Br > Cl > I! Thus, despite its attraction, a simple correlation of ${}^1J$(PtPt) with the *trans* influence of the terminal ligands is not supported by the experimental data.

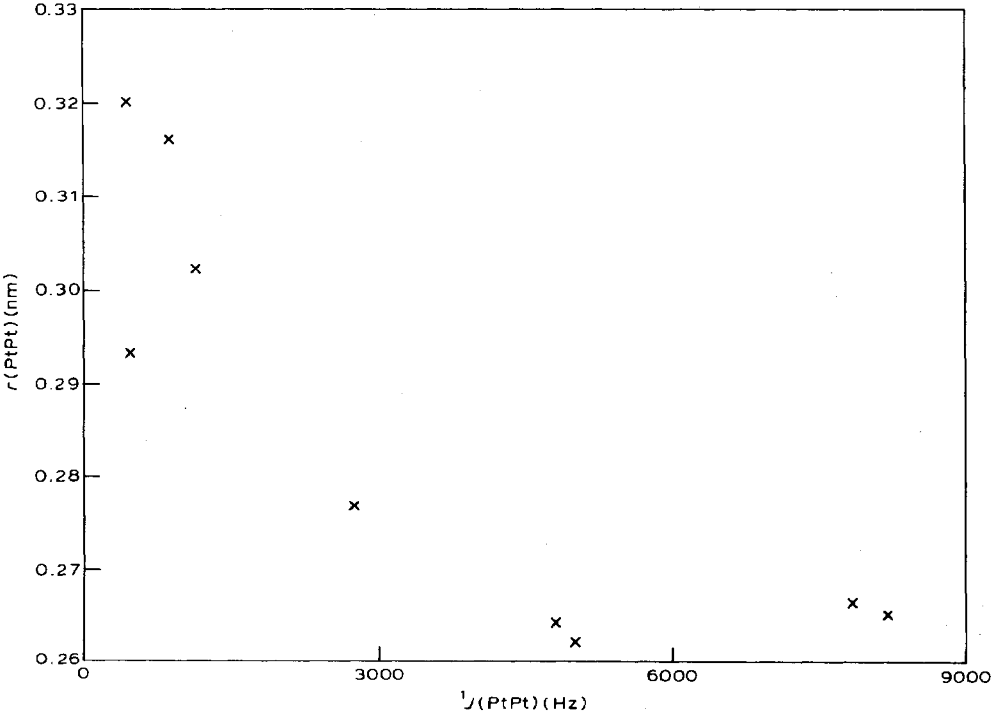


Fig. 13. A plot of r(PtPt) (nm) against ${}^1J$(PtPt) (Hz) for a wide range of complexes containing the $\{Pt_2(\mu\text{-dppm})_2\}$ skeleton.

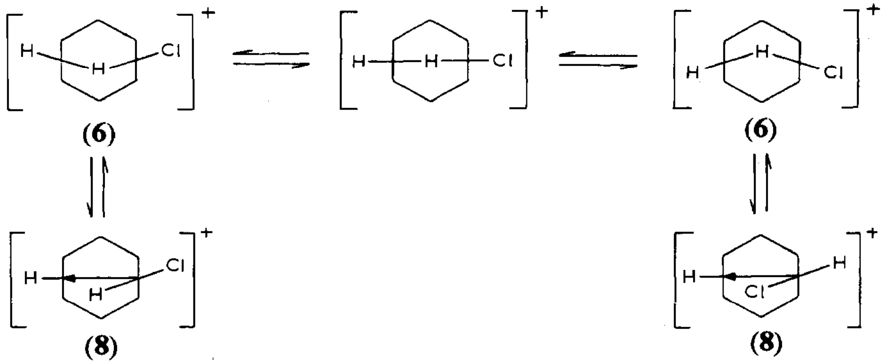
In considering complexes **1** and the 'A'-frame complexes derived from them, it is relevant to consider the extended Hückel molecular orbital (EHMO) calculations reported by Hoffman and Hoffmann [26], and to compare the predictions made in that paper with our new experimental findings. The EHMO calculations suggested that the degree of direct metal–metal bonding in complexes of skeleton **5** was determined by the nature of the bridging ligand, Y. If Y is a four-electron donor (such as Cl^-, S^{2-}, CH_2^{2-}, CO^{2-} or SO_2^{2-}), then the two new bridge bonding orbitals, of a_1 and b_2 symmetry, which are respectively M–M bonding and M–M antibonding in character, will both be filled. This results in no nett metal–metal bonding between the two platinum atoms. If Y is only a two-electron donor (such as H^-), however, then only the a_1 bonding combination of orbitals is occupied, resulting in a nett Pt–Pt bonding interaction. If one makes the reasonable assumption that the degree of metal–metal interaction will be reflected in the value of ^1J(PtPt), then it is possible to test these predictions. An examination of Tables 2 and 3 reveals considerable support for the theory. The ^1J(PtPt) values for the complexes **2**, which are lower (as would be expected) than for the complexes **1**, are in the range 3500–5500 Hz, and are significantly larger than those for $[Pt_2Cl_2(\mu\text{-}Y)(\mu\text{-dppm})_2]$ (Y = S, CH_2 or SO_2), which are all < 900 Hz. The only problems with the predictions of the EHMO calculations for $[Pt_2X_2(\mu\text{-}Y)(\mu\text{-dppm})_2]^{n+}$ arise when the terminal X ligands have a very high *trans*-influence. Thus, $[Pt_2Me_2(\mu\text{-Cl})(\mu\text{-dppm})_2]^+$, $[Pt_2Me_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ and $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ exhibit ^1J(PtPt) at 450, 464 and 530 Hz, respectively. The first complex, although having the smallest ^1J(PtPt) value of the three, does not differ from the last two in the manner expected. However, the reason for this must lie in the peculiarly low values of ^1J(PtPt) for the last two compounds, as the value of ^1J(PtPt) for $[Pt_2Me_2(\mu\text{-Cl})(\mu\text{-dppm})_2]^+$ is in the range found for the other complexes with four-electron donor bridges. Although the reason for this anomaly is not clear, it is interesting to note that the two complexes with the unusually low value of ^1J(PtPt) are also the complexes which show the smallest activation energies towards 'A'-frame inversion, the key step in which involves an intermediate with a linear Pt–H–Pt skeleton [29].

Finally, it is of interest to note that the values of ^1J(PtPt) for the two donor–acceptor metal–metal bonded complexes, $[Pt_2Me_3(\mu\text{-dppm})_2]^+$ and $[Pt_2H_2Cl(\mu\text{-dppm})_2]^+$, are of similar magnitude, and it was, indeed, the high value observed for this parameter of the latter complex which prompted our VT NMR study.

Implications of structure 8 for the photoelimination of H_2 from compound 4

Both Geoffroy [28] and Puddephatt [11] have observed the photoelimination of H_2 from $[Pt_2H_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ (**3**), and Geoffroy [28] has also observed a similar reaction for $[Pt_2H_2Cl(\mu\text{-dppm})_2]^+$ (**4**). For complex **3** in MeCN, the quantum yield for the photoproduction of dihydrogen was high ($\Phi = 0.62$; λ 366 nm), and a mechanism involving the facile photoelimination of two hydrogen atoms attached to the same platinum atom was envisaged [28]. For complex **4**, the quantum yield for the formation of dihydrogen was much lower ($\Phi = 0.06$; λ 336 nm), but to explain the surprising observation of any H_2 evolution at all, Geoffroy [28] was led to propose that the reaction must proceed via a photo-activated intermediate with both hydrides bound to the same platinum atom {such as **6** or **7**}, which was formed by an intramolecular hydride migration. However, the observation that $[Pt_2H_2Cl(\mu\text{-}$

dppm$)_2]^+$ possesses the 'T'-frame structure **8** and not the 'A'-frame structure **4** leads us to suggest that intermediate **6** is the photoactive species, and that it is formed by a thermal (rather than photochemical) route, as illustrated in eq. 4. This is the thermal



(4)

route by which "'A'-frame inversion" occurs, with $\Delta G^{\neq}$ 47.8 kJ mol^{-1} [29]. It occurs readily at ambient temperatures in fluid solution, and thus a significant quantity of intermediate **6** is present in thermal equilibrium with **8**.

Intermolecular proton transfer between [$Pt_2Cl_2(\mu$-dppm$)_2$] and [$Pt_2Cl_2(\mu$-H$)(\mu$-dppm$)_2]^+$

Although the aforementioned processes examined by dynamic NMR spectroscopy have been kinetically first-order, involving inversions of configuration (i.e. 'A'-frame inversion [29]), second-order reversible processes, frequently involving proton-transfer, can also be observed by this technique, and the Eyring equation used to calculate their free energy of activation [47]. The ^{31}P NMR spectra of the compounds reported originally [2] as "[$Pt_2Cl_2(\mu$-dppm$)_2$] · $0.5CH_2Cl_2$" and "[$Pt_2Cl_2(\mu$-dppm$)_2$] · C_6H_6" showed the presence of two or three platinum-containing components, and in each case the ^{31}P NMR signals from two of these components were seen to coalesce. As it was subsequently shown that the two components which showed this phenomenon were [$Pt_2Cl_2(\mu$-dppm$)_2$] and [$Pt_2Cl_2(\mu$-H$)(\mu$-dppm$)_2]^+$, it seemed likely that proton transfer was occurring between them. To test this hypothesis, an independent experiment was conducted, in which mixtures (1/2, 1/1 and 2/1) of pure [$Pt_2Cl_2(\mu$-dppm$)_2$] and [$Pt_2Cl_2(\mu$-H$)(\mu$-dppm$)_2]^+$ were dissolved in CD_2Cl_2, and the VT ^{31}P NMR spectra were recorded. All three mixtures yielded a value of T_c of -45°C, and since $\Delta\nu$ was 166.8 Hz, a value of $\Delta G^{\neq}$ of 44.1 kJ mol^{-1} was obtained for this intermolecular proton-transfer process. Comparison with the value of $\Delta G^{\neq}$ of 53.95 kJ obtained for the intramolecular 'A'-frame inversion of pure [$Pt_2Cl_2(\mu$-H$)(\mu$-dppm$)_2]^+$ indicates that the two processes are quite different, although the nett result of both processes is 'A'-frame inversion, since rapid proton transfer between **2** (X = Cl) and small amounts of **1** (X = Cl) results in the equivalencing of the H_α and H_β protons of the methylene group of the dppm ligands.

Finally, it should be noted that the observation of this proton-transfer reaction explains why ^{195}Pt NMR spectra of [$Pt_2Cl_2(\mu$-dppm$)_2$], at ambient temperature, were often broad and poorly resolved. The presence of **2** (X = Cl) as an impurity results in proton-transfer occurring, which broadens the signal due to **1** (X = Cl). Indeed, calculation of the coalescence temperature for the ^{195}Pt NMR spectra, using

$\Delta G^{\neq}$ 44.1 kJ mol^{-1} and $\Delta\nu$ 5500 Hz, yields a value of $T_c \sim -3$°C which suggests that at room temperature, a fast exchange of H^+ will be occurring, and that the ^{195}Pt signal will be very broad.

Experimental

The syntheses of $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2][PF_6]$, $[Pt_2H_2Cl(\mu\text{-dppm})_2][PF_6]$, $[Pt_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2]$, $[Pt_2Cl_2(\mu\text{-}S)(\mu\text{-dppm})_2]$ and $[Pt_2Cl_2(\mu\text{-}SO_2)(\mu\text{-dppm})_2]$ have been reported elsewhere [5,16]. $[PtBr_2(cod)]$ and $[PtI_2(cod)]$ [48] were used to prepare $[PtBr_2(dppm)]$ and $[PtI_2(dppm)]$ [2]. $[Pt_2Me_3(\mu\text{-dppm})_2][PF_6]$ and $[Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-dppm})_2][PF_6]$ were generously provided by Dr. M.P. Brown, to whom we are very grateful. NMR spectra were recorded on JEOL FX-90Q {ambient and variable temperature ^{31}P (36.27 MHz) and ^{195}Pt (19.16 MHz) NMR}, Bruker WH-90 {ambient ^1H (90.00 MHz) and ^{31}P (36.43 MHz) NMR}, Bruker WH-300 {ambient ^1H (300.13 MHz) and ^{31}P (121.49 MHz) NMR}, and Bruker WH-400 {ambient and variable temperature ^1H (400.13 MHz), ^{31}P (161.96 MHz) and ^{195}Pt (85.56 MHz) NMR} spectrometers.

$K_2[PtCl_4]$ was obtained from Johnson Matthey and dppm from Strem Chemical Co. CD_2Cl_2 (> 99.6%) was obtained from Aldrich Chemical Co., while $C_2D_2Cl_4$ (> 99%) was obtained from Kor Isotopes Ltd. $[NH_4][PF_6]$ used was of > 95% purity and obtained from Aldrich Chemical Co. Concentrated tetrafluoroboric acid (40%) was obtained from BDH. $Ag[PF_6]$ was obtained from Alfa-Ventron and was stored in a dessicator, to prevent hydrolysis. Methanol was dried by heating under reflux over magnesium turnings for ca. 6 h. Light petroleum (80–100°C) was redistilled and the fraction boiling between 80 and 100°C was collected and used.

Investigation of the nature and identity of the compound reported [2] as "$[Pt_2Cl_2(\mu\text{-dppm})_2] \cdot C_6H_6$"

$[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]Cl$ (0.3 g, 0.25 mmol) was suspended in benzene (13 cm^3), and concentrated hydrochloric acid (0.5 cm^3) was added. The mixture was heated under reflux for 5 min. A yellow solution was formed, decanted from a small amount of brown residue and allowed to cool. On slow addition of 2,2,4-trimethylpentane (50 cm^3) a fine lemon-yellow solid formed; the mixture was allowed to stand at 5°C overnight. The very fine solid was collected by filtration, washed with 2,2,4-trimethylpentane (5 cm^3) and dried in vacuo for ca. 4 h. The solid (ca. 100 mg) was dissolved in CD_2Cl_2 (2 cm^3) and the ^{31}P NMR (36.27 MHz) spectrum recorded. The temperature of the sample was then gradually decreased from ambient to −90°C, a spectrum being recorded at intervals.

The above experiment was repeated, but this time the yellow solution formed by the action of hydrochloric acid/benzene on $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2]Cl$ was decanted off the aqueous layer and then the volume of the benzene layer was reduced (to ca. 2–3 cm^3) by rotary evaporation; the ^{31}P NMR (36.27 MHz) spectrum was recorded of this solution in an 8.5 mm NMR tube inside a 10 mm NMR tube, with D_2O in the 10 mm tube to lock the spectrometer.

Investigation of the nature of the compound originally reported [2] as $[Pt_2Cl_2(\mu\text{-dppm})_2] \cdot 0.5CH_2Cl_2$

(i) $[Pt_2Cl_2(\mu\text{-}H)(\mu\text{-dppm})_2]Cl$ (originally formulated as "$[Pt_2Cl_2(\mu\text{-dppm})_2] \cdot C_6H_6$"). $[Pt_2Cl_2(\mu\text{-}H)(\mu\text{-dppm})_2]Cl$ (0.6 g, 0.47 mmol) was dissolved in CH_2Cl_2 (25 cm^3) and the solution filtered to remove impurities. On addition of 2,2,4-trimeth-

ylpentane a fine lemon-yellow solid was obtained and collected by filtration. After washing with 2,2,4-trimethylpentane (5 cm^3) the fine solid was dried in vacuo. The product was recrystallised twice and dried in vacuo. Its ^{31}P NMR spectrum was recorded in CD_2Cl_2 at −90°C.

(ii) [$Pt_2Cl_2(\mu$-$H)(\mu$-dppm$)_2$]Cl (vacuum decomposition). [$Pt_2Cl_2(\mu$-H)(μ-dppm$)_2$]Cl (0.5 g, 0.39 mmol) was placed in vacuo at room temperature for ca. 48 h and then the ^{31}P NMR spectrum was recorded in CD_2Cl_2 at −90°C.

New synthetic routes to [$Pt_2X_2(\mu$-dppm$)_2$] (X = Cl or Br)

Preparation of [$PtCl_2$(dppm)] from K_2[$PtCl_4$] [34]

K_2[$PtCl_4$] (1.40 g, 3.37 mmol) was dissolved in water (20 cm^3) and concentrated hydrochloric acid (10 cm^3) was added. To this solution propan-1-ol (435 cm^3) and dppm (1.29 g, 3.37 mmol) were added, and the mixture was heated under reflux for 20 min. The white solid [$PtCl_2$(dppm)] was collected by filtration, washed with diethyl ether (2 × 20 cm^3), and then dried in vacuo for 2 h. The filtrate was left to stand, and after a further 12 h, more [$PtCl_2$(dppm)] formed, which was subsequently collected by filtration and washed with diethyl ether (2 × 10 cm^3) and then dried in vacuo for 2 h. (1.79 g, 92%). (Found: C, 46.26; H, 3.43; Cl, 10.45. $C_{25}H_{22}Cl_2P_2Pt$ calcd.: C, 46.15; H, 3.38; Cl, 10.92%).

Preparation of crude [$Pt_2H_2(\mu$-$H)(\mu$-dppm$)_2$]Cl

(i) Using methanol and ethanol as solvents. Finely ground [$PtCl_2$(dppm)] (1.0 g, 1.54 mmol) was suspended in dry methanol (40 cm^3) and Na[BH_4] (0.5 g, 13.22 mmol) in absolute ethanol (25 cm^3) was added dropwise over a period of 1 h with continuous stirring under dinitrogen. Slowly the solution darkened first to yellow, then gradually to brown; an orange solid formed. Stirring was continued for 1 h after the completion of the addition of Na[BH_4], then the orange solid was collected by filtration, washed with methanol (20 cm^3) and diethyl ether (2 × 20 cm^3), and was dried in vacuo for ca. 2 h and stored away from strong light (0.86 g, 96%).

(ii) Using propan-2-ol as solvent. Finely ground [$PtCl_2$(dppm)] (0.5 g, 0.77 mmol) was suspended in dry propan-2-ol (30 cm^3), and Na[BH_4] (0.25 g, 6.61 mmol) in propan-2-ol (15 cm^3) was added over a period of 1 h with continuous stirring under dinitrogen. Slowly, the solution turned yellow, and then gradually darkened to brown; the brown suspension was stirred for a further 1 h. The brown solid was then collected by filtration, washed with propan-2-ol (20 cm^3) and diethyl ether (20 cm^3), and dried in vacuo for ca. 24 h (0.22 g). On addition of methanol (30 cm^3) to the brown solid, vigorous effervescence occurred and the solid turned orange. The reaction continued for about 2 min, whence the orange solid was collected by filtration, washed with methanol (20 cm^3) and diethyl ether (20 cm^3), and dried in vacuo for 24 h (0.15 g, 33.6%).

Preparation of [$Pt_2Cl_2(\mu$-dppm$)_2$] · 0.75CH_2Cl_2

[$Pt_2H_2(\mu$-H)(μ-dppm$)_2$]Cl (0.86 g, 0.72 mmol) was suspended in benzene (50 cm^3), and the solution was heated under reflux for ca. 2 min. Concentrated hydrochloric acid (4–5 cm^3) was added and the solution was heated under reflux for a further 10 min. The solution gradually became deep yellow, and after cooling, the excess solid was removed by filtration. The yellow benzene solution was decanted off the aqueous acidic layer, and an excess of light petroleum (b.p. 80–100°C) (ca. 200 cm^3) was added to yield a yellow solid precipitate of crude [$Pt_2Cl_2(\mu$-H)(μ-dppm)$_2$]Cl, that was collected by filtration. (The excess solid which was removed from the benzene solution can be returned to the reaction vessel, and the reaction repeated to ensure complete conversion of all the [$Pt_2H_2(\mu$-H)(μ-dppm)$_2$]Cl). The crude yellow solid was dissolved in CH_2Cl_2 (30 cm^3) and the solution was heated and evaporated to low volume (ca. 2–3 cm^3) to ensure complete dehydrochlorination. Further CH_2Cl_2 (3 cm^3) was added, followed by light petroleum (80–100°C) (50 cm^3), whence a yellow precipitate was formed. The suspension was heated to remove CH_2Cl_2; this caused coagulation of the precipitate, leaving the supernatant liquid above the yellow solid completely clear. The yellow solid was collected by filtration, washed with diethyl ether (2 × 20 cm^3) and dried in vacuo for 12 h. (0.41 g, 43.3%, based on [$PtCl_2$(dppm)]). (Found: C, 47.45; H, 3.52; Cl, 9.86. $C_{50.75}H_{45.5}Cl_{3.5}P_4Pt_2$ calcd.: C, 47.11; H, 3.52; Cl, 9.61%.

Preparation of [$Pt_2Br_2(\mu$-dppm)$_2$] · 0.85 CH_2Cl_2

[$Pt_2Cl_2(\mu$-dppm)$_2$] (0.35 g, 0.28 mmol) was dissolved in CH_2Cl_2 (25 cm^3), silver(I) hexafluorophosphate (0.4 g, 1.58 mmol) was added, and the solution stirred for 1.5 h at room temperature. The white precipitate of AgCl had darkened and was removed by filtration. [NEt_4]Br (1.5 g, 7.14 mmol) was then added in CH_2Cl_2 (20 cm^3) to the clear filtrate. The solution turned bright yellow, but became cloudy as the excess of silver ions were precipitated as AgBr. This was also removed by filtration yielding a golden yellow filtrate, which was washed with water (2 × 20 cm^3), to remove soluble tetraethylammonium salts. The volume of the solution was reduced (to ca. 2—3 cm^3), and then redistilled light petroleum (80–100°C) (30 cm^3) was added to yield a bright yellow precipitate. The excess of CH_2Cl_2 was removed by heating in a water bath, ensuring complete precipitation of the product. The solid was collected by filtration, washed with diethyl ether (20 cm^3) and dried in vacuo for 24 h (0.35 g, 93%). (Found: C, 43.92; H, 3.75; Hal, 15.98. $C_{50.85}H_{45.7}Br_2Cl_{1.7}P_4Pt_2$ calcd.: C, 43.97; H, 3.60; Hal, 15.94%).

Preparation of [$Pt_2I_2(\mu$-dppm)$_2$] · 0.75 CH_2Cl_2 [2]

[$Pt_2Cl_2(\mu$-dppm)$_2$] (0.4 g, 0.33 mmol) was suspended in a solution of iodide (0.26 g, 1.73 mmol) in propanone (40 cm^3). Initially the solution turned purple (due to the release of free iodine) but after 15 min the solution turned deep orange, and was stirred overnight. The crude orange-yellow crystals were collected by filtration and washed with water (10 cm^3), propanone (10 cm^3) and diethyl ether (5 cm^3). The propanone of solvation was removed by dissolving the complex in CH_2Cl_2 (30 cm^3) and evaporating the solution to dryness in a rotary evaporator. The solid was again dissolved in CH_2Cl_2 (30 cm^3), the process repeated, and the product recrystallised from CH_2Cl_2 and redistilled light petroleum (80–100°C). The orange-yellow solid formed was collected by filtration and dried in vacuo for 24 h (0.37 g, 81%). (Found: C, 43.07; H, 3.10; Hal., 19.10. $C_{50.75}H_{45.5}Cl_{1.5}I_2P_4Pt_2$ calcd.: C, 43.08; H, 3.13; Hal., 18.99%).

Preparation of solutions of [$Pt_2X_2(\mu$-H)(μ-dppm)$_2$]$^+$ (X = Cl, Br or I) in CD_2Cl_2

[$Pt_2X_2(\mu$-dppm)$_2$] (X = Cl, Br or I) (0.1 g) was dissolved in CD_2Cl_2 (2-3 cm^3); concentrated aqueous acid HY (X = Cl, Y = Cl; X = Br, Y = Br; X = I, Y = BF_4)

(ca. 4–5 cm^3) was added and the two immiscible layers were shaken vigorously for ca. 2 min. The solution was allowed to settle and the CD_2Cl_2 layer was carefully pipetted off into an NMR tube, and the ^1H, ^{31}P and ^{195}Pt NMR spectra of the sample were recorded.

Preparation of [$Pt_2X_2(\mu\text{-}H)(\mu\text{-}dppm)_2$][$BF_4$] (X = Cl, Br or I)

[$Pt_2X_2(\mu\text{-dppm})_2$] (X = Cl, Br or I) (0.15 g) was dissolved in CH_2Cl_2 (5 cm^3) and then concentrated tetrafluoroboric acid (40%) (ca. 4–5 cm^3) was added and the two immiscible liquids shaken vigorously. The two layers were allowed to settle out; the CH_2Cl_2 layer was removed by pipette, and hexane (ca. 20 cm^3) was added to this solution. A yellow precipitate formed, and was collected by filtration, washed with diethyl ether (10 cm^3) and dried in vacuo for ca. 15 min. (Prolonged evacuation results in loss of H[BF_4]). (X = Cl; 0.13 g, 83%: X = Br; 0.13 g, 79%: X = I; 0.11 g, 70%). (X = Cl, Found: C, 45.41; H, 3.36; Cl, 5.45. $C_{50}H_{45}BCl_2F_4P_4Pt_2$ calcd.: C, 45.56; H, 3.45; Cl, 5.38%. X = Br, Found: C, 42.60; H, 3.19; Br, 11.16. $C_{50}H_{45}BBr_2F_4P_4Pt_2$ calcd.: C, 42.71; H, 3.23; Br, 11.38. X = I, Found: C, 39.94, H, 2.92; I, 17.10. $C_{50}H_{45}BF_4I_2P_4Pt_2$ calcd.: C, 40.03; H, 3.03; I, 16.93%).

Appendices

(i) Analysis of the AA'A"A‴ XX' spin system

Despite the existence of good general treatments of the $A_nXX'A'_n$ spin system [49–51], it has been the experience of the authors that the analysis of the NMR spectra of {$Pt_2(\mu\text{-dppm})_2$} complexes has proved problematic for a number of workers in the field. In particular, the analysis of the X spectra is somewhat elusive. We therefore include here an explicit description of the analysis of both the A and X spectra of {$Pt_2(\mu\text{-dppm})_2$} derivatives, to give a value for $^1J(XX')$.

The most prominent features in the A spectra are a pair of lines at $\nu_A \pm \frac{1}{2}N'$, where $N' = J(AX) + J(AX')$; these two lines contain half the total intensity of the A spectrum with the remaining intensity being distributed over a further four pairs of lines, designated as $\chi_i(1)$, $\chi_i(2)$, $\chi_o(1)$ and $\chi_o(2)$. These pairs of lines are symmetrically disposed about ν_A at $\nu_A \pm \nu\{\chi_x(y)\}$ (x = i or o; y = 1 or 2), the inner (i) lines occurring within the pair of lines constituting the N' doublet and the outer (o) lines occurring outside the N' doublet. The separations, S_i or S_o, of each pair of χ_i or χ_o lines are given by:

$$S_i(y) = \{y^2L'^2 + [J(XX')]^2\}^{1/2} - \{(y-1)^2L'^2 + [J(XX')]^2\}^{1/2} \qquad \text{(A1)}$$

$$S_o(y) = \{y^2L'^2 + [J(XX')]^2\}^{1/2} + \{(y-1)^2L'^2 + [J(XX')]^2\}^{1/2} \qquad \text{(A2)}$$

where $y = 1$ or 2

$$L = |J(AX) - J(AX')|$$

The A spectrum due to the $AA'A''A'''XX'$ spin-system is shown in Fig. 14, and the important parameters are marked. In a real situation, this spin system only constitutes ca. 10% of the spectral intensity {cf. Fig. 3}. The intensity of the outer lines is significantly less than that of the inner lines. However, in the cases where both $\chi_o(1)$ and $\chi_i(1)$ are observable in the same spectrum {a situation invariably corresponding to small values of $^1J(XX')$}, the value of $^1J(XX')$ is given directly by:

$$|^1J(XX')| = |\nu\{\chi_i(1)\} - \nu\{\chi_o(1)\}| \qquad \text{(A3)}$$

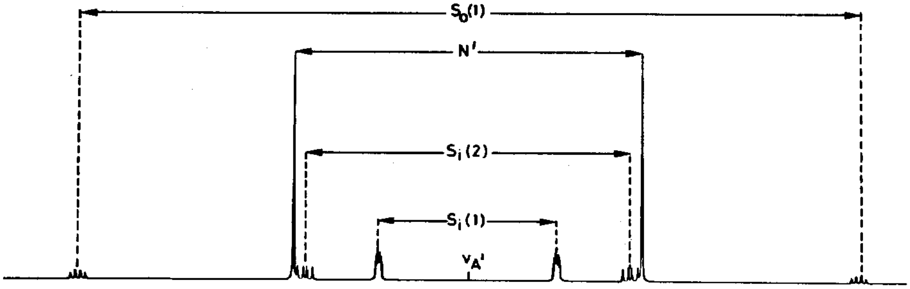


Fig. 14. Computer simulation of a typical A spectrum arising from the $AA'A''A'''XX'$ spin-system, showing the $\chi_i(1)$, $\chi_i(2)$, and $\chi_o(1)$ lines.

The more typical situation is when the χ_o lines are of too low an intensity to be observed. When only $\chi_i(1)$ lines are detected, then a rearrangement of eq. A1 gives:

$$|^1J(XX')| = \frac{L'^2 - S_i(1)^2}{2S_i(1)} \tag{A4}$$

If the $\chi_i(2)$ lines are also visible, then:

$$|^1J(XX')| = \frac{\{3S_i(1) + S_i(2)\}\{S_i(2) - S_i(1)\}}{2\{3S_i(1) - S_i(1) - S_i(2)\}} \tag{A5}$$

Also, if an independent check is required,

$$L' = \frac{S_i(1)S_i(2)\{S_i(1) + S_i(2)\}}{\{3S_i(1) - S_i(2)\}}$$

Use of eq. A4 was found to be more precise than eq. A5 for the calculation of $^1J(XX')$, but eq. A5 provides an independent corroboration of the calculation.

The most prominent features in the X spectrum are a pair of lines at $\nu_x \pm N'$. For large values of $^1J(XX')$ two lines, more intense than the N' lines, are observed on each side of ν_x. By computer simulation it was shown that the separation between each pair of lines on either side of ν_x (see Fig. 15) was equivalent to $S_i(1)$ observed in the A-spectrum. Thus applying eq. A4, $^1J(XX')$ was obtained. The prominent feature of these lines observed in the X spectra due to the $AA'A''A'''XX'$ spin system (in a real situation this spin system constitutes ca. 25% of the spectral intensity {cf. Fig. 4}) is that their relative intensity is much greater than the χ lines observed in the A spectrum, thus increasing the accuracy of the measurement of the parameter $S_i(1)$.

As $^1J(XX')$ decreases, new features appear in the X spectrum: weak closely spaced multiplets appear both outside and inside the outer N' lines (see Fig. 15), corresponding to the lines assigned in the A spectra as $\chi_o(1)$ lines. As with the A spectra when both $\chi_o(1)$ and $\chi_i(1)$ are observable, then $^1J(XX')$ is given directly by eq. A3.

(ii) Digital resolution of spectra

Digital resolution (DR) is defined as: (Sweep width in Hz)/(Number of data points). Typically, for a ^{31}P NMR spectrum, DR = $\frac{6000}{4000}$ = 1.5 Hz point^{-1}: for a ^{195}Pt NMR spectrum, DR = $\frac{30000}{4000}$ = 7.5 Hz point^{-1} (JEOL FX-90Q) or DR = $\frac{80000}{16000}$ = 5.0

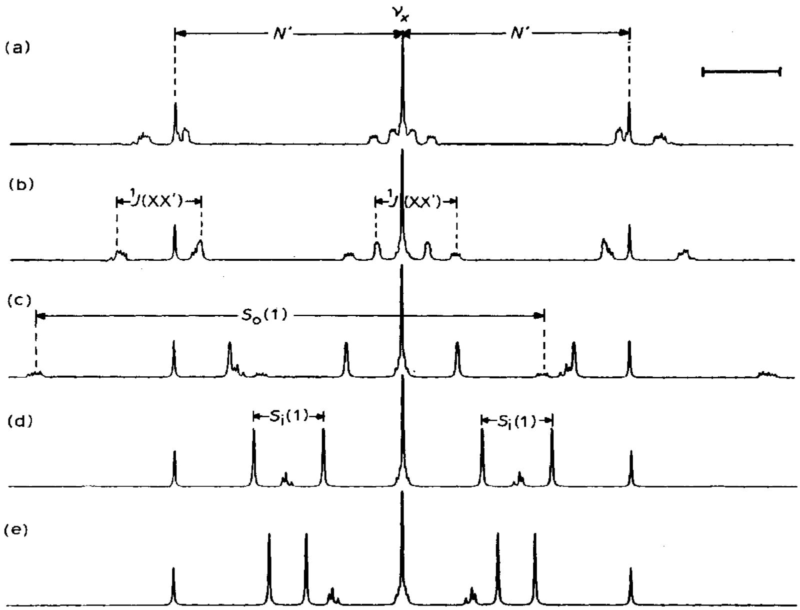


Fig. 15. Computer simulation of a typical X spectrum arising from the $AA'A''A'''XX'$ spin-system, demonstrating the dependence of the spectral form upon $^1J(XX')$, which takes the values of (a) 500, (b) 1000, (c) 2500, (d) 5000, and (e) 10000 Hz. The bar represents 1000 Hz.

Hz point^{-1} (Bruker WH-400). Thus, in terms of precision with respect to digital resolution, values obtained from a ^{31}P NMR spectrum are more accurate unless the lines being observed in the ^{31}P NMR spectra are less well defined than those seen in the ^{195}Pt NMR spectra, as is the case for the $\chi_i(1)$ and $\chi_o(1)$ lines.

(iii) Chemical shift reference for ^{195}Pt NMR spectra

Two contrasting methods of referencing ^{195}Pt NMR spectra are currently in use: (a) by comparison with a standard compound (e.g. $Na_2[PtCl_6]$ in D_2O) [35], or (b) by comparison with a frequency of 21.4 MHz on an NMR machine for which $Si(CH_3)_4$ resonates at exactly 100.00 MHz [36]. In our wide experience, the latter method (propounded by Goodfellow) is superior. The use of a standard such as $Na_2[PtCl_6]$, at some 3500 ppm to higher frequency than the majority of measured δ(Pt) values in the literature, is impracticable without defining a secondary standard, owing to the limited width of observation windows available with state-of-the-art spectrometers. The high frequency stability of modern instrumentation allows referencing to 21.4 MHz (scaled appropriately to the field strength of the spectrometer being used) to be made in a rapid, accurate and reproducible manner, and we have accordingly adopted this method of referencing in this manuscript.

Acknowledgements

We are extremely grateful to Dr. M.P. Brown, who supplied a number of the samples used in this study. We also wish to thank the S.E.R.C. for the award of a studentship (R.P.M.), and Dr. G. Hawkes and Mr. M. Buckingham (ULIRS

WH-400 NMR Service, Queen Mary College, University of London) and Mr. D. Parkinson (JEOL FX-90Q, Bedford and Royal Holloway New College, University of London) for their assistance with recording multinuclear NMR spectra.

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