Hydride Complexes of Six-co-ordinate Platinum

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Novel hydride complexes of six-co-ordinated platinum have been prepared in methylene chloride solution and studied by ^1H n.m.r. spectroscopy, double resonance experiments giving information about ^{31}P and ^{195}Pt nuclei. HX adds to *trans*-[$PtHY(PEt_3)_2$] (X,Y = Cl, Br, or I) to give *cis-trans*-[$PtH_2XY(PEt_3)_2$]. If X ≠ Y, halogen exchange occurs to give an approximately random mixture of dihydride products. Similarly HX adds to *trans*-[$PtY_2(PEt_3)_2$] to give $PtHXY_2(PEt_3)_2$, with H initially *trans* to X. Subsequent rearrangement gives the product with the lighter halogen *trans* to H. Addition of X_2 to *trans*-[$PtHX(PEt_3)_2$] (X = Cl or Br) does not give the expected $PtHX_3(PEt_3)_2$, but a mixture of $PtH_2X_2(PEt_3)_2$ and $PtX_4(PEt_3)_2$. The complexes *cis-cis-trans*-[$PtH_2X_2(PEt_3)_2$] (X = Cl or Br) were also characterised by C,H analysis and i.r. and Raman spectroscopy.

MANY examples are known of monohydride complexes of four-co-ordinated platinum; a large number are crystalline solids, stable at and above room temperature. Hydrides of six-co-ordinated platinum, however, are not so well characterised. Monohydride complexes have been isolated as intermediates in the oxidative addition of silyl and germyl halides to *trans*-[$PtI_2(PEt_3)_2$];[1] a solid adduct of HCl with *trans*-[$PtClH(PEt_3)_2$] has been described as a dihydride of six-co-ordinated platinum on the basis of its i.r. spectrum,[2] and C,H analysis.[2]

Other platinum dihydrides have been postulated. The preparations of $PtH_2(PPh_3)_n$ ($n = 2$, 3, and 4) have been described,[3,4] but the products have later all been shown not to be platinum hydrides.[5,6] The compound $PtCl_2H_2(PPh_3)_2$ has also been reported,[7] but it too has now been shown not to be a dihydride.[8] The only other reported dihydride is Pt(1-ethynylcyclohexanol)$_2H_2$-$(PPh_3)_2$:[9] the evidence for the existence of this is very limited, depending mainly on the observation of weak PtH_2^+ ions in the mass spectrum.

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We have prepared a series of mono- and di-hydride complexes of six-co-ordinated platinum by the reaction between hydrogen halides, HX, and *trans*-$[PtY_2(PEt_3)_2]$ or *trans*-$[PtHY(PEt_3)_2]$ in methylene chloride solution. The products have been characterised by ^1H n.m.r. spectroscopy, using heteronuclear double resonance to study the ^{195}Pt and ^{31}P spectra, and hence to show how many hydrogen ligands were bound to platinum; ^{195}Pt chemical shifts were also used to distinguish between complexes formed. I.r. and Raman spectroscopy, and C,H analyses were also used to characterise the complexes *cis-cis-trans*-$[PtH_2X_2(PEt_3)_2]$ (X = Cl or Br).

RESULTS AND DISCUSSION

Dihydride complexes.—When equimolar proportions of HX and *trans*-$[PtHX(PEt_3)_2]$ (X = Cl, Br, or I) were allowed to react together in methylene chloride in a sealed tube at 253 K, changes in the Pt*H* resonance and colour changes (X = Br or I) showed that a chemical change had occurred. The triplet Pt*H* resonance and the values of $^1J(^{195}Pt^{31}P)$ imply that the phosphorus atoms are mutually *trans* in the reaction product; the ^{195}Pt resonance showed the pattern of a triplet of triplets expected for a dihydride complex, with one of the triplet splittings equal to $^1J(^{195}Pt^1H)$ as measured directly from the ^1H spectrum. All the coupling constants are reduced in magnitude from their values in the parent complexes of four-co-ordinated platinum, which is consistent with the increase in co-ordination number of the metal atom.

Reaction of HX with *trans*-$[PtHY(PEt_3)_2]$ (X,Y = Cl, Br, or I; $X \neq Y$) at 183 K gave as the major product a compound with two Pt*H* resonances. Heteronuclear decoupling and the determination of $\delta(^{195}Pt)$ showed that both resonances were associated with hydrogens bound to the same platinum atom. When this solution was allowed to warm to 253 K, resonances due to $PtH_2X_2(PEt_3)$ and $PtH_2Y_2(PEt_3)_2$, weak in the initial spectra at 183 K, increased in relative intensity until they were comparable with the other two Pt*H* resonances. These results are consistent with initial formation of $PtH_2XY(PEt_3)_2$, and subsequent ' scrambling ' of halogens on a very roughly statistical basis:

$$2PtH_2XY(PEt_3)_2 \rightleftharpoons PtH_2X_2(PEt_3)_2 + PtH_2Y_2(PEt_3)_2$$

If this interpretation is correct, the hydride ligands in the mixed species must be mutually *cis*; if they were *trans*, they would be equivalent. We were unable to observe ^2J(HPtH) even at 183 K, although we believe that we would have detected splittings of the order of 0·5—1·0 Hz. Thus the stereochemistry of these dihydride complexes is established.

The reaction between HX and *trans*-$[PtHX(PEt_3)_2]$ is very rapid; n.m.r. spectra taken after *ca.* 1 min at 183 K showed that extensive reaction had occurred. The spectra are sharp at room temperature, showing that there is no rapid exchange with free HX, but over a few minutes hydrogen is evolved irreversibly; the order of stability is $Cl \gg Br > I$, which is the order of increasing *trans* influence. By removal of the solvent at 253 K, we were able to isolate *cis-cis-trans*-$[PtH_2X_2(PEt_3)_2]$ (X = Cl or Br), both white solids, which were stable enough to be characterised more fully by C,H analysis and i.r. and Raman spectroscopy (Table 1). For X = I an orange solid was obtained but it decomposed too readily for further study.

TABLE 1

Vibrational spectra (cm^{-1})

cis-cis-trans-$[PtCl_2H_2(PEt_3)_2]$		*cis-cis-trans*-$[PtBr_2H_2(PEt_3)_2]$		
I.r.[a]	Raman[b]	I.r.[a]	Raman[b]	Assignments
	2973w		2971w	ν(CH)
	2949m		2951m	
	2907m		2913s	
	2888w		2886w	
2263m,sh	2269(2)s	2252s	2254(2)s	ν(PtH)[c]
2251s	2264(2)m	2243s	2244(2)s	
	1459w		1455m	δ(CH)
	1427w		1426w	
1412m	1417w	1412m	1415w	
	1270w	1272s	1271s	ν(CC)
1263s		1260s		
1249s	1243w	1251s	1240w	
1048s	1055w	1050s	1055m	
		1046s		
1003s	1003w	1006s	1002m	
	987w		990w	
901w		903w		
892w		895w		
821s	823m	810s	809s	δ(PtH)
	784m		780m	
768vs,br	775m	768vs	765m	
	752w		745w	
	737vw			
701s	700m	700s	698s	
632m	638m	632m	638s	
577m	576m	548m	548s	δ(PtH)
	527vw			
435w		438w		
402m	404m	402m	404m	ν(PtP)
395w,sh	394m		394m	
359vw	364s	358w	364s	
348w		347w		
275m	284vs		284m	ν(PtX) +δ(PtX) +lattice modes
254s	256m	268w		
			222m	
	182vs,br		192vs	
	121vs		165m	

[a] Solid (Nujol mull). [b] Solid. [c] *cis-cis-trans*-$[PtH_2I_2(PEt_3)_2]$ (νPtH), 2210; *trans*-$[PtHI_3(PEt_3)_2]$ (νPtH) *ca.* 2210 cm^{-1}. Solution of the complexes *cis-cis-trans*-$[PtH_2X_2(PEt_3)_2]$ (X = Cl, Br, or I) gave 2256; 2232, and 2217 cm^{-1} respectively for ν(PtH).

We have tried to discover whether the initial addition is *cis* or *trans* by treating *trans*-$[PtHX(PEt_3)_2]$ with DY at 183 K, but even at this temperature the first spectrum obtained showed the presence of H *trans* to both X and Y. This implies that reversible *trans*-addition is not the only process going on under these conditions; H/D scrambling in the mixed species seems to be faster than the X/Y scrambling. We cannot conclude whether the initial addition of HX is *cis* or *trans*.

Monohydride Complexes.—When HI was allowed to react with *trans*-$[PtI_2(PEt_3)_2]$ in methylene chloride at 293 K, the solution darkened immediately; at 253 K a strong Pt*H* resonance was obtained, and heteronuclear double resonance showed the presence of one hydride *and two* mutually *trans* P-ligands bound to platinum. At higher temperatures the Pt*H* resonance collapsed, but it reappeared on cooling again; presumably rapid exchange with free HI occurs at the higher temperatures. In the analogous bromide system, a similar Pt*H* resonance was found, but only at temperatures below 200 K; in solutions containing comparable concentrations of starting materials, the Pt*H* resonance was much weaker for the bromide than for the iodide. Even at temperatures as low as 173 K we were unable to detect a Pt*H* resonance in solutions containing HCl and *trans*-[$PtCl_2(PEt_3)_2$].

The reaction between HX and *trans*-[$PtX_2(PEt_3)_2$] therefore appears to be an equilibrium, fast on the n.m.r. time scale at room temperature; the rates and instability constants decrease in the order X = (Cl>)Br > I:

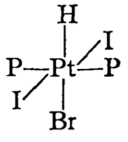
$$PtHX_3(PEt_3)_2 \rightleftharpoons PtX_2(PEt_3)_2 + HX$$

The change in equilibrium constant with halogen may be related to bond energies. Values for Pt–X bonds are not very reliable, but *E*(Pt–X) does not appear to be as sensitive to X as is *E*(H–X), which decreases markedly in the order Cl > Br > I. The equilibrium concentration of $PtCl_3H(PEt_3)_2$ might therefore be small. Even with a three-fold excess of HCl we were unable to detect the Pt*H* resonance of this species at 173 K, but we cannot say whether our failure is due to an unfavourable equilibrium constant, to too fast a reaction, or to a combination of the two.

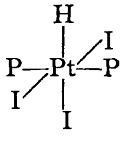
Reactions between HX and *trans*-[$PtY_2(PEt_3)_2$] led ultimately to halogen exchange but the resonance due to the species formed initially could be observed at low temperatures; in contrast to the behaviour of $PtH_2XY(PEt_3)_2$, halogen scrambling only occurred to a significant extent when the solution was allowed to warm from 183 to 253 K. This may be related to the high *trans* activating effect of H as a ligand. Furthermore, the rate of 'scrambling' in the monohydride system appears to decrease in the order Cl > Br > I. The ultimate products, too, are not random, but are those in which H is *trans* to the lightest halogen present; this is established from the ^1H chemical shift, which depends almost entirely on the *trans* ligand, and may be interpreted in terms of the weakening of the PtH bond by the *trans* influence of the heavier halogens.

Since the ^1H resonance of the initial product could be recorded before halogen exchange led to the formation of the most stable species, we were able to show by reaction between HX and *trans*-[$PtY_2(PEt_3)_2$] that the initial addition and elimination are *trans*. The halogen scrambling that occurs at higher temperatures must involve either *cis*-elimination of HY from the monohydride adduct, or some quite different process, such as ionic exchange of halogen.

These effects are illustrated in the spectra of the mixed bromo-iodo-complexes. When X = Br, Y = I, the product formed at 183 K is (I):

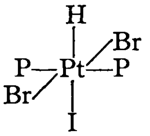


(I)

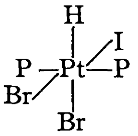


(II)

On warming, some halogen exchange occurs, but (I) is thermodynamically stable and persists as the main product at 253 K. A small amount of product (II) is also present at that temperature. When X = I, Y = Br, the initial product (III) has H *trans* to I; scrambling leads to the formation of products with H *trans* to Br, identified by their n.m.r. parameters (particularly ^{195}Pt chemical shift) as $PtBr_2HI(PEt_3)_2$ (IV, the major product) and $PtBrHI_2(PEt_3)_2$ (I).



(III)



(IV)

In the reaction of HCl with any dihalide, the lability of the adduct formed prevented us from establishing that initial *trans*-addition had occurred. Addition of HBr or HI to *trans*-[$PtCl_2(PEt_3)_2$] gave initial adducts with H *trans* to the heavier halogen. With HBr, scrambling was so rapid that we could not record all the n.m.r. parameters of this initial product, but the ^1H chemical shift showed that *trans*-addition had occurred. With HI, the spectrum of $PtHI_3(PEt_3)_2$ appeared as the solution warmed and the spectrum of $PtCl_2HI(PEt_3)_2$ decayed; ultimately this spectrum also diminished in intensity, the colour of the solution grew lighter, and all Pt*H* resonances disappeared.

Removal of the solvent from a solution of *trans*-[$PtHI_3(PEt_3)_2$] gave a red solid but this was too unstable to be characterised further.

Reaction of X_2 *with* trans-[$PtHX(PEt_3)_2$].—Addition of X_2 to *trans*-[$PtHX(PEt_3)_2$] under the conditions described above might have been expected to give similar monohydride complexes. When X = Cl, however, the only Pt*H* resonance observed at 253 K after reaction at that temperature was due to $PtCl_2H_2(PEt_3)_2$. Irradiation of ^{195}Pt while observing the Pt satellites of the methylene protons of the Et_3P groups showed that *trans*-[$PtCl_4(PEt_3)_2$] had also formed; the yellow colour of the solution was consistent with the presence of this compound. Reaction had occurred according to the equation:

$$2PtClH(PEt_3)_2 + 2Cl_2 \longrightarrow PtCl_2H_2(PEt_3)_2 + PtCl_4(PEt_3)_2$$

Reaction at 183 K did not reveal the presence of $PtCl_3H(PEt_3)$ as an intermediate at this temperature.

Reaction between Br_2 and *trans*-[$PtBrH(PEt_3)_2$] gave similar products; the presence of $PtBr_4(PEt_3)_2$ in the red solution was confirmed in the same way. [Spectra of $PtCl_4(PEt_3)_2$ and $PtBr_4(PEt_3)_2$ had previously been obtained using samples prepared from the appropriate halogen and platinum dihalide.] The ^1H resonance spectrum of the products of the reaction between I_2 and *trans*-$[PtHI(PEt_3)_2]$ at 253 K, however, showed that both $PtH_2I_2(PEt_3)_2$ and $PtHI_3(PEt_3)_2$ were present; we were unable either to detect the presence of any additional platinum complex of Et_3P, or to prepare a sample of $PtI_4(PEt_3)_2$ from I_2 and $PtI_2(PEt_3)_2$.

TABLE 2

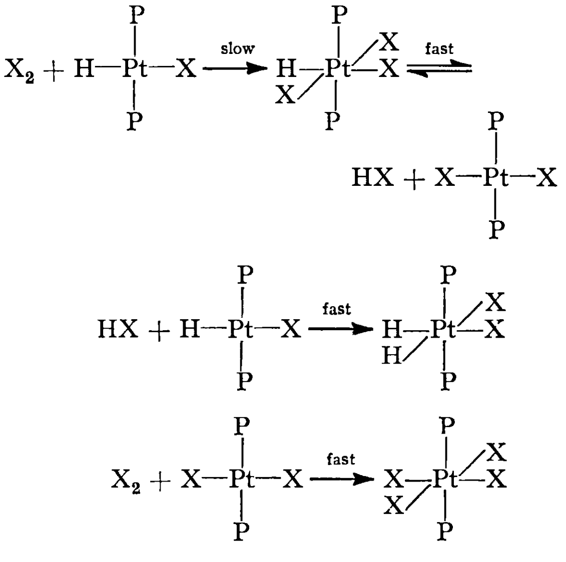
N.m.r. parameters of platinum hydride complexes

Compound	τ	$\delta(^{31}P)$ [a]	$\delta(^{195}Pt)$ [b]	$^1J(PtH)$	$^1J(PtP)$	$^2J(PH)$	T/K	Colour
trans-$[PtHI_3(PEt_3)_2]$	+26·41	−16·4	−662	+784	+1590	−5·5	233	Deep red
trans-trans-$[PtBrHI_2(PEt_3)_2]$	+28·75	−10·6	−320	−794	+1560	−5·5	193	Orange-red
cis-trans-$[PtBr_2HI(PEt_3)_2]$	+28·53	−4·9	+307	+831	*ca.* +1600	−5·5	213	Red
trans-trans-$[PtBr_2HI(PEt_3)_2]$	+26·41	−2·3	+734	+870	+1590	−4·5	193	Red
trans-$[PtBr_3H(PEt_3)_2]$	+28·33	+2·2	+1026	+845	+1578	−5·0	193	Yellow-orange
trans-trans-$[PtCl_2HI(PEt_3)_2]$	+26·48	+4·4	+1535	+942	+1675	−4·0	183	Light red
trans-trans-$[PtCl_2HBr(PEt_3)_2]$	+28·18	n.o.	n.o.	+944	n.o.	n.o.	183	Yellow
cis-cis-trans-$[PtH_2I_2(PEt_3)_2]$	+25·00	−1·4	−146	+1186	+1738	−5·8	253	Yellow
cis-trans-$[PtBrH_2I(PEt_3)_2]$	+26·82 [c]	+3·0	+207	+1176 [c]	+1710	−6·0 [c]	253	Yellow
	+25·00 [d]			+1220 [d]		−6·0 [d]		
cis-trans-$[PtClH_2I(PEt_3)_2]$	+28·03 [c]	+5·7	+395	+1132 [c]	+1732	−7·0 [c]	253	Pale yellow
	+25·09 [d]			+1240 [d]		−6·0 [d]		
cis-cis-trans-$[PtBr_2H_2(PEt_3)_2]$	+26·88	+7·2	+534	+1204	+1710	−6·3	253	Pale yellow
cis-trans-$[PtClBrH_2(PEt_3)_2]$	+28·09 [c]	+9·8	+708	+1168 [c]	+1770	−7·0 [c]	253	Very pale yellow
	+27·00 [d]			+1234 [d]		−7·0 [d]		
cis-cis-trans-$[PtCl_2H_2(PEt_3)_2]$	+28·17	+12·2	+881	+1176	+1769	−6·5	293	Colourless
trans-$[PtHI(PEt_3)_2]$ [e]	+22·65	+19·3	−325	+1369	+2660	−13·3	293	Very pale yellow
trans-$[PtBrH(PEt_3)_2]$ [e]	+25·55	+22·0	−126	+1331	n.o.	−13·7	293	Colourless
trans-$[PtClH(PEt_3)_2]$	+26·80	+22·8	0	+1275	+2730	−14·5	293	Colourless
Estimated errors	±0·03	±0·3	±1	±2	±20	±0·5		

n.o. = Not observed.

[a] P.p.m. to high frequency of external 85% H_3PO_4. [b] P.p.m. to high frequency of external 0·5M *trans*-$[PtClH(PEt_3)_2]$ in CH_2Cl_2. [c] H *trans* to lighter halogen. [d] H *trans* to heavier halogen. [e] Solvent C_6H_6. All others in CH_2Cl_2.

These observations are consistent with reactions (1)—(3). For X = Cl or Br, the equilibrium in step (1) is known from the above to be fast, as are the subsequent reactions (2) and (3). If the formation of the monohydride in step (1) is slow, the spectrum of this compound will not be observed. When X = I, since the compound $PtI_4(PEt_3)_2$ is not readily formed from I_2 and *trans*-$[PtI_2(PEt_3)_2]$, the equilibrium in step (1) will be maintained, giving a finite concentration of $PtHI_3(PEt_3)_2$. Some HI can undergo further reaction (2) giving $PtH_2I_2(PEt_3)_2$.



$$X_2 + H{-}\overset{P}{\underset{P}{Pt}}{-}X \xrightarrow{\text{slow}} H{-}\overset{P}{\underset{P}{Pt}}(X)_2{-}X \xrightleftharpoons{\text{fast}} HX + X{-}\overset{P}{\underset{P}{Pt}}{-}X \quad (1)$$

$$HX + H{-}\overset{P}{\underset{P}{Pt}}{-}X \xrightarrow{\text{fast}} H{-}\overset{P}{\underset{P}{Pt}}(H)(X){-}X \quad (2)$$

$$X_2 + X{-}\overset{P}{\underset{P}{Pt}}{-}X \xrightarrow{\text{fast}} X{-}\overset{P}{\underset{P}{Pt}}(X)(X){-}X \quad (3)$$

To determine the mode of addition, *trans*-$[PtHX(PEt_3)_2]$ has to be treated with XY or YZ, and the monohydride intermediate isolated. However, since step (1) and subsequent scrambling of products are fast this was not possible. Reaction of ICl with *trans*-$[PtHI(PEt_3)_2]$ at 183 K gave the three possible dihydrides, but no monohydride.

N.m.r. Parameters.—All the n.m.r. parameters measured are presented in Table 2.

The chemical shifts of all the Pt*H* protons in the six-co-ordinated platinum complexes are to low frequency of those of the four-co-ordinated analogues with the same ligand *trans* to H; the values for the latter are included for comparison in Table 2. The chemical shift of the Pt*H* within a group of similar compounds is determined mainly by the halogen in the *trans*-position; changing halogens in the *cis*-position has only a small effect. However, replacing a *cis*-hydrogen by a halogen (*i.e.* changing from dihydride to monohydride) changes the ^1H chemical shift substantially.

Variations in the ^{195}Pt and ^{31}P chemical shifts are more complex, and a full consideration of them will be given in a later paper.[10] Several interesting trends should, however, be mentioned here. Both $\delta(^{31}P)$ and $\delta(^{195}Pt)$ are in all cases shifted to higher frequency by substitution of lighter for heavier halogens. $\delta(^{31}P)$ for each of the monohydride complexes is to low frequency of the range found for the dihydrides. In contrast, the ranges of ^{195}Pt shifts are centred around the same value, but

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[10] D. W. W. Anderson, E. A. V. Ebsworth, and D. W. H. Rankin, *J.C.S. Dalton*, submitted for publication.

variations in shifts for monohydrides are greater than those for the dihydrides.

The magnitudes of the coupling constants ${}^1J({}^{195}\mathrm{Pt}{}^1\mathrm{H})$, ${}^1J({}^{195}\mathrm{Pt}{}^{31}\mathrm{P})$, and ${}^2J({}^{31}\mathrm{P}{}^1\mathrm{H})$ all decrease from the four- to the six-co-ordinated platinum complexes as expected with the corresponding decrease in *s*-orbital character in the bonds. There is also a considerable decrease in ${}^1J(\mathrm{PtH})$ and a smaller one in ${}^2J(\mathrm{PtP})$ from $\mathrm{PtH_2X_2(PEt_3)_2}$ to $\mathrm{PtHX_3(PEt_3)_2}$. This suggests that there is a decrease in covalency in the Pt–H bond in the same sense, an idea that is supported by the solubility of these complexes: both types of complex, but particularly the monohydrides, are almost insoluble in non-polar organic solvents.

In the monohydride series $\mathrm{PtHXYZ(PEt_3)_2}$, where H is *trans* to X, ${}^1J(\mathrm{PtH})$ increases in the order X,Y,Z = I,I,I < Br,I,I < Br,Br,I < Br,Br,Br < I,Br,Br < I,Cl,Cl < Br,Cl,Cl. There is therefore a corresponding increase in the *s*-orbital electron density of the Pt–H bond across this series. It has been suggested[11] that halogens do not have a strongly directed labilising influence; both *cis*- and *trans*-influences are significant. The above is then in the order expected from an increase in *cis–trans* influence of the halogens (and hence decrease in the Pt–H bond energy) in the order Cl < Br < I. In any case, the trends noted above may well be of value in the determination of structures of soluble complexes.

EXPERIMENTAL

Platinum complexes *trans*-$[\mathrm{PtHX(PEt_3)_2}]$, *trans*-$[\mathrm{PtX_2(PEt_3)_2}]$, and *trans*-$[\mathrm{PtX_4(PEt_3)_2}]$ were prepared by standard methods.[12-14] HI was obtained from aqueous solution using phosphorus pentoxide as a dehydrating agent, and was then purified by fractional condensation. Other reagents were purchased, and purified as necessary. Methylene chloride, dried over molecular sieve, was used as solvent for reactions of the platinum complexes. These reactions were all carried out in n.m.r. tubes. In a typical reaction, *trans*-$[\mathrm{PtClH(PEt_3)_2}]$ (0·832 g, 0·18 mmol) was dissolved in methylene chloride containing 10% tetramethylsilane (*ca.* 1 ml) and HCl (0·18 mmol) was condensed in at 77 K. The reagents were allowed to mix at 253 K, and the spectrum was recorded initially at this temperature.

The complexes *cis-cis-trans*-$[\mathrm{PtCl_2H_2(PEt_3)_2}]$ (Found: C, 28·75; H, 6·6. $\mathrm{C_{12}H_{32}Cl_2P_2Pt}$ requires C, 28·6; H, 6·4%) and *cis-cis-trans*-$[\mathrm{PtBr_2H_2(PEt_3)_2}]$ (Found: C, 24·25; H, 5·45. $\mathrm{C_{12}H_{32}Br_2P_2Pt}$ requires C, 24·3; H, 5·45%) were isolated by removal of the solvent under reduced pressure at 253 K.

I.r. spectra were recorded on a Perkin-Elmer 225 grating spectrometer, Raman spectra on a Cary 83 spectrometer using argon ion laser excitation at 488 nm, and n.m.r. spectra on a Varian Associates HA100 spectrometer operating at 100 MHz. The latter was double tuned to accept a second radio frequency, provided by a Schlumberger FS30 frequency synthesiser. The double resonance technique used has been described fully in a previous paper.[15]

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