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Synthetic and Structural Studies of Some Dinuclear Platinum(II) Dihydrido-Bridged Cations Containing both Four- and Five-Coordinate Metal Centers

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A general synthetic route has been developed to the air-stable complexes $[(PR_3)_2Pt(\mu\text{-}H)_2PtY(PR'_3)_2]^+$ (R = R′ = Et, c-Hx, and Ph for Y = H; R = R′ = Et for Y = Ph; R = Ph, R′ = c-Hx for Y = H). This consists of the in situ generation of a platinum dihydride, "$PtH_2(PR_3)_2$", from $[Pt(1,5\text{-}C_8H_{12})_2]$, PR_3, and H_2 and its subsequent trapping by a species of the type $[PtY((CH_3)_2CO)(PR'_3)_2]^+$ (Y = H or Ph, $(CH_3)_2CO$ = acetone). The trihydride $[(PEt_3)_2Pt(\mu\text{-}H)_2PtH(PEt_3)_2]^+$ is more conveniently prepared by reacting $[PtHCl(PEt_3)_2]$ with $NaBH_4$. ^1H, ^{31}P, and ^{195}Pt NMR data are used to deduce that in these compounds there are two hydrogen atoms bridging between two different platinum centers, one of which is four-coordinate and the other five-coordinate. The X-ray crystal structures of $[(PEt_3)_2Pt(\mu\text{-}H)_2PtY(PEt_3)_2][BPh_4]$ (Y = H and Ph) show that this type of structure is also present in the solid state.

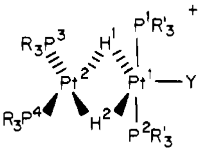
Introduction

Recently there have been a number of reports concerned with dinuclear platinum hydrides of various types.[2-9] Interest in such complexes is related to a number of factors, including their possible use as catalysts in processes of industrial importance, the activation of dihydrogen by low-valent metal centers, and the influence of ligands on complex geometry and its relationship to spectroscopic features.[10]

While investigating reactions of monohydride platinum(II) species, we observed[2] the unexpected formation of the dinuclear platinum hydride cation $[(PEt_3)_2HPt(\mu\text{-}H)PtPh(PEt_3)_2]^+$ (**1**), which contains a single hydride bridge. We now report the preparation of its isomer $[(PEt_3)_2Pt(\mu\text{-}H)_2PtPh(PEt_3)_2]^+$ (**2**), the syntheses of related trihydride complexes of the type $[(PR_3)_2Pt(\mu\text{-}H)_2PtH(PR'_3)_2]^+$ (**3**), and the X-ray crystal structures of $[(PEt_3)_2Pt(\mu\text{-}H)_2PtY(PEt_3)_2][BPh_4]$ (Y = H and Ph). The cationic hydride $[(PPh_3)_2Pt(\mu\text{-}H)_2PtH(PPh_3)_2]^+$ (**3c**) was the subject of a preliminary communication.[3]

Results.

Synthesis. Cations of the type $[(PR_3)_2Pt(\mu\text{-}H)_2PtY(PR'_3)_2]^+$ (**2, 3a–d**) were prepared in fair yield with use of the synthetic route



2, R = R′ = Et, Y = Ph
3a, R = R′ = Et, Y = H^3
b, R = R′ = c-Hx, Y = H^3
c, R = R′ = Ph, Y = H^3
d, R = Ph, R′ = c-Hx, Y = H^3

$$[Pt(1,5\text{-}C_8H_{12})_2] + 2PR_3 \xrightarrow[\text{toluene, 0 °C}]{H_2} \text{“}PtH_2(PR_3)_2\text{”}$$

$$\text{“}PtH_2(PR_3)_2\text{”} + trans\text{-}[PtY((CH_3)_2CO)(PR'_3)_2][BF_4] \xrightarrow[\text{acetone}]{} \mathbf{2}\text{ or }\mathbf{3}$$

There are two underlying concepts involved.

(a) A reactive platinum hydride species[11] is generated in situ from the oxidative addition of dihydrogen to a zerovalent bis(phosphine) platinum complex. (The activation of dihydrogen in this manner has been reported for the synthesis of a compound of the type $[LYPt(\mu\text{-}H)_2PtYL]$ (**4**), i.e., **4a** (L = $P(c\text{-}Hx)_3$ and Y = H),[4] and *trans*-$[PtH_2(PR_3)_2]$.[12-14] Furthermore, Yoshida et al.[14b] observed reversible hydrogen loss from certain *cis*-dihydride bis(phosphine) complexes.)

(b) A "Lewis acid", i.e., a complex with a vacant coordination site, can react with a "Lewis base", i.e., a transition-metal hydride, to form a "complex" in which one or more hydride atoms act as bridging ligands:

$$[MH_mL_n] + [M'L'_p] \rightarrow [L_nM(\mu\text{-}H)_mM'L'_p]$$

Shapley et al.[15] have used a similar scheme to rationalize the syntheses of various mixed-metal clusters, e.g., $[ReOs_3H_2(CO)_{10}]$, and have called it "metal hydride coupling".[15] In our particular system the cationic species can be considered as the Lewis acid and the reactive dihydride as the Lewis base, i.e.

$$\text{“}PtH_2(PR_3)_2\text{”} + [PtY((CH_3)_2CO)(PR'_3)_2]^+ \rightarrow [(PR_3)_2Pt(\mu\text{-}H)_2PtY(PR'_3)_2]^+$$

(R, R′ = Ph, c-Hx, or Et; Y = H or Ph; $(CH_3)_2CO$ = acetone)

This, however, is only a formal scheme since it cannot be used to predict the phosphine distribution in the product when the Lewis acid and Lewis base contain different tertiary phosphines; e.g., "$PtH_2[P(c\text{-}Hx)_3]_2$" and $[PtH((CH_3)_2CO)(PPh_3)_2]^+$ give the isomer $[(PPh_3)_2Pt(\mu\text{-}H)_2PtH(P(c\text{-}Hx)_3)_2]^+$ (**3d**). Compound **3a**, when obtained by the synthetic method

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(11) NMR studies of the reaction between $[Pt(1,5\text{-}C_8H_{12})_1]$, 2 PR_3, and H_2 show mixtures of products of differing composition depending on the nature of PR_3, the solvent, and the degree of H_2 saturation. These will be reported elsewhere.

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Table I. $^{195}Pt\{^1H\}$ NMR Data[a]

compd	solvent	$\delta(Pt^1)$	$\delta(Pt^2)$	J(Pt,Pt)
2	acetone-d_6	−4399	−5265	796
3a[b]	acetone-d_6	−4855	−5204	886
3b	CD_2Cl_2	−4812	−5328	268
3c	CD_2Cl_2	−4756	−5104	325
3d	CD_2Cl_2	−4908	−5255	701

compd	solvent	$\delta(Pt^1)$	J(Pt,P)
$[PtH((CH_3)_2CO)(P(c\text{-}Hx)_3)_2]^+$	acetone-d_6	−4668	2783
$[PtH((CH_3)_2CO)(PEt_3)_2]^{+}$[c]	acetone-d_6	−4703	2685
$[PtPh((CH_3)_2CO)(PEt_3)_2]^+$	acetone-d_6	−4052	2802
t-$[PtH_2(P(c\text{-}Hx)_3)_2]$	benzene-d_6	−5383	2873

[a] Relative to external Na_2PtCl_6, with J in Hz at 19.34 MHz. The compounds were measured at room temperature with Pt^1 and Pt^2 corresponding to the numbering in the figures. A negative sign denotes a shift to high field (low frequency). [b] At 273 K $\delta(Pt^1)$ and $\delta(Pt^2)$ are −4810 and −5163, respectively. [c] At 333 K.

described above, contained significant amounts of byproducts of similar solubilities from which it could not be conveniently separated. However, this complex could be satisfactorily obtained from the reaction of *trans*-$[PtHCl(PEt_3)_2]$ with $Na[BH_4]$ in a CH_3CN/H_2O medium. It is worth remarking that this reaction gives the hydrido-bridged binuclear complex and not the mononuclear hydrido complex *trans*$[PtH_2(PEt_3)_2]$ reported by Yoshida and Otsuka[14] and a number of other workers[10,16] using other routes.

Characterization. The pure compounds **2** and **3a–d** are all colorless or pale yellow solids with good air stability both in the solid state and in solution at room temperature. Their IR spectra allowed the identification of the $[BF_4]^-$ unit (ν_{B-F} ~1060 cm^{-1}) and gave an absorption between 2150 and 2250 cm^{-1} for the terminal hydride (when present), which, in some cases, was rather weak. There was also an ill-defined broad absorption in the region 2000–1500 cm^{-1}, which, in view of the results of Ciriano et al.,[5] may be associated with the vibrations of the bridging hydrido ligands.

The ^1H, ^{31}P, and ^{195}Pt NMR studies gave the structural information described below. The asymmetric dinuclear nature of the complexes **2** and **3a–d** was clearly demonstrated by the presence of two sets of resonances in their *^{195}Pt NMR spectra*. In addition, the multiplicity of these resonances established that each platinum atom was coordinated to two chemically equivalent tertiary phosphine ligands. Table I reports the appropriate chemical shift data and the values of the ^{195}Pt–^{195}Pt spin–spin coupling constants, ^2J(Pt,Pt) (for details of the assignment of Pt^1 and Pt^2 see the section on ^{31}P NMR). The principal NMR features are as follows.

(1) The shift of the five-coordinate center, Pt^1 (≃−4800 ppm for the trihydrides), occurs in the region associated with mononuclear platinum(II) complexes of the type *trans*-$[PtY((CH_3)_2CO)(PR_3)_2]^+$ (see Table I).

(2) The shift of the four-coordinate center, Pt^2 (≃−5200 ppm), is always to high field of that of Pt^1 and, at least for **3b**, the $\delta(^{195}Pt)$ value is remarkably similar to that of related *trans*-$[PtH_2(P(c\text{-}Hx)_3)_2]$ (see Table I).

(3) While there are only small changes in $\delta(^{195}Pt)$ when the phosphine ligands are varied, replacement of a terminal hydride by a phenyl group (**3a** compared to **2**) causes a significant downfield shift of $\delta(^{195}Pt^1)$, i.e., of the atom at which substitution has occurred, but has only a small effect on $\delta(^{195}Pt^2)$.

(4) The measured platinum–platinum coupling constants are toward the lower end of the range observed for this parameter and may be interpreted as indicating there is little direct metal–metal interaction.[10] Since this coupling is very sensitive to complex type and geometry, we cannot reliably interpret the very different values (268–886 Hz) for **2** and **3a–d**. For comparison, the measured values for **4b** (L = $PMe\text{-}t\text{-}Bu_2$ and Y = $Si(OEt)_3$) **1**, and $[(L\text{–}L)HPt(\mu\text{-}H)PtH(L\text{–}L)]^+$ ((L–L) = $t\text{-}Bu_2P(CH_2)_3P\text{-}t\text{-}Bu_2$) (**5a**), all of which contain hydrido bridges, are 92,[5] 366,[2] and 840 Hz,[7] respectively.

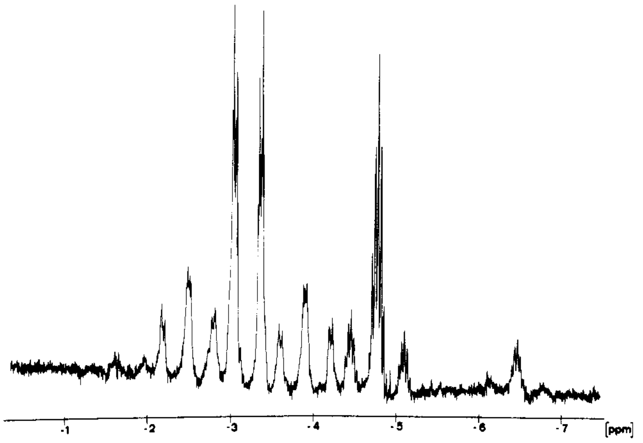

Figure 1. Hydride region of the 360-MHz ^1H NMR spectrum of $[(PPh_3)_2Pt(\mu\text{-}H)_2PtH(PPh_3)_2][BF_4]$.

The *$^{31}P\{^1H\}$ NMR spectra* of the complexes **2** and **3a–d** show, in each case, two sets of resonances each corresponding to one pair of phosphorus atoms. Both sets of resonances appear as a central triplet, owing to ^4J(P,P), with two sets of platinum satellites arising from ^1J(Pt,P) and ^3J(Pt,P). The chemical shifts, which fall in the range expected for platinum(II) complexes of these tertiary phosphine ligands,[17] and the relevant coupling constants are collected in Table II. It is found that $^1J(Pt^2,P)$ is always larger than $^1J(Pt^1,P)$ by 100–500 Hz while, in most cases, $^3J(Pt^2,P)$ is smaller than $^3J(Pt^1,P)$.

Unambiguous correlation of the phosphorus resonances to a particular platinum center was achieved by "off-resonance" ^1H decoupling of the hydride region. Under these conditions the resonances associated with P^3 appear as a broad doublet due to ^2J(P,H (trans)) while the set of resonances belonging to the other phosphorus atoms merely broaden. Since it is generally observed that values of ^2J(P,H) for platinum complexes are large (>100 Hz) for mutual trans arrangements and small (<25 Hz) for the corresponding cis forms, it was deduced that the splitting (in both magnitude and multiplicity) was consistent with the expected behavior of P^3 and P^4 on Pt^2.

In addition to the resonances attributable to the tertiary phosphine ligands the *^1H NMR spectra* of **2** and **3a–d** show a complex set of signals to high field of Me_4Si. For the trihydrides **3a–3d** the resonances attributable to two bridging hydrides and a unique terminal hydride can be clearly distinguished. The complexity of these resonances arises mainly from the strongly coupled spin system in conjunction with fairly small chemical shift differences and also in part to the occurrence of numerous overlapping ^{195}Pt satellites. The hydride region of the 360-MHz ^1H NMR spectrum of $[(PPh_3)_2Pt(\mu\text{-}H)_2PtH(PPh_3)_2]^+$ (**3c**) is shown in Figure 1. ^nJ(Pt,H) values were obtained directly from spectral separations, while simulation and iteration methods[18] were used to obtain the ^2J(P,H) values. The hydride signals shown in Figure 1 are interpreted in the following way.

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(18) LAME, LACOON with magnetic equivalence: C. W. Haig, University College, Swansea, England.

Table II. $^{31}P\{^1H\}$ NMR Data[a]

compd	$\delta(P^1)$	$\delta(P^3)$	$^4J(P^1,P^3)$	$^1J(Pt^1,P^1)$	$^3J(Pt^2,P^1)$	$^1J(Pt^2,P^3)$	$^3J(Pt^1,P^3)$
2a (R = R′ = Et, Y = Ph)	15.7	17.4	3	2608	29	2702	26
3a (R = R′ = Et, Y = H)	23.9	20.6	3	2538	23	2742	30
3b (R = R′ = c-Hx, Y = H)	38.7	38.5	3	2649	13	2864	49
3c[b] (R = R′ = Ph, Y = H)	26.6	31.9	2	2803	18	3008	42
3d (R = Ph, R′ = c-Hx, Y = H)	44.0	34.0	2	2576	18	3022	30

[a] Measured at room temperature (acetone-d_6). The numbering corresponds to that used in the figures. δ values are given with respect to external H_3PO_4, with J values given in Hz. [b] In CD_2Cl_2.

Table III. ^1H NMR Data[a]

compd	solvent	$\delta(H^1)$	$\delta(H^3)$	$^2J(H^1,H^3)$	$^1J(Pt^1,H^3)$	$^3J(Pt^2,H^3)$[c]	$^1J(Pt,H^{1,2})$[b]	$^2J(P,H)$[d]	$^2J(P^1,H^{1,2})$
2	acetone-d_6	−5.04					301, 598	105	6
3a	acetone-d_6	−3.55	−4.93	14	1316	192	361, 592	106	5
3b	CD_2Cl_2	−6.43	−8.61	12	1090	~220	415, 565	104	4
3c	acetone-d_6	−3.20	−4.75	14	1197	226	397, 601	110	5
3d	CD_2Cl_2	−4.14	−5.05	13	1247	246	392, 606	115	<5

[a] J values are in Hz. [b] Assignment of the individual J values to Pt¹ and Pt² was not made. [c] $^2J(P^1,H^3)$ and $J(P^3,H^3)$ are ≈10 Hz. [d] $^2J(P,H)\,|^2J(P^3,H^1) + {}^2J(P^4,H^1)| = |^2J(P^3,H^2) + {}^2J(P^4,H^2)|$.

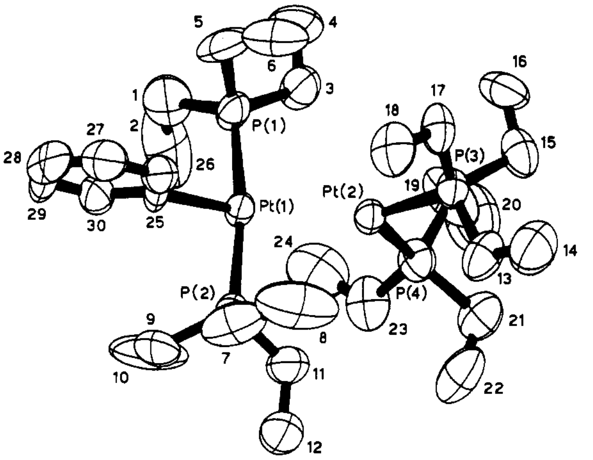

Figure 2. Perspective drawing of the binuclear cationic complex $[(PEt_3)_2Pt(\mu\text{-}H)_2PtPh(PEt_3)_2]^+$. The ellipsoids represent 50% probability.

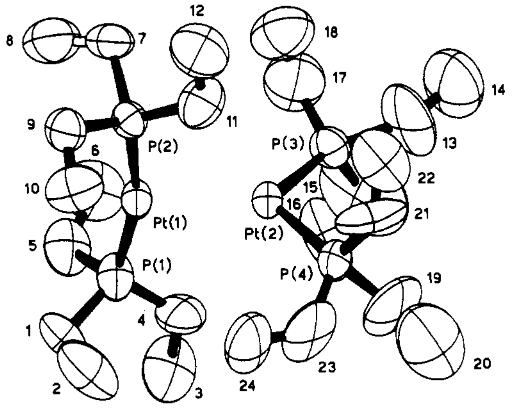

Figure 3. Perspective drawing of the binuclear cationic complex $[(PEt_3)_2Pt(\mu\text{-}H)_2PtH(PEt_3)_2]^+$. The ellipsoids represent 50% probability.

Table IV. Selected Distances (Å) in $[(PEt_3)_2Pt(\mu\text{-}H)_2PtPh(PEt_3)_2][BPh_4]$ (**2**) and in $[(PEt_3)_2Pt(\mu\text{-}H)_2PtH(PEt_3)_2][BPh_4]$ (**3a**)

	2	**3a**
Pt(1)···Pt(2)	2.819 (1)	2.826 (1)
Pt(1)–P(1)	2.289 (3)	2.287 (7)
Pt(1)–P(2)	2.295 (3)	2.284 (6)
Pt(1)–C(25)	2.074 (10)	
Pt(2)–P(3)	2.257 (3)	2.269 (6)
Pt(2)–P(4)	2.317 (3)	2.289 (6)
P(1)–C(1)	1.786 (13)	1.808 (23)
P(1)–C(3)	1.809 (13)	1.774 (26)
P(1)–C(5)	1.884 (15)	1.831 (24)
P(2)–C(7)	1.839 (15)	1.866 (24)
P(2)–C(9)	1.834 (16)	1.845 (23)
P(2)–C(11)	1.797 (12)	1.833 (24)
P(3)–C(13)	1.809 (11)	1.898 (23)
P(3)–C(15)	1.831 (11)	1.877 (49)
P(3)–C(17)	1.838 (13)	1.799 (31)
P(4)–C(19)	1.882 (13)	2.034 (42)
P(4)–C(21)	1.836 (14)	1.811 (55)
P(4)–C(23)	1.744 (14)	1.759 (39)

(1) δ −4.75, assigned to the terminal hydride, is of relative intensity 1 and shows satellites arising from short- and long-range platinum couplings ($^1J(Pt^1,H) = 1197$, $^3J(Pt^2,H) = 226$ Hz) and fine structure resulting from the four phosphorus atoms ($J(P,H) \simeq 10$ Hz) and the bridging hydrido ligands ($^2J(H,H) = 14$ Hz).

(2) δ −3.20, assigned to the bridging hydride resonance, is of relative intensity 2 and shows two distinct sets of platinum satellites ($^1J(Pt,H) = 601$ and 397 Hz). The obvious division of the main-line signals into two well-separated multiplets arises from the large value of $|^2J(P^3,H) + {}^2J(P^4,H)|$, a natural consequence of the fact that $^2J(P,H)$ is large (>100 Hz) for the trans geometry and small (<25 Hz) for cis arrangements.[19] The remaining multiplet structure arises from coupling to the terminal hydride and the phosphorus atoms P¹ and P². The derived data for **3c** together with those from the other hydrides **2**, **3a**, **3b**, and **3d** are to be found in Table III. It is apparent that, although there are only small chemical shift differences between the bridging and terminal hydride resonances, the former are invariably to lower field. Hydride chemical shifts are known to be particularly sensitive to the nature of the trans ligand,[20] and our data are consistent with the presence of trans hydride and/or phosphorus ligands. Typical data are −5.71 ppm for $[PtH(PPh_3)_3]^+(CDCl_3)$[16,21] and −2.22 ppm for *trans*-$[PtH_2(PEt_3)_2]$(benzene-d_6).[13] The values of $^1J(Pt^1,H)$ for the terminal hydride are of the expected magnitude. For the bridging hydride there are two, noticeably smaller, platinum couplings, $^1J(Pt^1$ or $Pt^2,H)$, but it was not possible to individually assign them.

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Table V. Selected Angles (deg) in $[(PEt_3)_2Pt(\mu\text{-}H)_2PtPh(PEt_3)_2][BPh_4]$ (**2**) and in $[(PEt_3)_2Pt(\mu\text{-}H)_2PtH(PEt_3)_2][BPh_4]$ (**3a**)

	2	**3a**
P(1)-Pt(1)···Pt(2)	93.3 (1)	97.2 (2)
P(2)-Pt(1)···Pt(2)	93.7 (1)	98.0 (1)
C(25)-Pt(1)···Pt(2)	158.5 (3)	
P(1)-Pt(1)-P(2)	171.1 (1)	164.7 (2)
P(1)-Pt(1)-C(25)	87.7 (3)	
P(2)-Pt(1)-C(25)	87.7 (3)	
Pt(1)···Pt(2)-P(3)	132.9 (1)	130.9 (2)
Pt(1)···Pt(2)-P(4)	124.5 (1)	125.1 (2)
P(3)-Pt(2)-P(4)	102.6 (1)	104.0 (2)
Pt(1)-P(1)-C(1)	113.5 (5)	113.3 (9)
Pt(1)-P(1)-C(3)	114.5 (4)	116.1 (9)
Pt(1)-P(1)-C(5)	115.3 (5)	112.0 (9)
C(1)-P(1)-C(3)	105.1 (7)	109.0 (12)
C(1)-P(1)-C(5)	103.2 (7)	98.5 (11)
C(3)-P(1)-C(5)	103.9 (6)	106.4 (12)
Pt(1)-P(2)-C(7)	117.2 (4)	113.5 (8)
Pt(1)-P(2)-C(9)	113.1 (5)	114.0 (8)
Pt(1)-P(2)-C(11)	115.7 (4)	115.8 (8)
C(7)-P(2)-C(9)	101.6 (8)	101.8 (10)
C(7)-P(2)-C(11)	104.7 (6)	102.4 (10)
C(9)-P(2)-C(11)	102.7 (7)	107.9 (11)
Pt(2)-P(3)-C(13)	110.9 (4)	117.1 (10)
Pt(2)-P(3)-C(15)	117.5 (4)	117.9 (15)
Pt(2)-P(3)-C(17)	116.4 (4)	114.8 (10)
C(13)-P(3)-C(15)	105.7 (6)	94.6 (17)
C(13)-P(3)-C(17)	105.4 (6)	107.6 (15)
C(15)-P(3)-C(17)	99.6 (5)	102.1 (18)
Pt(2)-P(4)-C(19)	110.3 (4)	107.5 (11)
Pt(2)-P(4)-C(21)	115.2 (4)	117.7 (16)
Pt(2)-P(4)-C(23)	116.0 (4)	119.8 (12)
C(19)-P(4)-C(21)	106.7 (6)	114.2 (20)
C(19)-P(4)-C(23)	104.7 (7)	93.3 (18)
C(21)-P(4)-C(23)	103.0 (6)	102.1 (20)

X-ray Crystal Structures of $[(PEt_3)_2Pt(\mu\text{-}H)_2PtPh(PEt_3)_2][BPh_4]$ (2) and $[(PEt_3)_2Pt(\mu\text{-}H)_2PtH(PEt_3)_2][BPh_4]$ (3a). Both crystal structures consist of the packing of well-separated tetraphenylborate anions and dinuclear platinum(II) dihydrido-bridged cations.

The relative positions of the heavy atoms of the complex cations, together with the numbering schemes, are shown in Figures 2 and 3; a selection of bond distances and angles are compiled in Tables IV and V.

In both structures the tetraphenylborate anion deviates from the T_d geometry as already observed:[22,23] the B–C bond lengths are equivalent and average 1.68 (3) Å for both **2** and **3a**; the C–B–C angles range from 105 to 112° for both structures.

The two dinuclear cationic complexes comprise two different platinum-containing units. The first, based on Pt(1), is T-shaped in **2** with trans phosphorus atoms and a terminal phenyl group and is almost linear in **3a** with trans phosphorus atoms. The second, containing Pt(2), is V-shaped with cis phosphorus atoms in both complexes. These two fragments are roughly perpendicular in the two complexes: the dihedral angle between their planes is 86.0° in **2** and 88.6° in **3a**.

The Pt(1)–Pt(2) distance (2.819 (1) Å in **2**, 2.826 (1) Å in **3a**) is closer to that of the dihydrido-bridged species **4c** (L = $P(c\text{-}Hx)_3$ and Y = $Si(OEt)_3$, 2.692 (3) Å)[5] than to that (3.093 Å) found in the monohydrido-bridged complex $[(PEt_3)_2HPt(\mu\text{-}H)PtPh(PEt_3)_2][BPh_4]$ (**1**), an isomer of **2**.[2]

In both structures the hydride ligands were not located; however, their approximate positions can be inferred from the arrangement of the heavier atoms. To a first approximation the coordination around Pt(1) could be described as trigonal bipyramidal with two bridging hydride ligands and a terminal phenyl group in **2**, or two bridging and one terminal hydride ligand in **3a**, occupying equatorial sites. The coordination around Pt(2) could be described as square planar with cis hydride (bridging) and phosphorus atoms, in both complexes.

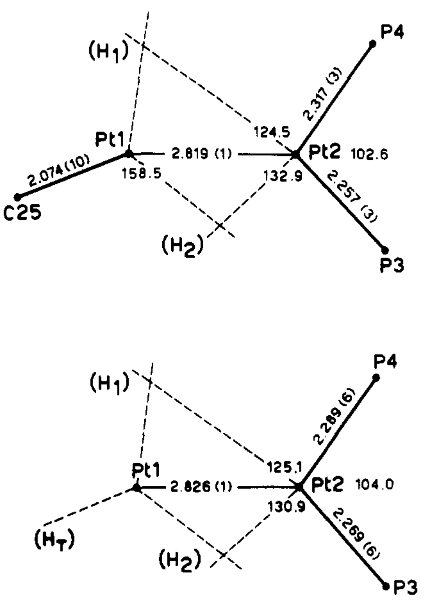

Figure 4. Top: Content of the coordination plane for the binuclear complex $[(PEt_3)_2Pt(\mu\text{-}H)_2PtPh(PEt_3)_2]^+$. The light lines represent the theoretical directions of the Pt–H bonds. A regular trigonal-bipyramidal coordination is assumed around Pt(1) and a distorted-square-planar coordination around Pt(2). The deformation of the P(3)–Pt(2)–P(4) angle is assumed as entirely affecting the Pt–H directions. Bottom: Content of the coordination plane for the binuclear complex $[(PEt_3)Pt(\mu\text{-}H)_2PtH(PEt_3)_2]^+$. The light lines represent the theoretical directions of the Pt–H bonds. In this case the regular trigonal-bipyramidal coordination around Pt(1) is constructed by starting from a Pt–H_T (terminal hydride) direction assumed as lying on the Pt(1)–C(25) bond of complex **2**. A distorted-square-planar coordination was assumed around Pt(2), and the deformation of the P(3)–Pt(2)–P(4) angle is assumed as entirely affecting the Pt–H directions.

The positions of the heavy atoms suggest that in both **2** and **3a** the two hydrido bridges are geometrically different and that the $Pt(\mu\text{-}H)_2Pt$ moiety can be defined as unsymmetrical. Thus (i) the Pt(1)–Pt(2) direction does not bisect the P(3)–Pt(2)–P(4) angle as the Pt(1)–Pt(2)–P(3) and Pt(1)–Pt(2)–P(4) angles are 132.9 (1) and 124.5 (1)° in **2** and 130.9 (2) and 125.1 (2)° in **3a**, (ii) the Pt–P bond lengths at Pt(2) are significantly different, with Pt(2)–P(3) being 2.257 (3) Å in **2** and 2.269 (6) Å in **3a**, while Pt(2)–P(4) is 2.317 (3) Å in **2** and 2.289 (6) Å in **3a**, and (iii) the Pt(1)–C(25) bond in **2** is not collinear with the Pt(1)–Pt(2) direction, with C(25)–Pt(1)–Pt(2) being 158.5 (3)°.

Using these data, one can represent the bridging interactions in extreme forms as shown in Figure 4. In particular the long Pt(2)–P(4) distance would then be a result of the strong trans influence of the hydride ligand H(2), which is bonded to Pt(2).

A nonlinear arrangement of the phenyl group and the two platinum atoms was also observed in the monohydrido-bridged complex **1**, an isomer of **2**.[2] Also in **1** the difference in the two Pt(2)–P bond lengths is significant, but no clear explanation is evident at the moment.

Table VI reports the observed Pt–Pt distances in binuclear platinum complexes containing one or more hydrido bridges. As can be seen, Pt–Pt distances in **2** and **3a** are significantly shorter than in **1**, where only one hydrido bridge exists. On the other hand, they are significantly longer than in **5b**[24] and

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(22) R. E. Cramer and J. T. Huneke, *Inorg. Chem.*, **17**, 365 (1978).

(23) M. Di Vaira and A. B. Orlandini, *J. Chem. Soc., Dalton Trans.*, (1972) 1704.

(24) H. D. Kaesz and G. Minghetti, private communication.

Table VI. Pt–Pt Distances, Number of Hydrido Bridges, and Coordination Number of the Platinum Atoms in Some Binuclear Hydrido-Bridged Platinum Complexes[a]

compd	Pt^1-Pt^2, Å	no. of bridging H atoms[b]	Pt^1 and Pt^2 coordination polyhedra	ref
$[(PEt_3)_2Pt(\mu\text{-}H)_2PtPh(PEt_3)_2]^+$ (**2**)	2.819 (1)	2 unsym	square planar trigonal bipyramidal	present work
$[(PEt_3)_2Pt(\mu\text{-}H)_2PtH(PEt_3)_2]^+$ (**3a**)	2.826 (1)	2 unsym	square planar trigonal bipyramidal	present work
$[(PEt_3)_2HPt(\mu\text{-}H)PtPh(PEt_3)_2]^+$ (**1**)	3.093 (1)	1	square planar square planar dihedral angle ~90°	2
$[(dppe)Pt(\mu\text{-}H)_2PtH(dppe)]^+$ (**5b**)	2.728 (1)	2 sym	square planar trigonal bipyramidal, H axial	24
$[LYPt(\mu\text{-}H)_2PtYL]$ (**4c**)	2.692 (3)	2 sym	square planar square planar dihedral angle 21°	5
$[(dbpp)Pt(\mu\text{-}H)_xPtH_{3-x}(dbpp)]^+$ (**5a**)	2.768 (2)	1	trigonal bipyramidal[c] trigonal bipyramidal	7

[a] Abbreviations: dppe = $Ph_2PCH_2CH_2PPh_2$; L = $P(c\text{-}Hx)_3$; Y = $SiMe_3$; dbpp = $t\text{-}Bu_2P(CH_2)_3P\text{-}t\text{-}Bu_2$. [b] In this context the term symmetrical or unsymmetrical is not referred to each hydrido bridge but to the $Pt(\mu\text{-}H)_2Pt$ moiety. [c] One of the bonds of the set is the Pt–Pt bond.

Table VII. Analytical Data for Complexes **2** and **3a–d**

compd	% yield	mp, °C	% C calcd	% C found	% H calcd	% H found
$[Pt_2H_2Ph(PEt_3)_4][BF_4]$ (**2**)	22	>180 dec	35.02	34.99	6.56	6.63
$[Pt_2H_3(PEt_3)_4][BPh_4]$ (**3a**)	91	120–125 dec	48.65	48.64	7.06	6.97
$[Pt_2H_3(P(c\text{-}Hx)_3)_4][BF_4]$ (**3b**)	32	>165 dec	53.99	54.30	8.50	8.73
$[Pt_2H_3(PPh_3)_4][BF_4]$ (**3c**)	41	>190 dec	56.55	56.22	4.15	4.23
$[Pt_2H_3(PPh_3)_2(P(c\text{-}Hx)_3)_2][BF_4]$ (**3d**)	34	>200 dec	55.24	55.14	6.37	6.32

in **4c**,[5] for which the $Pt(\mu\text{-}H)_2Pt$ moiety may be assumed symmetrical. With regard to these two complexes, it has to be underlined that also in **5b** each hydrido bridge can be considered symmetrical, while in **4c** each single bridge can be considered unsymmetrical but the two of them are symmetrically related.

It seems that, apart from the complex **4c**, dihydrido-bridged binuclear platinum complexes would prefer an arrangement given by one square-planar and one trigonal-bipyramidal platinum with coincident equatorial planes.

The Pt–Pt distances in **2** and **3a** are also slightly but significantly longer than in **5a**, which has been described as a monohydrido-bridged species.[7] However, the data reported in Table VI indicate that the structure of **5a** might also be considered as involving the presence of two unequal hydrido bridges between one cis square-planar and one trigonal-bipyramidal Pt, in an arrangement similar to that of **5b**, but much distorted, with the axial H bent toward the other platinum.

The data reported in Table VI suggest that the Pt–Pt separation could be indicative of the number and the type of hydrido bridges. One bridge gives a distance of ~3.1 Å, two unsymmetrical bridges give ~2.8 Å, and two symmetric bridges give ~2.7 Å.

Discussion

In recent years there have been a number of reports of dinuclear platinum(II) hydrides that may be readily classified according to whether they possess a (μ-H) or $(\mu\text{-}H)_2$ bridge in their static structure, e.g., in the solid state. Of the former type are the complexes $[YPt(\mu\text{-}H)(\mu\text{-}Ph_2PCH_2PPh_2)_2PtY]^+$ (Y = Cl and H) (**6**),[9] in which the diphosphine ligands bridge the metal centers, and $[(PEt_3)_2HPt(\mu\text{-}H)PtPh(PEt_3)_2]^+$ (**1**), in which the single (μ-H) bridge is the only group binding the platinum centers together. On the basis of solid-state evidence complexes of type **5**, e.g., with L–L = 1,2-bis(diphenylphosphino)ethane, 1,2-bis(diphenylarsino)ethane, and $R(t\text{-}Bu)P(CH_2)_nPR(t\text{-}Bu)$ (R = Ph or *t*-Bu, *n* = 2; R = *t*-Bu, *n* = 3), in which the bidentate ligands chelate at each metal center, can be described as possessing two (μ-H) bridges and one terminal hydride. However, in solution they undergo extremely facile exchange of terminal and bridging hydrides and the NMR data suggest that the *fast-exchange* limit can be described as corresponding to a structure in which a $(\mu\text{-}H)_3$ bridge is present. Complexes of type **4** possess a $(\mu\text{-}H)_2$ bridge, and a variable-temperature NMR study of **4b** showed the dihydrido ligands to be dynamic in solution. The complexes **2** and **3a–d** are unusual in possessing both a four- and a five-coordinate metal center in solution. NMR studies on the trihydride members have shown no indication of exchange between the two bridging and one terminal hydride at room temperature, indicating the greater stability of the doubly over the singly bridged geometry. It is of course apparent that **2** and **3a–d** are related to the dinuclear cationic hydrides **5** and **6** in having the same number and type of donor ligand atoms and hence the same number of valence electrons (30). This relationship is particularly clear for **2**, for which we have already reported the isolation of its isomer **1**,[2] a complex with a single (μ-H) bridge and a coordination geometry analogous to that of the hydrides **6**. Another aspect of the asymmetric complexes **3a–3d** is the stability of the geometric arrangement for a range of phosphines (PEt_3, PPh_3, and $P(c\text{-}Hx)_3$) varying considerably in bulk and basicity; it should be noted that **3b** contains formally mutually cis- and trans-coordinated tricyclohexylphosphine ligands. It is therefore apparent that the dynamic behavior in the trihydrides mentioned above is related to the geometric restraints imposed by the bidentate ligands rather than to any inherent electronic factors concerned with the electron-deficient bridge bonds. In recent years there has been increasing evidence of the importance of such bonds in transition-metal chemistry, though the concept of the three-center two-electron bond has long been considered of wide applicability in main-group chemistry. It is now known that an M(μ-H)M bridge is expected (and found) to be nonlinear with a degree of metal–metal bonding.[25] In species with a dihydride bridge the description is similar and the solid-state geometry of **2** and**3a** not only suggests the presence of two bent bridge bonds but also indicates that these are inequivalent.

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(25) R. Bau, Ed., "Transition Metal Hydrides", Adv. Chem. Ser. No. 167, American Chemical Society, Washington, DC, 1978.

Table VIII. Summary of Crystal Data and Intensity Collection Details for the Compounds $[(PEt_3)_2Pt(\mu\text{-}H)_2PtY(PEt_3)_2]X$

compd	$Y = Ph, X = BPh_4^-$	$Y = H, X = BPh_4^-$
formula	$C_{54}H_{87}BP_4Pt_2$	$C_{48}H_{83}BP_4Pt_2$
fw	1261.18	1185.08
a, Å	14.492 (4)	15.971 (6)
b, Å	14.450 (3)	21.615 (7)
c, Å	13.788 (2)	16.630 (6)
α, deg	92.62 (2)	90
β, deg	93.55 (2)	99.40 (3)
γ, deg	94.41 (2)	90
V, $Å^3$	2869 (1)	5323 (3)
Z	2	4
density, g cm^{-3} calcd	1.460	1.479
obsd[a]	1.46 (1)	1.47 (1)
space group	$P\bar{1}$	$P2_1/n$
cryst dimens, mm^3	0.20 × 0.22 × 0.30	0.15 × 0.25 × 0.35
radiation	graphite-monochromatized Mo Kα	
μ, cm^{-1}	50.6	54.5
scan mode	ω scan	
scan range, deg	1	
bkgd counts	0.5 scan time at ±0.8°	
2θ limits, deg	3-56	
total no. of observns	±*h*,*k*,±*l*, 14540	*h*,*k*,±*l*, 14090
no. of unique data $F_o^2 > 3\sigma(F_o^2)$	6700	3070
final no. of variables	363	309
final *R*, R_w	0.052, 0.046	0.051, 0.050

[a] Measured by flotation in $CdCl_2$ solutions.

Table IX. Final Positional Parameters (× 10^4) for Non-Hydrogen Nongroup Atoms (Standard Deviations Given in Parentheses)

	x	*y*	*z*
	$[(PEt_3)_2Pt(\mu\text{-}H)_2PtPh(PEt_3)_2][BPh_4]$ (**2**)		
Pt(1)	2401.4 (3)	3207.7 (3)	1003.2 (3)
Pt(2)	2679.8 (3)	1832.7 (3)	2354.2 (3)
P(1)	3732 (2)	2955 (2)	254 (2)
P(2)	970 (2)	3496 (2)	1518 (2)
P(3)	3428 (2)	1868 (2)	3842 (2)
P(4)	2068 (2)	303 (2)	2143 (2)
B	7649 (8)	2847 (9)	4776 (9)
C(1)	3596 (10)	2955 (12)	−1042 (9)
C(2)	2896 (13)	2307 (14)	−1438 (11)
C(3)	4206 (8)	1864 (9)	511 (9)
C(4)	5022 (10)	1577 (11)	−81 (11)
C(5)	4735 (9)	3849 (10)	568 (11)
C(6)	5068 (10)	3925 (13)	1571 (12)
C(7)	923 (9)	4460 (9)	2428 (11)
C(8)	1429 (11)	4258 (16)	3378 (12)
C(9)	169 (10)	3829 (15)	536 (11)
C(10)	−10 (14)	3141 (23)	−190 (14)
C(11)	328 (7)	2529 (8)	2004 (9)
C(12)	−639 (8)	2618 (10)	2239 (10)
C(13)	2624 (8)	1962 (10)	4788 (8)
C(14)	2971 (10)	2091 (11)	5818 (10)
C(15)	4095 (7)	880 (8)	4136 (9)
C(16)	4897 (9)	788 (9)	3514 (10)
C(17)	4331 (8)	2823 (8)	4124 (8)
C(18)	3973 (9)	3798 (8)	4177 (9)
C(19)	3007 (10)	−481 (8)	1867 (12)
C(20)	2696 (13)	−1391 (13)	1593 (14)
C(21)	1497 (9)	−162 (8)	3190 (10)
C(22)	647 (10)	282 (10)	3436 (10)
C(23)	1225 (9)	62 (9)	1187 (9)
C(24)	1480 (12)	195 (13)	211 (12)
C(25)	2463 (7)	4514 (7)	436 (8)
C(26)	2817 (7)	5255 (7)	1058 (7)
C(27)	2894 (8)	6155 (8)	716 (9)
C(28)	2650 (8)	6329 (9)	−173 (10)
C(29)	2284 (8)	5578 (8)	−846 (9)
C(30)	2191 (7)	4688 (10)	−537 (8)
	$[(PEt_3)_2Pt(\mu\text{-}H)_2PtH(PEt_3)_2][BPh_4]$ (**3a**)		
Pt(1)	2960.9 (3)	3473.0 (4)	1554.7 (5)
Pt(2)	2082.9 (6)	2918.6 (4)	2786.2 (5)
P(1)	1852 (4)	3492 (3)	426 (4)
P(2)	4265 (4)	3543 (3)	2404 (3)
P(3)	1857 (4)	1909 (3)	3073 (4)
P(4)	1388 (4)	3445 (3)	3731 (4)
B	2404 (16)	5041 (11)	7143 (14)
C(1)	1713 (16)	4234 (10)	−111 (16)
C(2)	1527 (21)	4730 (14)	464 (19)
C(3)	858 (16)	3238 (10)	663 (16)
C(4)	69 (19)	3256 (12)	−78 (18)
C(5)	2067 (16)	3026 (11)	−492 (15)
C(6)	2363 (19)	2424 (12)	−210 (18)
C(7)	4999 (15)	2902 (11)	2224 (13)
C(8)	5134 (18)	2844 (13)	1327 (16)
C(9)	4879 (15)	4231 (10)	2182 (14)
C(10)	4419 (16)	4800 (11)	2332 (14)
C(11)	4274 (16)	3504 (11)	3576 (15)
C(12)	5071 (19)	3502 (13)	4113 (17)
C(13)	1856 (22)	1690 (15)	4249 (21)
C(14)	1748 (23)	1049 (16)	4533 (20)
C(15)	776 (29)	1579 (21)	2676 (27)
C(16)	391 (19)	1722 (13)	1859 (18)
C(17)	2539 (21)	1372 (14)	2638 (21)
C(18)	3372 (20)	1448 (14)	3078 (19)
C(19)	202 (26)	3080 (18)	3629 (26)
C(20)	−306 (27)	3267 (18)	4011 (26)
C(21)	1929 (33)	3539 (21)	4836 (32)
C(22)	2620 (17)	3251 (11)	5244 (17)
C(23)	1006 (25)	4197 (17)	3471 (24)
C(24)	1388 (20)	4654 (3)	2990 (18)

This contrasts sharply with the solution NMR spectra, which show that both bridging hydride ligands are equivalent. However, the interaction of these hydrogen atoms with Pt^1 and Pt^2 are different.

It is hoped that further studies, in particular structural investigations by neutron diffraction, will provide further information about this interesting class of compounds.

Experimental Section

General experimental conditions were as described in previous publications.[2,3] ^1H, ^{31}P, and ^{195}Pt NMR spectra were measured at 90, 36.43, and 19.34 MHz, respectively, on a Bruker HX 90 spectrometer. ^1H NMR spectra at 360 and 250 MHz were obtained with Bruker HXS 360 and WM 250 spectrometers, respectively.

Preparation of Complexes. These were prepared by using exactly the same method and the stoichiometry described elsewhere[3] unless otherwise noted below.

(1) For the synthesis of **2**, the crude product obtained from $[Pt(COD)_2]$, PEt_3, $[PtPh((CH_3)_2CO)(PEt_3)_2]^+$, and H_2 was washed with Et_2O and recrystallized from MeOH at −20 °C.

(2) The method using $[Pt(COD)_2]$, PEt_3, $[PtH((CH_3)_2CO)(PEt_3)_2]^+$, and H_2 gave an oily product containing **3a** contaminated with a byproduct of very similar solubility characteristics. Pure **3a** was obtained as follows: 47 mg of $NaBH_4$ was added to a solution of 510 mg of *trans*-$[PtHCl(PEt_3)_2]$ in 1 mL of dry acetonitrile. The reaction was started by adding about 0.04 mL of water. After 1 h 5 mL of water was added, resulting in the formation of two phases. The yellow organic phase was separated, and 1 equiv of KBF_4 was added. The product was precipitated with water and filtered off. The more stable BPh_4^- salt was obtained by dissolving the precipitate in acetone, adding 1 equiv of $NaBPh_4$, evaporating the solvent, extracting the residue with CH_2Cl_2, and precipitating the product with methanol (yield 91%).

(3) For the synthesis of **3b**, the crude product obtained from $[Pt(COD)_2]$, $P(c\text{-}Hx)_3$, $[PtH((CH_3)_2CO)(P(c\text{-}Hx)_3)_2]^+$, and H_2 was washed with Et_2O and recrystallized from CH_2Cl_2/Et_2O.

(4) For the synthesis of **3d**, the crude product obtained from $[Pt(COD)_2]$, $P(c\text{-}Hx)_3$, $[PtH((CH_3)_2CO)(PPh_3)_2]^+$, and H_2 was washed with Et_2O and recrystallized from CH_2Cl_2/Et_2O.

The analytical data for the complexes are given in Table VII.

X-ray Crystal Structure Determinations. The complexes **2** and **3a** were prepared as their $[BPh_4]^-$ salts by treatment of an acetone solution of the $[BF_4]^-$ complexes with an excess of $NaBPh_4$ in methanol. The precipitate was filtered off, washed with methanol and water, and dried. Crystals suitable for X-ray measurements were grown by dissolving the crude products in acetone, adding methanol, and storing the solutions at −22 °C.

Collection and Reduction of X-ray Data of $[(PEt_3)_2Pt(\mu\text{-}H)_2PtPh(PEt_3)_2][BPh_4]$ (2) and $[(PEt_3)_2Pt(\mu\text{-}H)_2PtH(PEt_3)_2][BPh_4]$

(**3a**). Preliminary photograph studies revealed that the crystals of **2** are triclinic while those of **3a** are monoclinic.

Cell constants were obtained by least-squares refinement of the setting angles of 15 reflections centered on a Syntex $P2_1$ computer-controlled diffractometer. A summary of crystal parameters and experimental data is given in Table VIII.

The intensities of 3 standard reflections were measured after every 100 reflections. They were found to decrease gradually during the course of the data collection, reaching at the end of the run the maximum decay of 20% for **2** and 23% for **3a**. Linear correction factors to account for the loss of intensity were therefore applied to the reflections of both compounds. The reflections were then processed as described by Bachechi et al.[26] with ignorance factors $p = 0.011$ and 0.012 for **2** and **3a**, respectively. They were also corrected for shape anisotropy as described in the literature.[27] For **2** 6700 and for **3a** 3070 reflections had $I > 3\sigma(I)$ and were used in subsequent calculations.

Solution and Refinement of the Structures. The structures of **2** and **3a** were solved by the heavy-atom method and refined by least-squares procedures. The isotropic refinements converged at $R = 0.058$ and 0.066 for **2** and **3a**, respectively.

At this stage, for each structure, the phenyl groups of the $[BPh_4]^-$ anion were treated as rigid groups and restricted to their idealized geometry ($6/mmm$ symmetry, $d(C-C) = 1.392$ Å, $d(C-H) = 1.0$ Å). All the nongroup non-hydrogen atoms were allowed to vibrate anisotropically while for the group atoms only the group isotropic thermal parameters were refined. The fixed contributions of the cation hydrogen atoms (except the hydrides) were included in the calculation with idealized positions $d(C-H) = 1.0$ Å, H-C-H = 109.5°, and isotropic thermal parameters of the nearest carbon atoms. Convergence was reached at $R = 0.052$ and 0.051 ($R_w = 0.046, 0.050$) for **2** and **3a**, respectively.

During the isotropic refinement of **3a** abnormally high temperature factors for the carbon atoms of the ethyl groups bound to P(3) and P(4) were observed. Zonal Fourier difference maps revealed clear evidence of disorder. a series of calculations was then made, in which the disorder was assumed to result in fractional carbon atoms, over a range of 40° around Pt(2)–P(3) and Pt(2)–P(4) directions.

Successive Fourier difference summations indicated that the treatment was proper, although a more elaborate fractionation of the atoms could have been a better model. However, this model of rotational disorder would require a large and scarcely rewarding use of computer time since the coordination geometry around the platinum atoms would remain virtually unaffected. Thus, it was decided to continue the refinement without taking into account the disorder.

For both compounds a series of difference Fourier maps was then calculated with a gradual lowering of the cutoff $(\sin\theta)/\lambda$ limit to enhance the hydrogen contribution to the diffraction effects as described by La Placa et al.[28] None of the residual peaks so obtained corresponded to chemically reasonable sites for the terminal and bridging hydrido ligands.

Refinements were carried out with a block-diagonal approximation of the equation matrix. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 4F_o^2/\sigma(F_o^2)$.

Scattering factors and anomalous dispersion terms were taken from ref 29.

The calculations were performed with local programs on the Univac 1110 computer of the University of Rome[30] and on the HP 21MX minicomputer of the CNR Research Area.[31]

Final positional parameters for the non-hydrogen atoms of the two cationic complexes are given in Table IX. The corresponding anisotropic thermal parameters and the positional and thermal parameters of the $[BPh_4]^-$ nonhydrogen atoms, Tables X and XI, are available as supplementary material.

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Registry No. **2**, 84623-72-3; **3a**, 81800-05-7; **3b**, 84709-75-1; **3c**, 69277-93-6; **3d**, 84623-74-5; $[Pt(1,5-C_8H_{12})_2]$, 12130-66-4; *trans*-$[PtPh((CH_3)_2CO)(PEt_3)_2][BF_4]$, 76297-58-0; *trans*-$[PtH((CH_3)_2CO)(PEt_3)_2][BF_4]$, 84623-75-6; *trans*-$[PtH((CH_3)_2CO)(P(c\text{-}Hx)_3)_2][BF_4]$, 84623-77-8; *trans*-$[PtH((CH_3)_2CO)(PPh_3)_2][BF_4]$, 37036-05-8.

Supplementary Material Available: Listings of structure factor amplitudes and anisotropic thermal parameters (Table X) and positional and thermal parameters for non-hydrogen atoms (Table XI) (65 pages). Ordering information is given on any current masthead page.

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