

SYNTHETIC AND SPECTROSCOPIC STUDIES OF SOME MONO-HYDRIDO-BRIDGED COMPLEXES OF PLATINUM(II)

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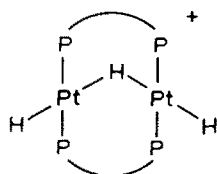
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Summary

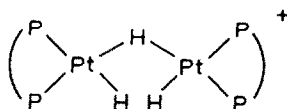
The mono-hydrido-bridged complexes $[(\text{PEt}_3)_2(\text{Ar})\text{Pt}(\mu_2\text{-H})\text{Pt}(\text{Ar})(\text{PEt}_3)_2][\text{BPh}_4]$ ($\text{Ar} = \text{Ph}$, 4-MeC₆H₄ and 2,4-Me₂C₆H₃) have been obtained by treating *trans*- $[\text{Pt}(\text{Ar})(\text{MeOH})(\text{PEt}_3)_2][\text{BF}_4]$ with sodium formate and Na[BPh₄]. The cations $[(\text{PEt}_3)_2(\text{Ar})\text{Pt}(\mu_2\text{-H})\text{Pt}(\text{Ar}')(\text{PEt}_3)_2]^+$ ($\text{Ar} = \text{Ph}$ and $\text{Ar}' = 2,4\text{-Me}_2\text{C}_6\text{H}_3$ and 2,4,6-Me₃C₆H₂) have been identified in solution. Their ¹H- and ³¹P-NMR data are reported. The X-ray crystal structure of $[(\text{PEt}_3)_2(\text{Ph})\text{Pt}(\mu_2\text{-H})\text{Pt}(\text{Ph})(\text{PEt}_3)_2][\text{BPh}_4]$ is reported.

Introduction

The formation of binuclear hydrido-bridged complexes is being reported with increasing frequency [1]. Among these the mono-hydrido-bridged species have received particular attention mainly because of the deviation from linearity of the M–H–M bond [2]. In recent years several types of hydrido-bridged compounds of platinum(II) have been obtained, mainly using chelating phosphine ligands, e.g.,

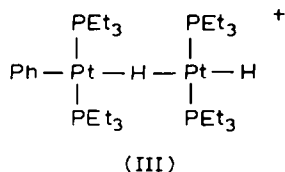


(I)

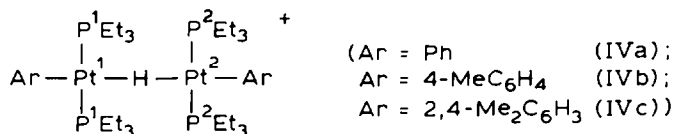


(II)

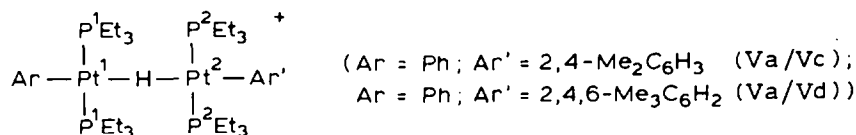
$\text{Ph}_2\text{PCH}_2\text{PPh}_2$ which gives compounds of type I [3], $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ [4] and $^t\text{Bu}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}^t\text{Bu}_2$ [5] which give compounds of type II. However, it has also been shown that mono-hydrido-bridged complexes of platinum(II) can be obtained even using monodentate phosphine ligands, e.g., compound III is readily formed from the reaction of *trans*- $[\text{PtH}(\text{NO}_3)(\text{PEt}_3)_2]$ with $\text{Na}[\text{BPh}_4]$ in methanol [6].



This paper describes a convenient synthetic method for the preparation of symmetrical mono-hydrido-bridged di-platinum complexes of type IV, some of their reactions, their NMR spectroscopic characterization and the X-ray crystal structure of $[(\text{PEt}_3)_2(\text{Ph})\text{Pt}(\mu_2\text{-H})\text{Pt}(\text{Ph})(\text{PEt}_3)_2][\text{BPh}_4]$. The formation of two unsymmetrical

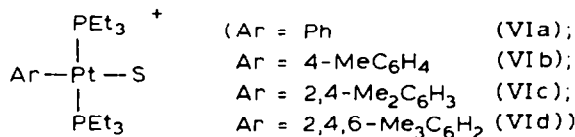


compounds, Va/Vc and Va/Vd, their disproportionation reactions and NMR spectra are also reported.



Preparative studies

Sodium formate reacts with cations VIa to VIc (prepared in situ from the corresponding complexes *trans*- $[\text{PtCl}(\text{Ar})(\text{PEt}_3)_2]$ and AgBF_4 in methanol or acetone) to give hydrido-bridged species IVa to IVc.



(S = methanol or acetone)

A ^{31}P NMR study of this reaction (see Fig. 1) shows that compounds of type IV are formed as indicated in Scheme 1. The formation of hydrido species by decomposition of formate complexes has been previously reported [7]. As can be seen on Fig. 1, this reaction cannot be used to prepare the mononuclear complex *trans*- $[\text{PtH}(\text{Ph})(\text{PEt}_3)_2]$ (VIIIa) even when an excess of formate is employed. This observa-

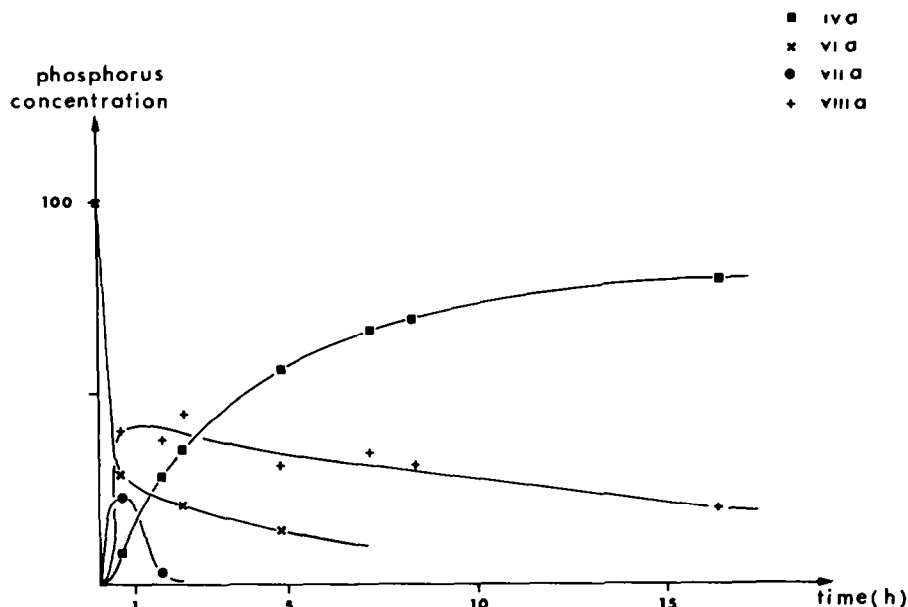
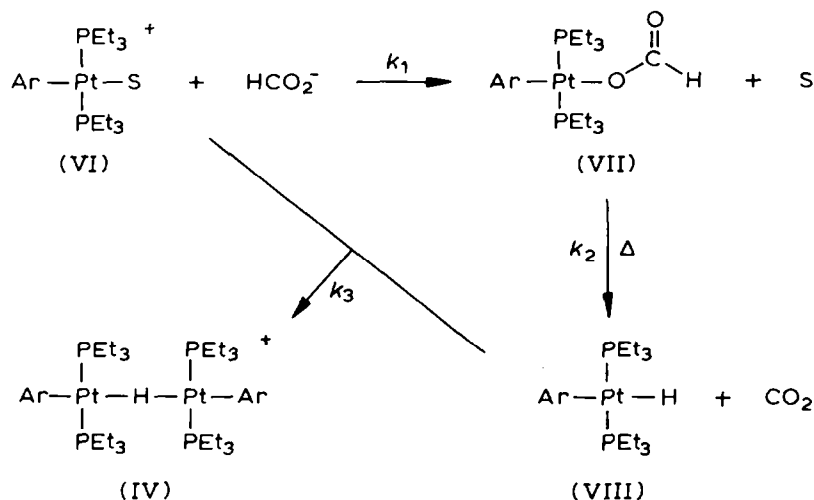
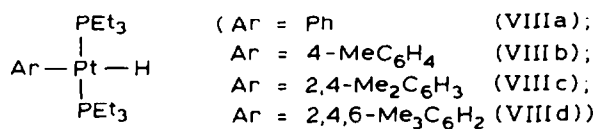


Fig. 1. Time-dependence of the product distribution in the reaction of sodium formate with *trans*-[Pt(acetone)(Ph)(PEt₃)₂]⁺ (VIa) in acetone-*d*₆. (The reaction was monitored by ³¹P NMR; the phosphorus concentration is in arbitrary units normalized to ΣP = 100; a 3-fold excess of formate was used).

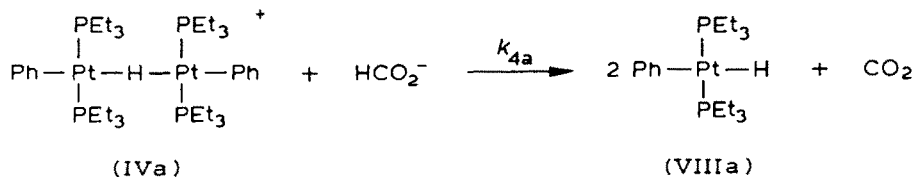


SCHEME 1

tion can be accounted for by assuming that the rate of formation of VIIIa from VIIa, k_{2a} , is slower than the rate of formation of the binuclear species (IVa) from



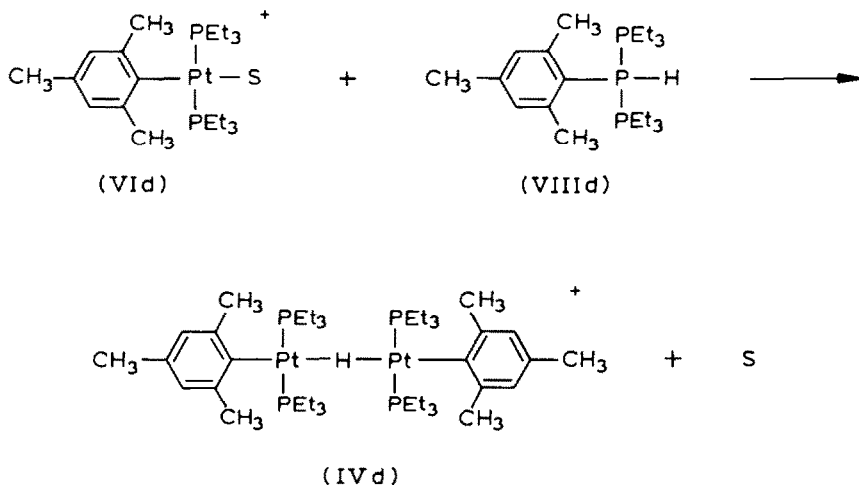
VIa and VIIIa, k_{3a} , and that the rate constant k_{4a} for the reaction below is very small. Support for this hypothesis is provided by an independent study of this



reaction, carried out in acetone at room temperature, which gave a mixture of ca. 75% IVa and ca. 25% VIIIa after 25 days even when a three-fold excess of formate was used.

On the other hand, the reaction of formate with the mesityl solvento complex VIId yields only the mononuclear hydrido complex VIIId. As it is known [8] that replacement of a phenyl by a mesityl group in complexes of the type *trans*-[PtCl(Ar)(PEt₃)₂] slows down the rate of chloride substitution by a factor of ca. 100, it could be presumed that this factor, when applied to the reactions of Scheme 1, would be sufficient to make $k_2 > k_3$.

However, the sole formation of VIIId during the reaction of VIId with formate may also be due to the inherent instability of the hydrido-bridged complex IVd in the solvent medium used. Thus, the reaction below when carried out in acetone or



methanol, did not give detectable amounts of the binuclear species IVd, i.e., if an equilibrium is established this is completely shifted towards the left hand side.

Supporting evidence for the easy dissociation of the binuclear hydrido-bridged complex of type IV, in solution of weak donor solvents, when the aryl group carries α -methyl substituents, is provided by the following set of observations:

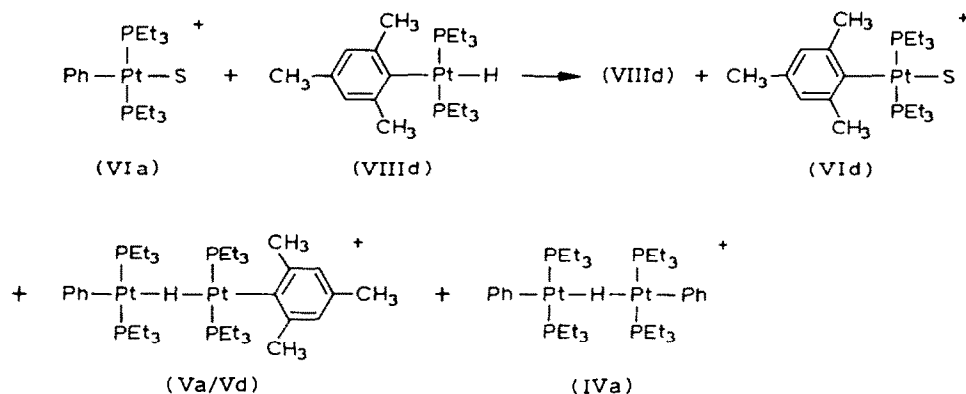
(a) compounds IVa and IVb (Ar = Ph and 4-MeC₆H₄) are not dissociated in either acetone or dichloromethane;

(b) compound IVc (Ar = 2,4-Me₂C₆H₃) is slightly dissociated, at room temperature, into VIc and VIIC in acetone but not dissociated in dichloromethane solution.

These results could be due to steric effects as molecular models show that

formation of the binuclear unit poses very stringent requirements on the possible arrangements of the ethyl groups. Alternatively, the apparent weakness of the Pt–H–Pt bridging unit could be, at least in part, of electronic origin. It is expected that the presence of methyl groups on the phenyl ligand would increase its electron donor capacity and this, in turn, would cause an increase in negative charge on the hydride ligand, making it a better electron donor towards the cation VI_d. On the other hand, the effect of methyl substitution on cations VI would be expected to show the opposite trend, i.e., VI_d would be the weakest electron acceptor. The instability of IV_d would then have to be rationalized by assuming that methyl substitution causes a more marked decrease in acceptor capacity of cation VI_d than an increase in donor ability of hydride VIII_d.

In order to obtain additional evidence on the relative importance of electronic and steric effects on the stability of the Pt–H–Pt bridging unit, the reaction between VIII_d and VI_a, in acetone or methanol, was carried out with the results shown below:

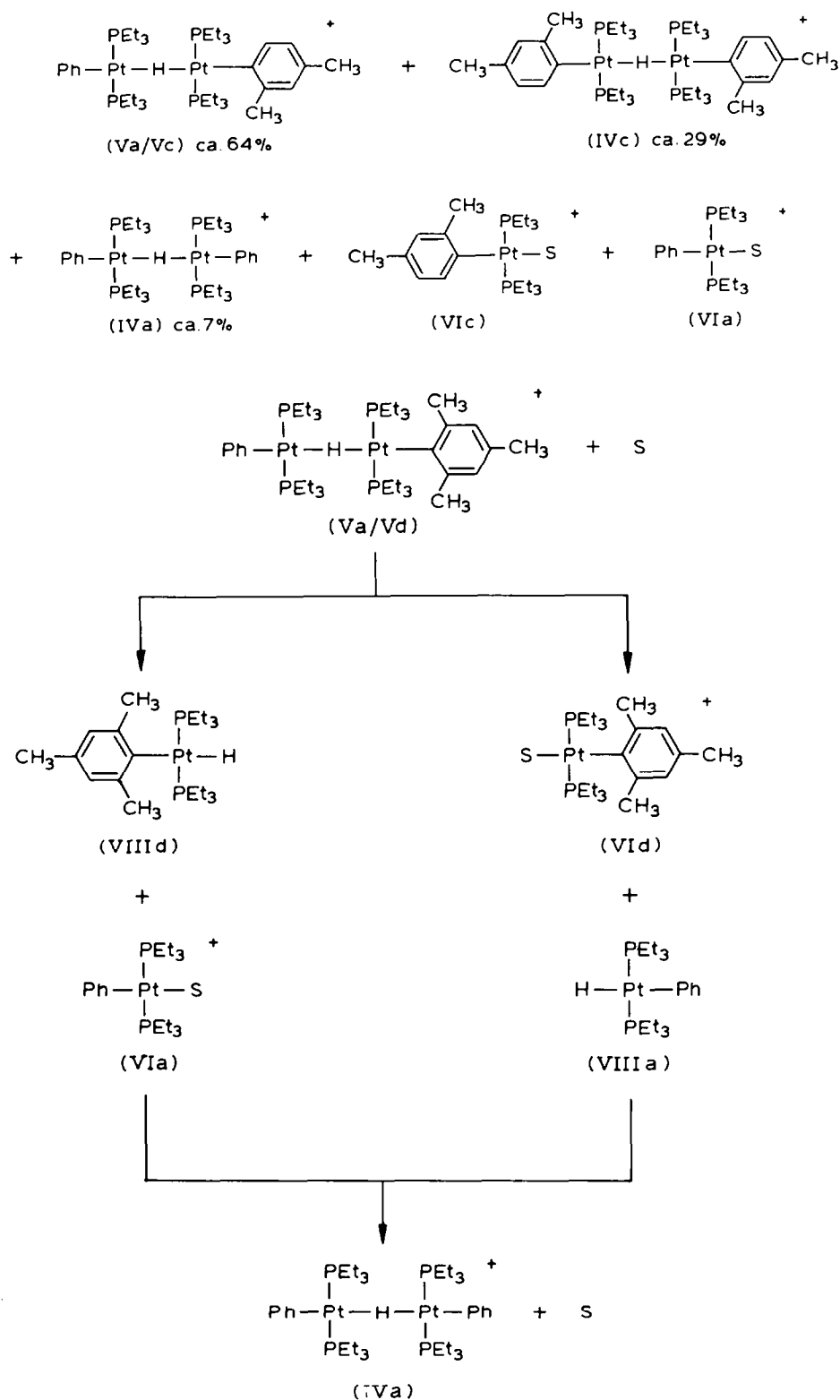


Reaction time	Temp. (°C)	Product distribution (Va/Vd) / (IVa)
30 min	0	no reaction
12 h	10	4/1
40 h	RT	1/60

Thus, the kinetically controlled product Va/V_d is formed, but this rearranges slowly to the thermodynamically favoured mixture of the phenyl binuclear IV_a and the solvated mesityl cation VI_d. It can then be deduced that the easy dissociation of the Pt–H–Pt is attributable to weak bonding interaction caused by mutual steric repulsions of the organic substituents on the two sides of the binuclear species.

The pathway of the above disproportionation can be written as shown in Scheme 2.

The ease of cleavage of the Pt–H–Pt bridging unit and the occurrence of subsequent disproportionation reactions is also shown by the reaction of IV_c (the hydrido-bridged compound with xyllyl groups) with VI_a (the phenyl cation). When this reaction is carried out in methanol or acetone solution for five hours at room temperature, the following mixture of compounds is obtained:



SCHEME 2

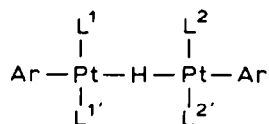
Summing up, binuclear species with bridging hydride ligands of type IV are preferentially formed even in oxygen-donor solvents, as long as the aryl groups terminally bonded to the platinum atoms do not have *o*-methyl substituents. Thus, the preparation of a wide variety of mono-hydrido-bridged di-platinum species does not require the use of chelating phosphine ligands.

NMR spectra

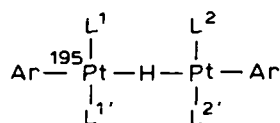
The ^{31}P , ^1H and, for some compounds, the ^{195}Pt NMR spectra were recorded and the parameters obtained are given in Tables 1 and 2. These data have been used for the structural assignments made above and the discussion of the types of spectra is given below.

Symmetric compounds IVa, IVb and IVc

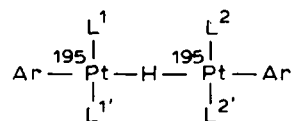
A discussion of the ^{31}P NMR spectra of these species requires consideration of the existence of the following isotopomers (their relative abundances and spin systems are shown in brackets). A schematic representation of the signal pattern expected for these three isotopomers is shown in Fig. 2 and the observed and simulated spectra of compound IVa are shown in Fig. 3. The ^{31}P NMR data for compounds IV are summarized in Table 1.



(IV/0: 43.82% ; A_4)



(IV/1: 44.75%; $A_2A_2'X$)



(IV/2: 11.42% ; $A_2A_2'XX'$)

($L = ^{31}\text{PEt}_3$)

It should be noted that the sub-spectrum of isotopomer IV/2 gives a direct reading of the value of $^2J(\text{Pt}, \text{Pt})$ and that this spectrum, together with that of isotopomer IV/1, allows the determination of the relative signs of $^1J(\text{Pt}, \text{P})$ and $^3J(\text{Pt}, \text{P})$. It should also be noted that in compounds of type IV ^{13}C -satellites are frequently observed in the ^{31}P NMR spectra of the isotopomers IV/0. The relative abundance of that isotopomer with one ^{13}C atom in the $\text{P}(\text{CH}_2\text{CH}_3)_3$, i.e., with $>\text{P}^{13}\text{CH}_2\text{CH}_3$, is 3.3% for each phosphorus atom. These data are also included in Table 1.

The significant ^1H NMR spectral data are summarized in Table 2. The high field part of the spectrum (hydride region) appears as a quintet for isotopomer IV/0, a doublet of quintets for isotopomer IV/1 and a triplet of quintets for isotopomer IV/2.

While the resonances due to the organic substituents in compounds IVa and IVb

TABLE 1. ^{31}P AND ^{195}Pt NMR SPECTRA ^a OF COMPLEXES $[(\text{PEt}_3)_2\text{ArPt}(\mu_2\text{-H})\text{PtAr}'(\text{PEt}_3)_2][\text{BPh}_4]$

	Ar	Ar'	$\delta(\text{P})$ (ppm)	$^1J(\text{Pt}, \text{P})$ (Hz)	$^3J(\text{Pt}, \text{P})$ (Hz)	$^1J(\text{P}, \text{C})$ (Hz)	$\delta(\text{Pt})$ (ppm)	$^2J(\text{Pt}, \text{Pt})$ (Hz)
(IVa)	Ph	Ph	8.2	2675	6.6	17.2	-4549	164.0
(IVb)	4-MeC ₆ H ₄	4-MeC ₆ H ₄	8.3	2682	6.4	17.3		163.1
(IVc)	2,4-Me ₂ C ₆ H ₃	2,4-Me ₂ C ₆ H ₃	7.3	2703	2.7			
(IVa/IVc) ^b	Ph	2,4-Me ₂ C ₆ H ₃	8.5 ^{c,d}	2687	3.3			
			7.6 ^{c,e}	2692	4.4			
(IVa/IVd) ^b	Ph	2,4,6-Me ₃ C ₆ H ₂	8.2 ^d	ca. 2693				
			4.7 ^f	ca. 2690				

^a The spectra were measured in acetone-*d*₆ at 36.43 and 53.53 MHz for ^{31}P and ^{195}Pt respectively. $\delta(^{195}\text{Pt})$ is given relative to $[\text{PtCl}_6]^{2-}$. A negative sign indicates a resonance to high field of the reference. ^b This complex was only identified in solution. ^c When the ^{31}P NMR spectrum is recorded at 101.4 MHz these two phosphorus atoms become inequivalent and an AB type pattern is observed. The splitting between the two central resonances is ca. 2 Hz. ^d Resonance of PEt_3 *cis* to Ph. ^e Resonance of PEt_3 *cis* to 2,4-Me₂C₆H₃. ^f Resonance of PEt_3 *cis* to 2,4,6-Me₃C₆H₂.

TABLE 2. ^1H NMR SPECTRA ^a OF CATIONS $[(\text{PEt}_3)_2\text{ArPt}(\mu_2\text{-H})\text{PtAr}'(\text{PEt}_3)_2]^+$

	Ar	Ar'	$\delta(\text{H})$ (ppm)	$^1J(\text{Pt}, \text{H})$ (Hz)	$^2J(\text{P}, \text{H})$ (Hz) ^b	$\delta(\text{H}(\text{CH}_3))$ (ppm) ^{c,d}	$\delta(\text{H}(\text{CH}_2))$ (ppm) ^{c,e}	$^3J(\text{H}, \text{H})$ (Hz) ^{c,f}	$\delta(\text{H}(\text{CH}_3))$ (ppm) ^g	$^4J(\text{Pt}, \text{H})$ (Hz) ^h	$\delta(\text{H}(\text{CH}_3))$ (ppm) ⁱ
(IVa)	Ph	Ph	-13.07 ^j	447	8.6	1.19 ^{k,l}	1.95 ^{m,n}	7.3			
(IVb)	4-MeC ₆ H ₄	4-MeC ₆ H ₄	-12.99 ^j	448	8.5	1.18 ^k	2.06 ^m	7.3			2.23 ^o
(IVc)	2,4-Me ₂ C ₆ H ₃	2,4-Me ₂ C ₆ H ₃	-12.74 ^j	445	8.2	1.107 ^{k,l,q}	1.77 ^{m,n,q}	7.7	2.46 ^p	7.7	2.23 ^o
						1.121 ^{k,l,q}	1.82 ^{m,n,q}	7.7			
(IVa/IVc)	Ph	2,4-Me ₂ C ₆ H ₃	-13.04	443 447	8.4						

^a Measured at 250 MHz in acetone-*d*₆ (IVa and IVb) and in CD₂Cl₂ (IVc and IVa/IVc). ^b Coupling between the bridging hydride and the phosphorus atoms. ^c Data obtained also by recording the ^1H NMR spectra with simultaneous ^{31}P decoupling. ^d Chemical shift of the CH₃ group in PEt_3 . ^e Chemical shift of the CH₂ group in PEt_3 . ^f Coupling between the H atoms of the CH₂ and CH₃ groups in PEt_3 . ^g Chemical shift of the H atom in the *o*-CH₃ of the 2,4-Me₂C₆H₃ group. ^h Coupling between the platinum atom and the H atom of the *o*-CH₃ group in 2,4-Me₂C₆H₃. ⁱ Chemical shift of the H atom of the *p*-CH₃ group in 4-MeC₆H₄ or 2,4-Me₂C₆H₃. ^j Quintet with Pt satellites. ^k Pseudo-quintet. ^l This quintet reduces to a triplet when the spectrum is recorded with simultaneous ^{31}P decoupling. ^m Complex multiplet. ⁿ This multiplet reduces to a quartet when the spectrum is recorded with simultaneous ^{31}P decoupling. ^o Singlet. ^p Singlet with platinum satellites, see footnote (g). ^q This multiplet reduces to a singlet when the spectrum is recorded with simultaneous ^{31}P heterodecoupling and CH₂ homodecoupling for the observation of $\delta(\text{H}(\text{CH}_3))$ and CH₃ homodecoupling for the observation of $\delta(\text{H}(\text{CH}_2))$. These two singlets occur with a relative intensity of 1/1.

can be described as normal (see Table 2), it should be pointed out that the spectrum of compound IVc shows two CH_2 and two CH_3 sets of resonances arising from the ethyl groups of the phosphine ligands. Each of these sets of signals appears as a single resonance when observed with simultaneous hetero-decoupling of ^{31}P and homo-decoupling of the methyl protons for the observation of the signals due to the CH_2 groups or of the methylene protons to observe the resonances of the CH_3 groups.

Although the crystal structure of compound IVc is not known, it can be presumed to be analogous to that of compound IVa, (see Figs. 5 and 6). Thus, in the absence of free rotation about the Pt-H-Pt bond, (see Fig. 7), L^1 and L^1' (corresponding to P(1) and P(2) respectively) will not be equivalent and the same will be true for L^2 and L^2' (corresponding to P(3) and P(4) respectively), giving rise to two sets of

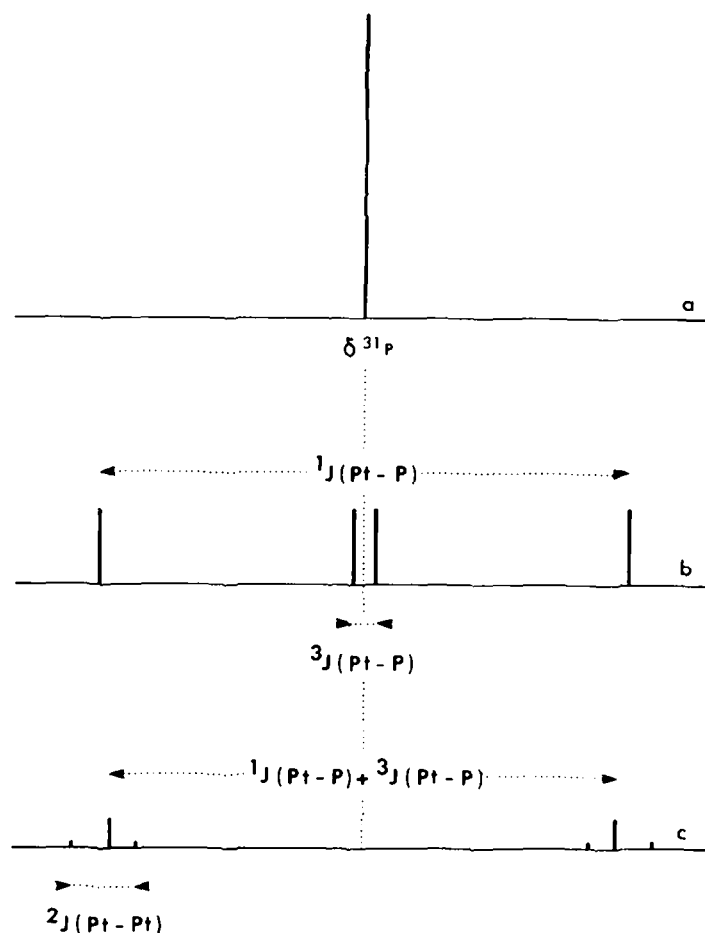
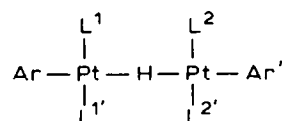


Fig. 2. Schematic representation of the ^{31}P NMR signal pattern for a symmetrical bridged diplatinum complex of the type $[(\text{PEt}_3)_2(\text{Ar})\text{Pt}(\mu_2\text{-H})\text{Pt}(\text{Ar})(\text{PEt}_3)_2]^+$ (IV) (with approximate relative intensities); (a) isotopomer without ^{195}Pt (IV/0); (b) isotopomer with one ^{195}Pt (IV/1); (c) isotopomer with two ^{195}Pt (IV/2) (in that case $^1J(\text{Pt-P})$ and $^3J(\text{Pt-P})$ are of opposite signs; $^4J(\text{P-P}) = 0$; isotopomers with ^{13}C are ignored).

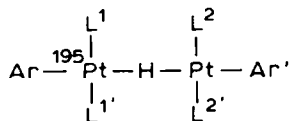
signals mentioned above. It should be noted, however, that no ^{31}P -inequivalence is apparent between L^1 and L' and between L^2 and $\text{L}^{2'}$.

Asymmetric compounds Va/Vc and Va/Vd

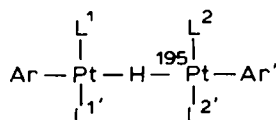
The interpretation of the ^{31}P NMR spectra of these compounds requires consideration of the occurrence of the four isotopomers shown below (their relative abundances and spin systems are given in brackets, $\text{L} = ^{31}\text{PEt}_3$).



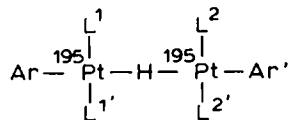
(V/O: 43.82%; A_2M_2)



(V/1x: 22.38%; $\text{A}_2\text{M}_2\text{X}$)



(V/1y: 22.38%; $\text{A}_2\text{M}_2\text{Y}$)



(V/2: 11.42%; $\text{A}_2\text{M}_2\text{XY}$)

The spectrum of this isotopomeric mixture will give a pattern corresponding to the superposition of the sub-spectra shown in Fig. 4. The ^{31}P NMR data for compounds of this type are given in Table 1.

As mentioned earlier the ^{31}P NMR spectrum of the symmetrical compound with *m*-xylyl group, IVc, did not show inequivalence of the phosphorus atoms. While the P atom inequivalence is not observable in compound Va/Vc, when the spectrum is recorded at 36.43 MHz, it becomes apparent as a ca. 2 Hz splitting at 101.4 MHz.

The ^1H NMR spectra of the asymmetrical compounds are more complex than those of the corresponding symmetrical compounds and as compounds Va/Vc and Va/Vd could not be obtained in the pure state no attempt was made to make complete assignment of the resonances observed.

Crystal structure of $[(\text{PEt}_3)_2(\text{Ph})\text{Pt}(\mu_2\text{-H})\text{Pt}(\text{Ph})(\text{PEt}_3)_2][\text{BPh}_4]$

The crystal structure consists of the packing of well separated tetraphenyl borate anions and dinuclear platinum(II) monohydrido-bridged cations.

The relative positions of the heavy atoms of the complex cation, together with the numbering scheme, are shown in Fig. 5; a selection of bond distances and angles is in Fig. 6 and Table 3.

The tetraphenyl borate anion shows the usual distortions from the ideal geometry [9,10]: the B-C bond lengths are equivalent and average to 1.65 Å and the C-B-C angles range from 108 to 111°.

The structure of the cation consists of two platinum-containing units. Both of them are T-shaped with *trans*-phosphorus atoms and a terminal phenyl group. The two units are roughly normal forming a dihedral angle of 80.9°. In both units the coordination of the platinum atoms can be described as square-planar with the fourth coordination site, *trans* to the phenyl group, being occupied by the hydrido

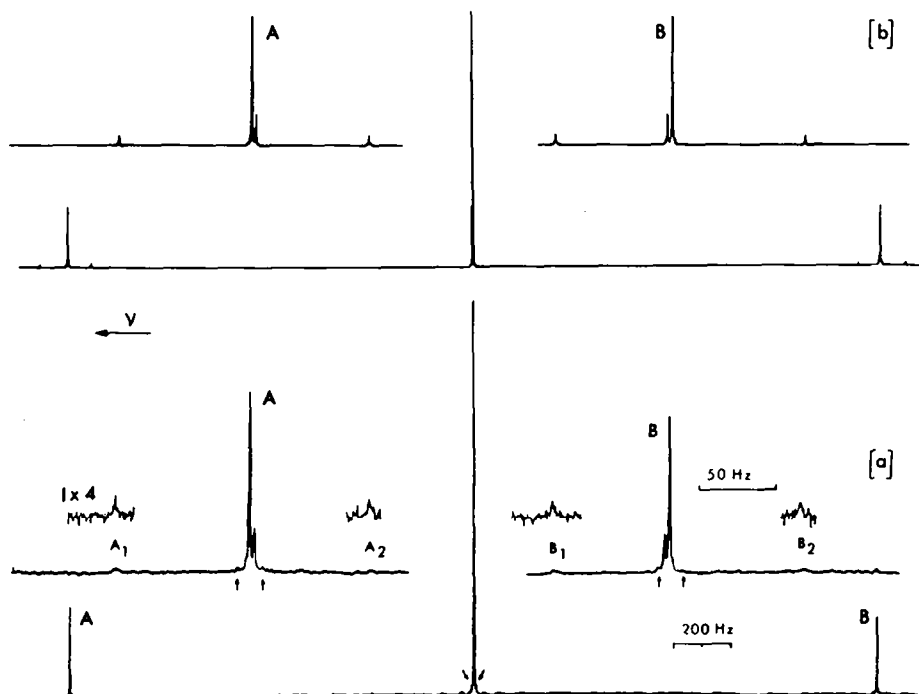


Fig. 3. Observed (a) and simulated (b) ^{31}P NMR spectra of $[(\text{PEt}_3)_2(\text{Ph})\text{Pt}(\mu_2\text{-H})\text{Pt}(\text{Ph})(\text{PEt}_3)_2][\text{BPh}_4]$ (IVa). The simulated spectrum was obtained using the PANIC program on the Bruker Aspect 2000 computer; Note (a) the broadness and weakness (with respect to simulated spectrum) of the lines A_1 , A_2 , B_1 , B_2 , owing to the chemical shift anisotropy relaxation of ^{195}Pt ; (b) the ^{13}C satellites on the central line and on the A and B lines (identified by arrows).

ligand. This latter has not been directly located by this analysis, but its position can be inferred from the NMR data and from the arrangement of the heavy atoms. These also show that the Pt–H–Pt bond is bent as the Pt(1)–Pt(2)–C(55) and Pt(2)–Pt(1)–C(25) are $162.4(6)$ and $162.9(6)^\circ$ respectively. Deviation from linearity of the Pt–H–Pt angles which has also been observed in the unsymmetrical monohydrido-bridged complex III [6] as well as in the dihydrido-bridged complexes $[(\text{PR}_3)_2\text{Pt}(\mu_2\text{-H})_2\text{PtY}(\text{PR}_3)_2]^+$ (Y = H or Ph) [11]. The equal values of the angles Pt(1)–Pt(2)–C(55) and Pt(2)–Pt(1)–C(25) in compound IVa indicate that the hydrido ligand lies in a symmetric position with respect to the two platinum atoms, as can be seen in the schematic representation of the bridging unit in Fig. 6.

The planes of the phenyl groups bound to the platinum atoms are about normal to the respective planes of coordinates of the platinum atoms which, in turn, are nearly normal to each other. The relative orientations of those four planes are shown in Fig. 7.

The coordination geometries of the two metal atoms are similarly distorted. The platinum atoms lie about $0.2 \text{ \AA}$ above the planes defined by the respective phosphorus and carbon donor atoms and the angles at the metals sensibly deviate from the theoretical values. The same distortions, although less severe, are present in the CP_2Pt fragment of compound III, as can be seen on the data shown in Table 4.

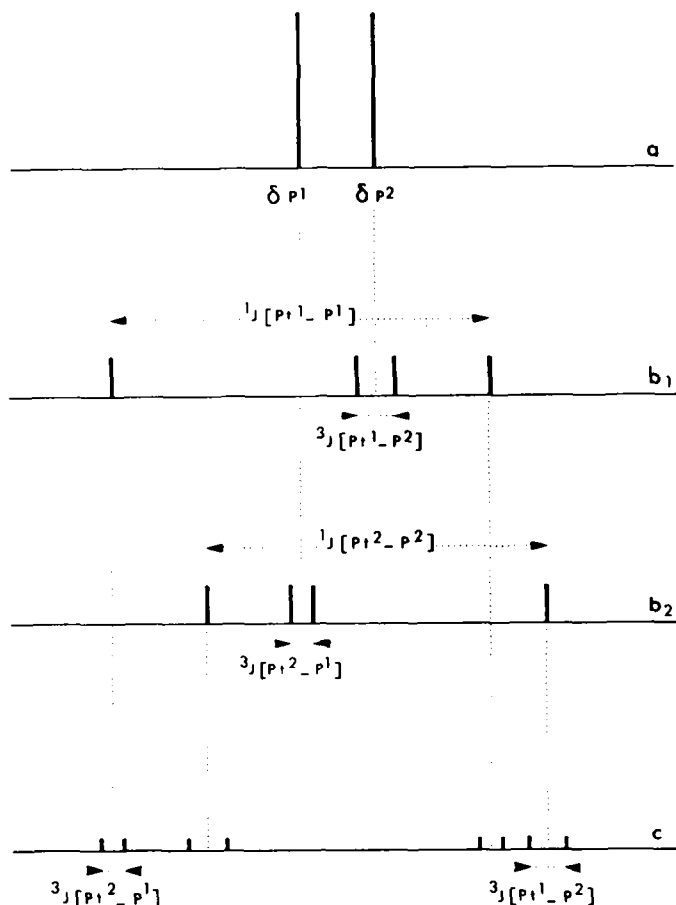


Fig. 4. Schematic representation of the ^{31}P NMR signal pattern for an unsymmetrical bridged diplatinum complex (with approximate relative intensities); (a) isotopomer without ^{195}Pt ($V/0$); (b_1) isotopomer with $^{195}\text{Pt}^1$ ($V/1x$); (b_2) isotopomer with $^{195}\text{Pt}^2$ ($V/1y$); (c) isotopomer with two ^{195}Pt ($V/2$); ($^4J(\text{P-P}) = 0$; isotopomers with ^{13}C are ignored).

The four Pt–P bond lengths are equivalent (2.303(7) to 2.318(7) Å) and comparable with those found in compound III. In this latter there is a significantly shorter Pt(2)–P bond length (2.260 Å), which cannot be explained at the moment.

The Pt(1)–Pt(2) distance of 3.238(1) Å is significantly longer than that observed in the related monohydrido bridged complex III (3.093(1) Å). This difference seems to reflect the variation in the “donor-acceptor” interactions [1] which occur in the symmetrical phenyl-substituted compound IVa with respect to the unsymmetrical phenyl-hydrido complex III. This observation, indicating a rather weak Pt–H–Pt interaction in compound IVb, can be used to rationalize the decreasing strength of the bridging interaction in compounds of type IV in the order $\text{Ph} > 4\text{-MeC}_6\text{H}_4 > 2,4\text{-Me}_2\text{C}_6\text{H}_3 > 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$.

TABLE 3

SELECTED DISTANCES (Å) AND ANGLES (°) IN $[(\text{PEt}_3)_2(\text{Ph})\text{Pt}(\mu_2\text{-H})\text{Pt}(\text{Ph})(\text{PEt}_3)_2]^+[\text{BPh}_4]^-$ (IVa)

Pt(1)···Pt(2)	3.238(1)	C(9)–C(10)	1.596(44)
Pt(1)–P(1)	2.306(6)	C(11)–C(12)	1.529(36)
Pt(1)–P(2)	2.312(6)	C(13)–C(14)	1.477(47)
Pt(1)–C(25)	2.053(19)	C(15)–C(16)	1.477(42)
Pt(2)–P(3)	2.303(7)	C(17)–C(18)	1.462(40)
Pt(2)–P(4)	2.318(7)	C(19)–C(20)	1.513(42)
Pt(2)–C(55)	2.046(22)	C(21)–C(22)	1.431(44)
P(1)–C(1)	1.851(25)	C(23)–C(24)	1.585(39)
P(1)–C(3)	1.840(26)	C(25)–C(26)	1.325(31)
P(1)–C(5)	1.947(30)	C(26)–C(27)	1.469(34)
P(2)–C(7)	1.899(26)	C(27)–C(28)	1.342(41)
P(2)–C(9)	1.869(29)	C(28)–C(29)	1.340(44)
P(2)–C(11)	1.816(25)	C(29)–C(30)	1.396(38)
P(3)–C(13)	1.907(33)	C(30)–C(25)	1.358(31)
P(3)–C(15)	1.860(34)	C(55)–C(56)	1.446(32)
P(3)–C(17)	1.826(26)	C(56)–C(57)	1.370(34)
P(4)–C(19)	1.825(26)	C(57)–C(58)	1.381(39)
P(4)–C(21)	1.931(33)	C(58)–C(59)	1.433(38)
P(4)–C(23)	1.797(28)	C(59)–C(60)	1.347(36)
C(1)–C(2)	1.494(39)	C(40)–C(55)	1.390(32)
C(3)–C(4)	1.545(37)	B–C(31)	1.651(33)
C(5)–C(6)	1.356(42)	B–C(37)	1.685(32)
C(7)–C(8)	1.446(39)	B–C(43)	1.594(33)
		B–C(49)	1.675(33)
P(1)–Pt(1)···Pt(2)	105.6(2)	C(21)–P(4)–C(23)	98.8(13)
P(2)–Pt(1)···Pt(2)	85.4(2)	P(1)–C(1)–C(2)	115.2(17)
C(25)–Pt(1)···Pt(2)	162.4(6)	P(1)–C(3)–C(4)	116.6(18)
P(1)–Pt(1)–P(2)	167.6(2)	P(1)–C(5)–C(6)	113.5(22)
P(1)–Pt(1)–C(25)	87.3(6)	P(2)–C(7)–C(8)	111.7(17)
P(2)–Pt(1)–C(25)	83.3(6)	P(2)–C(9)–C(10)	115.8(18)
Pt(1)···Pt(2)–P(3)	88.6(2)	P(2)–C(11)–C(12)	118.1(12)
Pt(1)···Pt(2)–P(4)	102.3(2)	P(3)–C(13)–C(14)	114.7(21)
Pt(1)···Pt(2)–C(55)	162.9(6)	P(3)–C(15)–C(16)	116.8(20)
P(3)–Pt(2)–P(4)	165.9(2)	P(3)–C(17)–C(18)	114.8(19)
P(3)–Pt(2)–C(55)	85.5(7)	P(4)–C(19)–C(20)	115.4(18)
P(4)–Pt(2)–C(55)	86.4(7)	P(4)–C(21)–C(22)	117.9(20)
Pt(1)–P(1)–C(1)	111.4(8)	P(4)–C(23)–C(24)	113.0(18)
Pt(1)–P(1)–C(3)	113.5(8)	C(25)–C(26)–C(27)	121.5(21)
Pt(1)–P(1)–C(5)	118.2(9)	C(26)–C(27)–C(28)	120.7(27)
C(1)–P(1)–C(3)	102.4(12)	C(27)–C(28)–C(29)	116.1(28)
C(1)–P(1)–C(5)	102.2(12)	C(28)–C(29)–C(30)	122.8(25)
C(3)–P(1)–C(5)	107.0(12)	C(29)–C(30)–C(25)	122.3(23)
Pt(1)–P(2)–C(7)	110.5(8)	C(30)–C(25)–C(26)	115.7(19)
Pt(1)–P(2)–C(9)	114.4(8)	Pt(1)–C(25)–C(26)	118.8(15)
Pt(1)–P(2)–C(11)	116.4(9)	Pt(1)–C(25)–C(30)	125.0(17)
C(7)–P(2)–C(9)	107.7(11)	C(55)–C(56)–C(57)	119.7(20)
C(7)–P(2)–C(11)	103.8(11)	C(56)–C(57)–C(58)	122.6(24)
C(9)–P(2)–C(11)	102.6(12)	C(57)–C(58)–C(59)	115.8(23)
Pt(2)–P(3)–C(13)	115.2(11)	C(58)–C(59)–C(60)	123.4(23)
Pt(2)–P(3)–C(15)	117.2(9)	C(59)–C(60)–C(55)	120.0(22)
Pt(2)–P(3)–C(17)	108.7(9)	C(60)–C(55)–C(56)	118.0(20)
C(13)–P(3)–C(15)	107.3(14)	Pt(2)–C(55)–C(56)	121.8(15)

TABLE 3 (continued)

C(13)–P(3)–C(17)	101.5(13)	Pt(2)–C(55)–C(60)	119.5(16)
C(15)–P(3)–C(17)	105.5(12)	C(31)–B–C(37)	108.4(17)
Pt(2)–P(4)–C(19)	115.4(9)	C(31)–B–C(43)	108.3(17)
Pt(2)–P(4)–C(21)	118.7(9)	C(31)–B–C(49)	110.6(19)
Pt(2)–P(4)–C(23)	112.7(9)	C(37)–B–C(43)	110.3(20)
C(19)–P(4)–C(21)	103.0(12)	C(37)–B–C(49)	107.7(17)
C(19)–P(4)–C(23)	106.2(12)	C(43)–B–C(49)	111.4(17)

Experimental

The infrared spectra were recorded on samples in KBr discs, on a Beckman, Model 4250, spectrophotometer. The ^{31}P NMR spectra were measured using acetone- d_6 solutions, in 10 mm sample tubes, using a Bruker HX 90 E spectrometer. A positive sign of the chemical shift denotes a resonance to low field of the reference. The ^1H spectra were obtained using a Bruker WM 250 spectrometer, the samples being dissolved in acetone- d_6 unless stated otherwise.

The complexes were prepared under oxygen-free, dry nitrogen.

trans-[PtBr(4-MeC₆H₄)(PEt₃)₂]

A solution of K₂(PtCl₄) (0.66 g, 1.6 mmol), in water (4.6 ml) was added slowly to a solution of KOH (0.37 g, 6.5 mmol) and triethylphosphine (1.4 ml, 9.5 mmol) in ethanol (14 ml) and water (0.5 ml). The mixture was stirred for 1 h at room temperature and then for 3.5 h at 60°C. The colourless solution was taken to dryness

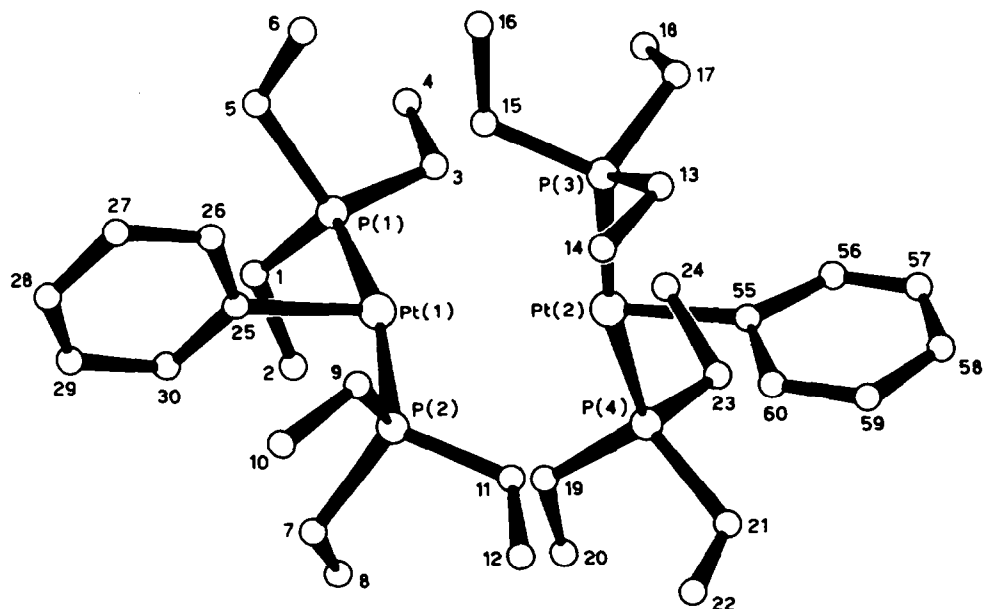


Fig. 5. Perspective drawing of the cationic complex $[(\text{PEt}_3)_2(\text{Ph})\text{Pt}(\mu_2\text{-H})\text{Pt}(\text{Ph})(\text{PEt}_3)_2]^+$.

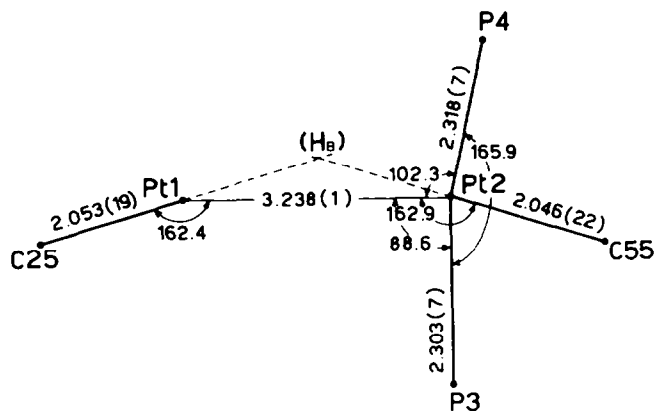


Fig. 6. Content of the equatorial plane of the cationic complex $[(\text{PEt}_3)_2(\text{Ph})\text{Pt}(\mu_2\text{-H})\text{Pt}(\text{Ph})(\text{PEt}_3)_2]^+$. The broken lines represent the theoretical directions of the Pt-H bonds.

under vacuum and the reddish, oily residue was extracted with hexane (2×10 ml). The extracts were filtered off, the solvent evaporated under reduced pressure and the residue heated to 50°C under vacuum for 5 h. The oily $[\text{Pt}(\text{PEt}_3)_3]$ [12] thus obtained was treated with *p*-bromotoluene (2.05 g, 12.0 mmol) in toluene (10 ml) and the mixture was heated first to 80°C for 1.5 h and then to 120°C for 3 h. The solvent was evaporated under reduced pressure and the yellowish residual oil was recrystallized from petroleum ether (b.p. $80\text{--}95^\circ\text{C}$). The white crystalline product (m.p. 137°C) was obtained in 51% yield. Found: C, 37.97; H, 6.12; P, 10.14; Br, 13.17. $\text{C}_{25}\text{H}_{25}\text{BrP}_2\text{Pt}$ calcd.: C, 37.88; H, 6.19; P, 10.28; Br, 13.26%.

$\delta(^{195}\text{Pt})$ -4352 ppm; $\delta(^{31}\text{P})$ 12.4 ppm; $^1J(\text{Pt}, \text{P})$ 2781 Hz; $\delta(\text{H}(\text{CH}_3 \text{ of Et}))$ 0.8–1.1 ppm (m); $\delta(\text{H}(\text{CH}_2 \text{ of Et}))$ 1.5–1.8 ppm (m); $\delta(\text{H}(\text{CH}_3))$ 2.15 ppm (s); $\delta(\text{H}_a(\text{H meta to CH}_3))$ 7.18 ppm (d); $^3J(\text{Pt}, \text{H}_a)$ 67 Hz; $\delta(\text{H}_b(\text{H ortho to CH}_3))$ 6.70 ppm (d); $^3J(\text{H}_a, \text{H}_b)$ 8 Hz.

TABLE 4

COMPARISON AMONG THE CP_2Pt UNITS IN THE COMPLEXES $[(\text{PEt}_3)_2(\text{Ph})\text{Pt}(\mu_2\text{-H})\text{Pt}(\text{Ph})(\text{PEt}_3)_2]^+ [\text{BPh}_4]^-$ (IVa) and $[(\text{PEt}_3)_2(\text{Ph})\text{Pt}(\mu_2\text{-H})\text{PtH}(\text{PEt}_3)_2]^+ [\text{BPh}_4]^-$ (III)

	III ⁶	IVa	
	Pt(1) unit	Pt(1) unit	Pt(2) unit
P(x)–Pt–P(y)	169.5(1)°	167.6(2)°	165.9(2)°
P(x)–Pt–C	88.3(3)°	87.3(6)°	86.4(7)°
P(y)–Pt–C	87.6(3)°	83.3(6)°	85.5(7)°
Pt displacement from the P(x)P(y)C plane	0.20 Å	0.18 Å	0.25 Å
(x = 1 and y = 2 for Pt(1) while x = 3 and y = 4 for Pt(2))			

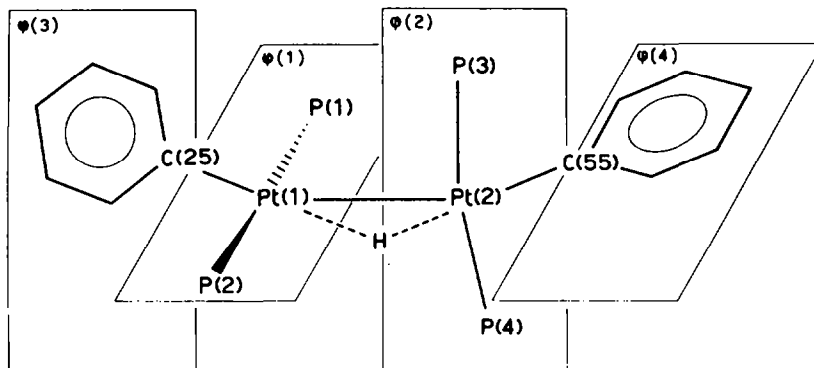


Fig. 7. Relative orientations of the planes of coordination of the platinum atoms and those of the phenyl ligands in the cationic complex $[(\text{PEt}_3)_2(\text{Ph})\text{Pt}(\mu_2\text{-H})\text{Pt}(\text{Ph})(\text{PEt}_3)_2]^+$. ψ_1/ψ_2 80.9, ψ_1/ψ_3 = 90.5, ψ_2/ψ_4 85.7°.

trans-[PtBr(2,4-Me₂C₆H₃)(PEt₃)₂]

This was prepared and purified in the same way as the *p*-tolyl derivative. K₂-[PtCl₄] (0.34 g, 0.8 mmol), triethylphosphine (0.68 g, 4.5 mmol) and 1-bromo-2,4-dimethylbenzene (1.1 g, 6.0 mmol) gave white crystals, of m.p. 152°C, in 52% yield. Found: C, 39.68; H, 6.35; P, 9.96; Br, 12.30. C₂₆H₂₇BrP₂Pt calcd.: C, 38.97; H, 6.38; P, 10.05; Br, 12.96%. $\delta(^{195}\text{Pt})$ -4368 ppm; $\delta(^{31}\text{P})$ 11.2 ppm; $^1J(\text{Pt}, \text{P})$ 2780 Hz; $\delta(\text{H}(\text{CH}_3 \text{ of Et}))$ 0.8–1.3 ppm (m); $\delta(\text{H}(\text{CH}_2 \text{ of Et}))$ 1.3–1.9 ppm (m); $\delta(\text{H}_a(\text{CH}_3 \text{ para to Pt}))$ 2.15 ppm (s); $\delta(\text{H}_c(\text{CH}_3 \text{ ortho to Pt}))$ 2.35 ppm (s); $^4J(\text{Pt}, \text{H}_c)$ 7 Hz; $\delta(\text{H}_{d,e}(\text{ortho H atoms}))$ 6.4–6.9 ppm (m); $\delta(\text{H}_b(\text{H between CH}_3 \text{ groups}))$ 7.1–7.6 ppm (m).

trans-[PtBr(2,4,6-Me₃C₆H₂)(PEt₃)₂]

Similarly K₂[PtCl₄] (1.50 g, 3.7 mmol), triethylphosphine (3.0 ml, 20 mmol) and bromomesitylene (4.3 ml, 28.5 mmol), gave white crystals of product in 51% yield [8]. $\delta(^{195}\text{Pt})$ -4372 ppm; $\delta(^{31}\text{P})$ 9.3 ppm; $^1J(\text{Pt}, \text{P})$ 2790 Hz; $\delta(\text{H}(\text{CH}_3 \text{ of Et}))$ 0.8–1.3 ppm (m); $\delta(\text{H}(\text{CH}_2 \text{ of Et}))$ 1.4–1.9 ppm (m); $\delta(\text{H}_c(\text{CH}_3 \text{ para to Pt}))$ 2.15 ppm (s); $\delta(\text{H}_a(\text{CH}_3 \text{ ortho to Pt}))$ 2.48 ppm; $^4J(\text{Pt}, \text{H}_a)$ 8 Hz; $\delta(\text{H}_b(\text{H between CH}_3 \text{ groups}))$ 6.60 ppm; $^4J(\text{Pt}, \text{H}_b)$ 15 Hz.

$[(\text{PEt}_3)_2\text{PhPt}(\mu_2\text{-H})\text{PtPh}(\text{PEt}_3)_2][\text{BPh}_4]$ (IVa)

A solution of AgBF₄ (0.29 g, 1.50 mmol), in methanol (5 ml) was added to a suspension of *trans*-[PtClPh(PEt₃)₂] [13] (0.82 g, 1.50 mmol) in methanol (10 ml). The mixture was stirred for 30 min and the solid filtered off. Solid sodium formate (0.051 g, 0.75 mmol) was added to the colourless filtrate. The formate dissolved within a few minutes and then Na[BPh₄] (0.34 g, 1.00 mmol) in methanol (3 ml) was added. The solution was stirred until gas evolution stopped (ca. 45 min) and the solvent was then evaporated under reduced pressure. The residual yellow oil was dissolved in the minimum amount of acetone and the product precipitated as a white powder by addition of methanol. Pure IVa was obtained in 55% yield by recrystallization from acetone/methanol. Found: C, 53.87; H, 7.01; P, 10.04. IVa calcd.: C, 53.89; H, 6.86; P, 9.26%. $\nu(\text{Pt-H})$ 1700–1800 cm⁻¹ (m, very broad).

$[(\text{PEt}_3)_2(4\text{-MeC}_6\text{H}_4)\text{Pt}(\mu_2\text{-H})\text{Pt}(4\text{-MeC}_6\text{H}_4)(\text{PEt}_3)_2][\text{BPh}_4] \text{ (IVb)}$

IVb was obtained in 50% yield as described for IVa, starting from *trans*-[PtBr(4-MeC₆H₄)(PEt₃)₂]. Found: C, 54.43; H, 7.00; P, 8.67. IVb calcd.: C, 54.54; H, 7.01; P, 9.07%. $\nu(\text{Pt-H})$ 1700–1800 cm⁻¹ (m, very broad).

$[(\text{PEt}_3)_2(2,4\text{-Me}_2\text{C}_6\text{H}_3)\text{Pt}(\mu_2\text{-H})\text{Pt}(2,4\text{-Me}_2\text{C}_6\text{H}_3)(\text{PEt}_3)_2][\text{BPh}_4] \text{ (IVc)}$

IVc was obtained in 75% yield as described for IVa, starting from *trans*-[PtBr(2,4-Me₂C₆H₃)(PEt₃)₂]. Found: C, 55.24; H, 7.17; P, 8.48. IVc calcd.: C, 55.17; H, 7.16; P, 8.89%. $\nu(\text{Pt-H})$ 1700–1800 cm⁻¹ (very broad).

trans-[PtH(2,4,6-Me₃C₆H₂)(PEt₃)₂] (VIIId)

An equimolecular mixture of VIII d and *trans*-[Pt(MeOH)(2,4,6-Me₃C₆H₂)(PEt₃)₂]⁺ (VI d) was obtained when *trans*-[PtBr(2,4,6-Me₃C₆H₂)(PEt₃)₂] [8] was treated first with AgBF₄ and then with formate as described for the synthesis of IVa. Compound VIII d was prepared in 70% yield by carrying out this reaction using a 1/1 ratio of platinum-bromo complex and formate. Found: C, 44.91; H, 7.72; P, 10.99. VIII d calcd.: C, 45.72; H, 7.67; P, 11.23%. $\nu(\text{Pt-H})$ 1910 cm⁻¹ (vs). $\delta(^{31}\text{P})$ 16.35 ppm (acetone-*d*₆); $^1\text{J}(\text{Pt}, \text{P})$ 2825 Hz; $\delta(^1\text{H}(\text{hydride}))$ -6.38 ppm (acetone-*d*₆); $^1\text{J}(\text{Pt}, \text{H})$ 639 Hz; $^2\text{J}(\text{P}, \text{H})$ 19.0 Hz; $\delta(\text{H}(\text{CH}_3 \text{ of Et}))$ 1.05 ppm (pseudo sextet); $\delta(\text{H}(\text{CH}_2 \text{ of Et}))$ 1.63 ppm (complex multiplet); $\delta(\text{H}(\text{o-CH}_3 \text{ of mesityl}))$ 2.30 ppm; $^4\text{J}(\text{Pt}, \text{H})$ 5 Hz; $\delta(\text{H}(\text{p-CH}_3 \text{ of mesityl}))$ 2.23 ppm.

When this latter method was used in an attempt to prepare pure [PtH(2,4-Me₂C₆H₃)(PEt₃)₂] (VIIIc) from the corresponding bromo-complex, a mixture of VIIIc (ca. 30%) and IVc was obtained.

Single crystals of $[(\text{PEt}_3)_2\text{PhPt}(\mu_2\text{-H})\text{PtPh}(\text{PEt}_3)_2]^+ [\text{BPh}_4]^-$ (IVa) suitable for diffraction analysis, were obtained from acetone/methanol.

Crystal data

[C₆₀H₉₁BP₄Pt₂], *M* = 1337.3. Monoclinic, *a* 13.733(6), *b* 21.462(7), *c* 21.727(7) Å, β 95.85(3)°, *V* 6371(4) Å³, *Z* = 4, *D*_c 1.394 g cm⁻³, *F*(000) = 2675, space group *P*2₁/c(*C*_{2h}⁵, No. 14), Mo-*K*_α radiation, λ 0.71069 Å, (Mo-*K*_α) 45.6 cm⁻¹.

X-Ray measurements

A preliminary photograph study allowed the derivation of the space group from the systematically absent reflections. A single crystal of approximate dimensions 0.25 × 0.30 × 0.50 mm³ was selected and used for all the measurements. The cell constants were determined from the setting angles of 15 reflections centered on a Syntex P2₁ computer controlled diffractometer equipped with a graphite monochromator. The intensities of 16570 reflections with 3° ≤ θ ≤ 28° were measured by ω -scan technique. The intensities of three standard reflections were periodically remeasured throughout the data collection. They were found to decrease gradually, reaching the maximum decay of 16% at the end of the run. Linear correction factors were therefore applied to account for the loss of intensity. The reflections were then processed as described elsewhere [14], using an ignorance factor *p* = 0.013 and corrected for shape anisotropy as described in the literature [15]. Only 4930 independent reflections met the condition *I* > 3σ(*I*) and were used in the subsequent calculations.

TABLE 5

FINAL ATOMIC POSITIONAL PARAMETERS ($\times 10^4$) FOR THE NON-HYDROGEN ATOMS

Atom	x	y	z
Pt(1)	2658(1)	4959(0)	3012(0)
Pt(2)	578(1)	4941(0)	2165(0)
P(1)	2843(5)	5963(3)	3382(3)
P(2)	2679(5)	3896(3)	2837(3)
P(3)	1383(5)	5255(3)	1338(3)
P(4)	-524(5)	4792(3)	2892(3)
B	4833(20)	2853(13)	16(14)
C(1)	2988(18)	5986(12)	4238(11)
C(2)	2256(22)	5612(13)	4546(12)
C(3)	1755(19)	6454(11)	3191(12)
C(4)	1828(23)	7138(13)	3413(13)
C(5)	3970(20)	6441(14)	3175(13)
C(6)	3925(25)	6601(15)	2569(14)
C(7)	2948(19)	3458(11)	3594(12)
C(8)	2255(19)	3612(12)	4030(13)
C(9)	3591(22)	3639(11)	2307(11)
C(10)	4270(23)	3067(18)	2543(14)
C(11)	1551(18)	3546(12)	2489(11)
C(12)	1517(19)	2838(12)	2414(12)
C(13)	1309(23)	4688(16)	659(14)
C(14)	1972(31)	4147(13)	747(15)
C(15)	2686(25)	5490(12)	1503(13)
C(16)	3144(19)	5797(14)	996(12)
C(17)	758(20)	5936(12)	983(12)
C(18)	719(21)	6473(13)	1393(16)
C(19)	120(19)	4710(13)	3690(12)
C(20)	-701(25)	4637(14)	4168(12)
C(21)	-1413(20)	4094(17)	2792(13)
C(22)	-1004(21)	3480(13)	2822(15)
C(23)	-1405(19)	5410(23)	2894(11)
C(24)	-917(20)	6077(24)	2980(13)
C(25)	4104(14)	4820(10)	3323(10)
C(26)	4779(16)	4940(10)	2944(9)
C(27)	5822(20)	4821(13)	3128(15)
C(28)	6129(23)	4636(11)	3705(13)
C(29)	5441(22)	4592(11)	4098(12)
C(30)	4447(18)	4683(10)	3916(11)
C(31)	4349(11)	2281(8)	392(6)
C(32)	3789(11)	2418(8)	876(6)
C(33)	3346(11)	1938(8)	1178(6)
C(34)	3462(11)	1321(8)	997(6)
C(35)	4022(11)	1184(8)	513(6)
C(36)	4466(11)	1665(8)	211(6)
C(37)	4008(10)	3083(8)	-567(9)
C(38)	3013(10)	3022(8)	-500(9)
C(39)	2318(10)	3201(8)	-980(9)
C(40)	2617(10)	3442(8)	-1527(9)
C(41)	3612(10)	3503(8)	-1593(9)
C(42)	4308(10)	3324(8)	-1114(9)
C(43)	5797(11)	2598(7)	-250(7)
C(44)	6728(11)	2756(7)	21(7)
C(45)	7555(11)	2549(7)	-242(7)

TABLE 5 (continued)

Atom	x	y	z
C(46)	7451(11)	2184(7)	-776(7)
C(47)	6519(11)	2027(7)	-1047(7)
C(48)	5692(11)	2234(7)	-784(7)
C(49)	5080(13)	3467(8)	483(7)
C(50)	5561(13)	3363(8)	1070(7)
C(51)	5789(13)	3864(8)	1468(7)
C(52)	5536(13)	4469(8)	1278(7)
C(53)	5055(13)	4573(8)	690(7)
C(54)	4827(13)	4072(8)	292(7)
C(55)	-546(17)	4708(10)	1515(10)
C(56)	-1323(19)	5142(9)	1321(10)
C(57)	-2131(18)	4939(14)	955(13)
C(58)	-2205(2)	4343(12)	714(12)
C(59)	-1420(22)	3928(12)	916(13)
C(60)	-651(17)	4094(11)	1317(11)

Structure determination and refinement

The structure was solved by heavy atom method and refined by least-squares procedures. The isotropic refinement converged at $R = 0.069$.

Afterwards the phenyl groups of the $[\text{BPh}_4]^-$ anion were constrained to 6/mmm symmetry, $d(\text{C}-\text{C})$ 1.395 and $d(\text{H}-\text{H})$ - 1.08 Å but the carbon atoms were assigned individual isotropic thermal parameters. The hydrogen contributions of the ethyl groups were neglected while those of the phenyl ligands were taken into account. All the non-group, non-hydrogen atoms were allowed to vibrate anisotropically. The refinement converged at $R = 0.059$ and $R_w = 0.063$. A final electron density map did not reveal residual peaks which could be interpreted as the bridging hydrido ligand.

The refinement was carried out by blocked full matrix and the function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o) + b|F_o|^2$. Scattering factors and anomalous dispersion terms were taken from the International Tables of X-Ray Crystallography [16]. The calculations were carried out on the HP21 MX minicomputer of the NRC Research Area of Rome, using local programs and on the IBM 3330/168 computer of CNUCE, Pisa, using the SHELX system (G.M. Sheldrick).

The final positional atomic parameters are listed in Table 5. Tables of thermal atomic parameters and observed and calculated structure factors are available from the authors.

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