Binuclear Hydridoplatinum(II): One-Pot Synthesis, INS Spectra and X-ray Crystal Structure of $[Pt_2(dcype)_2(H)_3][BPh_4]$ {dcype = 1,2-Bis(dicyclohexylphosphanyl)ethane}

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The binuclear platinum(II) hydride $[Pt_2(dcype)_2(H)_3][Cl]$ (**1b**) has been isolated in high yields by treatment of $Pt(dcype)Cl_2$ with $NaBH_4$ (molar ratio 1:2) in ethanol solution at room temperature. This one-pot synthesis is not straightforward when starting from diphenylphosphanylalkane complexes. The compounds $[Pt_2(dppp)_2(H)_3][OH]$ (**3b**) and $[Pt_2(dppb)_2(H)_3][OH]$ (**4**) were isolated by starting from the mononuclear hydrides {*cis*-$[Pt(P\text{-}P)(H)_2]$} while mixtures of both binuclear {$[Pt_2(dppe)_2(H)_3]^+$, **5**} and trinuclear {$[Pt_3(dppe)_3(H)_3]^+$, **6**} trihydrides were obtained with the dppe ligand. Various salts of the cation **1**, $[Pt_2(dcype)_2(H)_3][X]$ (X = BF_4, **1a**; OH, **1c**; BPh_4, **1d**), were isolated either from $[Pt(dcype)(\mu\text{-}OH)]_2[BF_4]_2$ (**2**) by a general procedure (**1a**), or by decomposition of the complex *cis*-$[Pt(dcype)(H)_2]$ in solution (**1c**), as well as by metathesis reactions (**1a**, **1c**, and **1d**). Compounds **1a**, **1b**, and **1d** react with CO under mild conditions to afford the corresponding Pt^I binuclear hydrides $[Pt_2(dcype)_2(\mu\text{-}CO)(\mu\text{-}H)][X]$ (X = Cl, **7a**; BF_4, **7b**; BPh_4, **7c**). The binuclear core of cation **1** is broken by KCN in methanol solution, yielding the mononuclear complex *cis*-$[Pt(dcype)(CN)(H)]$ (**8**). The complexes **1a**–**d**, **2**, **7a**–**c**, and **8** have been characterised by FAB MS, IR, and NMR (^1H, ^{31}P, and ^{195}Pt) spectroscopic techniques; the **1** and **7** cations show fluxional behaviour on the NMR timescale. The structure of compound **1d** was determined, at 200 K, by single-crystal X-ray diffraction. All the hydrido ligands were located. The Pt–Pt separation is 2.696(1) Å and the coordination geometry around each platinum centre can be regarded as distorted square planar. Incoherent Inelastic Neutron Scattering (INS) spectra were obtained for **1a** and $[Pt_2(dppe)_2(H)_3][BF_4]$ (**5a**); the spectra reflect the different geometries of the two "$P_4Pt_2(H)_3$" cores as found by single-crystal structure determinations.

Introduction

Since the first examples − $[Pt_2(PR_3)_2(H)_2(SiR_3)_2]$, reported by M. Green and co-workers[1] − binuclear platinum hydrides have been a topic of continuous interest. Besides complexes with monodentate tertiary phosphanes[2] or exobidentate (bridging) diphosphane,[3] a number of species with chelating diphosphanes (P-P) have also been described.[4−6] These complexes include 30-electron species, both neutral $[Pt(P\text{-}P)(H)]_2$[5] and cationic $[Pt_2(P\text{-}P)_2(H)_3]^+$,[4] as well as 28-electron $[Pt(P\text{-}P)(H)]_2{}^{2+}$ species.[6] The observed differences in their formation, spectroscopic properties and molecular structures seem to be largely dependent on the ancillary diphosphanyl ligand. Moreover, when chelating diphosphanes have been used, only a few examples of mononuclear *cis*-dihydrides {*cis*-$[Pt(P\text{-}P)(H)_2]$} have been described.[4d,5a,5c,7]

The trihydrido cations {$[Pt_2(P\text{-}P)_2(H)_3]^+$} have been widely investigated. In solution they show fluxional behaviour on the NMR timescale over a wide temperature range, at least down to 183 K. Typically, only one resonance for the hydrides is observed in the ^1H NMR spectrum, coupled to four ^{31}P and two ^{195}Pt magnetically equivalent nuclei. In the solid state, however, two distinct types of structure have been observed, with either a $(H)Pt(\mu\text{-}H)_2Pt$ or a $(H)Pt(\mu\text{-}H)Pt(H)$ core. The former arrangement, with two bridging

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and one terminal hydride, implies different environments for the two platinum atoms, as found in the structures of $[Pt_2\{Ph_2P(CH_2)_2PPh_2\}_2(H)_3]^+$ [4c,8] and $[Pt_2\{(Ph_2PC_5H_4)_2Fe\}_2(H)_3]^+$.[4f] On the other hand, the coordination geometries of the two platinum atoms in the structures of $[Pt_2(dtbpp)_2(H)_3]^+$ [4b] and $[Pt_2(butaphos)_2(H)_3]^+$ [4g] are approximately the same, and are consistent with the presence of two terminal and one bridging hydrides.

Different factors could be considered in order to explain the observed differences in the solid state, in particular: (i) the influence of the bite angle of the chelating ligands, and (ii) the steric demand of the substituents on the phosphorus atoms. Moreover, more subtle factors, such as crystal-packing forces, could also be responsible for the existence of different structures involving small energy differences.

In pursuit of our interest in platinum polynuclear hydrides, we report here the synthesis of the complexes $[Pt_2(dcype)_2(H)_3][X]$ (X= BF_4, **1a**; Cl **1b**; OH, **1c**; BPh_4, **1d**) and the X-ray crystal structure of the BPh_4 salt. In addition, the Incoherent Inelastic Neutron Spectra of complexes **1a** and $[Pt_2(dppe)_2(H)_3][BF_4]$ (**5a**) are also reported.

Complex **1b** can be obtained in good yields directly from $[Pt(dcype)Cl_2]$ by a one-pot reaction. This synthetic approach has also been used with less sterically demanding bis-diphenylphosphanylalkanes: satisfactory yields have been obtained in the case of dppp $\{[Pt_2(dppp)_2(H)_3]^+$, **3**} and dppb $\{[Pt_2(dppb)_2(H)_3]^+$, **4**} ligands, but the quantitative conversion of $Pt(P-P)Cl_2$ was only obtained when the corresponding mononuclear hydrides {*cis*-$[Pt(P-P)(H)_2]$} were isolated and then converted into the corresponding binuclear cations. With dppe mixtures, both binuclear $\{[Pt_2(dppe)_2(H)_3]^+$, **5**} and trinuclear $\{[Pt_3(dppe)_3(H)_3]^+$, **6**} trihydrides were obtained.

The $[Pt_2(dcype)_2(H)_3][X]$ species react with CO under mild conditions to give the binuclear p1atinum(I) hydrides $[Pt(dcype)_2(\mu-CO)(\mu-H)]^+$ (X = Cl, **7a**; BF_4, **7b**; BPh_4, **7c**).

The monuclear hydrido complex *cis*-[Pt(dcype)(CN)(H)] (**8**) has been obtained from the reaction between **1b** and KCN in methanol solution.

A preliminary report of this work has already appeared.[9]

Throughout this paper the chelating diphosphanyl ligands (P-P) are indicated as follows: dcype, 1,2-bis(dicyclohexylphosphanyl)ethane; dtbpe, 1,2-bis(di-*tert*-buthylphosphanyl)ethane; dppe, 1,2-bis(diphenylphosphanyl)ethane; dfepe, 1,2-bis[bis(perfluoroethyl)phosphanyl]ethane $(C_2F_5)_2PCH_2CH_2P(C_2F_5)$; dtbpp, 1,3-bis(di-*tert*-butylphosphanyl)propane; dippp, 1,3-bis(diisopropylphosphanyl)propane; dppp, 1,3-bis(diphenylphosphanyl)propane; butaphos, 1-(diphenylphosphinoxy)-2-[*N*-ethyl-*N*-(diphenylphosphanyl)amino]butane; dppb, 1,4-bis(diphenylphosphanyl)butane.

Results and Discussion

Our previously reported platinum binuclear trihydrides $[Pt_2(P-P)_2(H)_3]^+$ were synthesised from two different intermediates: cationic bis-pyrazole adducts (i) or μ-hydroxo binuclear cations (ii), as summarised in Scheme 1.

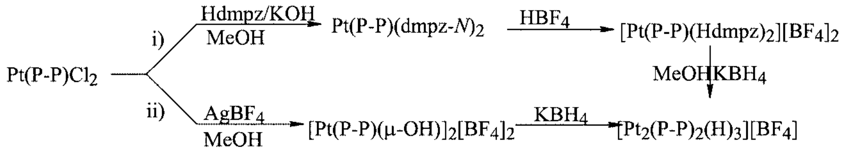
In the current case (P-P = dcype), attempts to operate according to path (i) were unsuccessful, owing to difficulties in isolating the pyrazolato precursor. Similarly, pathway (ii) was also unsatisfactory; compound $[Pt_2(dcype)_2(H)_3][BF_4]$ (**1a**) was isolated, but yields were erratic and often modest.[10] Analytical and NMR spectroscopic data suggested the formation of complex reaction mixtures in the first step: the synthesis of the binuclear μ-hydroxo complex $[Pt(dcype)(\mu-OH)]_2[BF_4]_2$ (**2**). The $^{31}P\{^1H\}$ NMR spectra of the crude products showed, besides the signals of compound **2**, a number of resonances in the 55−75 ppm range, probably due to other platinum species with oxygen donors. The values of the $^1J_{P,Pt}$ coupling constants, 3900−3400 Hz, suggest species with a *trans* P−Pt−O arrangement with anionic (OH or OR) rather than neutral (H_2O or CH_3OH) ligands (e.g. ref.[11b]). The chelating behaviour of dcype is confirmed by the large ^{31}P downfield shift with respect to the free ligand (Δδ = 50−70 ppm).

An analytical sample of the intermediate **2** was isolated from the crude product as a less soluble species in acetone. Its spectroscopic (IR, $^{31}P\{^1H\}$ NMR, and FAB MS) properties (see Exp. Sect.) are highly reminiscent of those of homologous cations with various bis(diphenylphosphanyl)alkanes.[11]

The cation $[Pt_2(dcype)_2(H)_3]^+$ (**1**) had previously been detected in solution by multinuclear NMR spectra either as the final product of the decomposition of *cis*-$[Pt(dcype)(H)_2]$[7b] or as that of the protonation of the platinum(I) dihydride $[Pt(dcype)(H)]_2$,[5a] this compound also being reversibly obtained from *cis*-$[Pt(dcype)(H)_2]$[5a] (see Scheme 2).

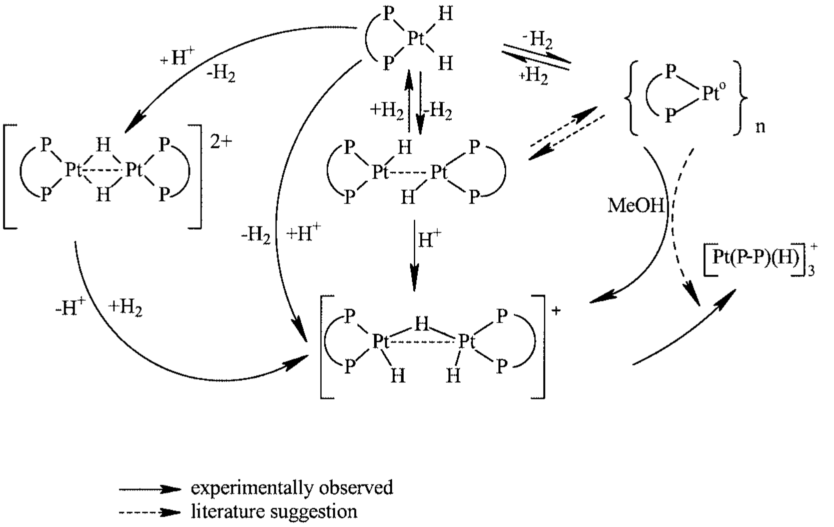
It therefore seemed that cation **1** might be directly obtainable in a one-pot reaction, through the controlled decomposition of *cis*-$[Pt(dcype)(H)_2]$. Indeed, we were able to obtain the complex $[Pt_2(dcype)_2(H)_3][Cl]$ (**1b**) in high yields by treatment of a dichloromethane solution of $[Pt(dcype)Cl_2]$ with an ethanol solution of $NaBH_4$ (Pt/BH_4^- mo1ar ratio 1:2) at room temperature (under dinitrogen atmosphere). At lower reaction temperatures the yield was decreased and unchanged $[Pt(dcype)Cl_2]$ was recovered. Significant amounts of the mononuclear dihydride *cis*-$[Pt(dcype)(H)_2]$ have occasionally been detected in the crude products of synthesis reactions of compound **1b**; these could be converted into the compound $[Pt_2(dcype)_2(H)_3][OH]$ (**1c**) by treatment with wet methanol.

The corresponding tetrafluoroborate **1a** and the tetraphenylborate $[Pt_2(dcype)_2(H)_3][BPh_4]$ (**1d**) were easily obtained from **1b** through a metathesis reaction with a large excess of the sodium salt of the appropriate anion in methanol solution. Moreover, the more nucleophilic CN^- anion disrupts the binuclear core. Under analogous experimental conditions, complex **1b** and KCN react to give, in high yields, the mononuclear hydride *cis*-[Pt(dcype)(CN)(H)] (**8**), which in turn, in $CDCl_3$ solution, slowly decomposes to afford mixtures of *cis*-$[Pt(dcype)Cl_2]$ and *cis*-[Pt(dcype)(CN)(Cl)] (**9**). This decomposition path gave a clue for



Hdmpz = 3,5-dimethylpyrazole

Scheme 1



Scheme 2. For a detailed discussion of the steps summarised in this scheme see references [4−8]

reliable assignment of the NMR parameters of complex **8** (see Exp. Sect.), which indicate a larger *trans* influence from the terminal hydride [$^1J_{P(trans\text{-}H)\text{-}Pt}$ = 1714 Hz] than from the cyanide ligand [$^1J_{P(trans\text{-}CN)-Pt}$ = 2706 Hz].

A significant improvement was obtained on carrying out the synthesis of compound **1b** starting from [Pt(COD)Cl$_2$], the commonest precursor of Pt(P-P)Cl$_2$ species. Yields of **1b** close to 65% were obtained under the same experimental conditions by sequential addition of dcype ligand and NaBH$_4$ to a dichloromethane solution of [Pt(COD)Cl$_2$].

The role of the mononuclear *cis*-[Pt(P-P)(H)$_2$] complexes to give platinum polyhydrides is summarised in Scheme 2.

It is also worth notice that the neutral Pt^I and 28 e$^-$ dihydrido species have been isolated only with aliphatic diphosphanes and that the complex *cis*-[Pt(dcype)(H)$_2$] seems to be the unique complex that acts as an effective precursor of all the known types of binuclear polyhydrides.

Thus, if the *cis*-[Pt(P-P)(H)$_2$] complexes are assumed to function as effective precursors in the formation of the binuclear trihydrides directly from [Pt(P-P)Cl$_2$], a dimerisation (see Scheme 2) aimed at a one-step synthesis could be envisaged under experimental conditions designed to enhance the lifetime of the mononuclear *cis*-dihydrides and avoid total dihydrogen loss (the most favoured reaction). We tested this approach to obtain complexes bearing bis(diphenylphosphanyl)alkane derivatives (dppe, dppp, and dppb) as ligands.

As far as we know, only two examples of *cis*-[Pt(P-P)(H)$_2$] compounds with (diphenylphosphanyl)alkane ligands (P-P = dppp, dppb) have been isolated and characterised; both are unstable in the absence of a dihydrogen atmosphere.[7c] In the dppe case, the mononuclear hydride was reported to be a source either of Pt^0 species[7a] or of various hydrides.[4d] Carmichael and co-workers inferred from a VT. NMR study (from 233 K to room temperature) that the hydride formation follows the sequence:[4d] *cis*-[Pt(dppe)(H)$_2$], [Pt(dppe)(H)]$_2$, [Pt$_2$(dppe)$_2$(H)$_3$]$^+$, and then [Pt$_3$(dppe)$_3$(H)$_3$]$^+$.

We carried out a few attempts under different conditions (see Exp. Sect.) starting from the appropriate [Pt(P-P)Cl$_2$] precursor and obtained the binuclear hydrides [Pt$_2$(P-P)$_2$(H)$_3$][Cl] (P-P = dppp, **3a**; P-P = dppe, **5b**). However the one-pot reaction was unattractive, due to the unsatisfactory yields. With the dppe ligand, the major product was always the trinuclear cation [Pt$_3$(dppe)$_3$(H)$_3$]$^+$ (**6**),[4d,12] the product of a formal addition of a (P-P)Pt^0 fragment to the binuclear cation **5**.

However, compounds [Pt$_2$(P-P)$_2$(H)$_3$][OH] (P-P = dppp, **3b**; P-P = dppb, **4**) were obtained in nearly quantitative yields, provided that the corresponding mononuclear hydrides were isolated. These were quickly converted into **3b** and **4**, respectively, after dissolution, under dinitrogen, in common organic solvents (e.g. chloroform).

The same conversion also occurs in the solid state: after two months, a not carefully stored sample of *cis*-[Pt(dppp)$(H)_2$] was found to have been fully converted into compound **3b**. Dimerisation reactions in the solid state are not unprecedented, but in the present case, in addition to a facile H_2 loss, the process requires a proton source, reasonably atmospheric moisture. In solution we cannot exclude different processes, as previously suggested for, for example, the formation of the cations $[Pt_2\{R_2P(CH_2)_nPR_2\}_2(H)_3]^+$ [R = *t*Bu, $n = 2$ (dtbpe), 3 (dtbpp)].[4b]

In the case of the dppe ligand, the one-pot reaction seems to be more profitable for synthesis of the trinuclear **6** species than of the binuclear **5**. The yield of compound **6**, calculated from the amounts of [Pt(dppe)Cl_2] consumed, reached 65%, a significant improvement with respect to the values obtained with other precursors {26% from the hydride **5** and from $[Pt(dppe)(\mu\text{-}OH)]_2^{2+}$, and 30% from $[Pt(dppe)(Hdmpz)_2]^{2+}$},[12b] which in turn require at least two other synthetic steps from [Pt(dppe)Cl_2]. On the other hand, the isolation of the *cis*-[Pt(dppe)$(H)_2$] is ruled out by its well established instability, even though its formation during the one-pot reaction is suggested by the occasional presence in the ^1H NMR spectra of a complex multiplet [hydrido region in $(CD_3)_2CO$: $\delta \approx -3.6$, $^2J_{P-H} \approx 168$ and 10 Hz] with satellites (1:4:1; $^1J_{Pt-H} \approx 880$ Hz).

All the compounds **1−8** reported here have been identified by analytical and spectroscopic data, while the solid-state structure of complex **1d** has been established by single-crystal X-ray diffraction at 200 K.

The spectroscopic data for cation **1** are consistent with those reported for the analogous hydrides and are not significantly affected by the nature of the counter-ions.

The IR spectra show a strong and broad ν_{Pt-H} vibration at 1980 cm^{-1} (in CH_2Cl_2), not observed in the corresponding deuterides and thus attributable to terminal Pt−H bonds.

The ^1H, $^{31}P\{^1H\}$, and ^{195}Pt NMR spectra confirm fluxional behaviour, not frozen at least down to 183 K. The hydrido resonance appears as a typical quintet with four satellites (intensity ratios: 1:8:18:8:1) indicating the magnetic equivalence of the four phosphorus and two platinum atoms.

Consistently, the $^{195}Pt\{^1H\}$ NMR spectra show the resonance of the most abundant isotopomer (^{195}Pt-Pt: 44.8%) as a triplet of triplets. In the $^{195}Pt\{^{31}P\}$ spectrum the central resonance is split into a quadruplet, giving unequivocal evidence for the number of hydrido ligands.

This determination is obviously a crucial point for the correct assignment of a new compound to the appropriate family of the different binuclear hydrides, namely the 30 e^- species $\{[Pt(P\text{-}P)(H)]_2$ or $[Pt_2(P\text{-}P)_2(H)_3]^+\}$ or the 28 e^- derivatives $\{[Pt(P\text{-}P)(H)]_2^{2+}\}$. As these compounds are often formulated on the basis of spectroscopic data in solution, it is worth comparing their relevant IR and NMR spectroscopic properties (see Table 1).

In the IR spectra, the region of the terminal Pt−H stretching seems to be a diagnostic feature: the 28 e^- species do not in fact show any vibration in this region, while one or two bands are observed in the case of 30 e^- complexes (the Pt^{II} cations and the neutral Pt^I species, respectively).

In the NMR spectra the multiplicities of the main resonances, as well as the satellites' intensities, have no diagnostic value, owing to the fluxionality and identical nuclearity mentioned above. Significant differences between various NMR parameters are observed, however. Provided that the same diphosphanyl ligand is present, the following points can be used in order to distinguish the different binuclear hydrides: (i) greater $^1J_{H-Pt}$ values are associated with 28 e^- species, (ii) shifts towards higher field of the hydrido resonances and smaller $^2J_{P,P}$ values are observed in the case of the 30 e^- cations, and (iii) the neutral Pt^I complexes show the greatest $^2J_{P,Pt}$ values.

These observations allowed, inter alia, the proposal of a binuclear platinum(I) dihydride $[Pt(dppp)(H)]_2$ [^1H NMR in CD_2Cl_2 (hydrido region): $\delta = -1.5$ (quintet with 1:8:18:8:1 satellites, $^1J_{Pt-H} = 529$, $^2J_{P-H} = 39$ Hz) ppm; $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = 19.2$, $^1J_{P,Pt} = 2420$, $^2J_{P,Pt} = 318$, $J_{P-P} = 37$ Hz] as a by-product in the crude mixtures isolated in the attempts to synthesise cation **3** directly from Pt(dppp)Cl_2.

Compounds **1a**, **1b**, or **1c** do not react with excess $NaBH_4$, unlike **5**, which gave rise to the trinuclear cation **6** $[Pt_3(dppe)_3(H)_3]^+$. We observe that these trinuclear hydrides are not known with diphosphanyl ligands that stabilise mononuclear *cis*-dihydrides in respect to Pt^0 species (i.e., with dppp, dppb, dtbpe, dtbpp, dippp, and dcype ligands).

Compounds **1a**, **1b**, and **1d** react with CO to give the corresponding μ-hydrido μ-carbonyl platinum(I) derivatives $[Pt_2(dcype)_2(\mu\text{-}H)(\mu\text{-}CO)][X]$ (X = Cl, **7a**; BF_4, **7b**; BPh_4, **7c**), isolated as blue-green powders. The reactions, carried out as reported previously for the analogous species with various diphosphanyl ligands,[4e,13] seem to be dependent on the counter-ions: species **7b** and **7c** are in fact obtained nearly quantitatively, while the yields of **7a** are lower, due to the formation of minor by-products often including [Pt(dcype)Cl_2].

Their spectroscopic features (IR and NMR spectra) are reminiscent of those observed for the homologous complexes with different diphosphanes either of platinum[4e,13] or of palladium.[14] The IR spectra show the strong absorption due to the bridging carbonyl group at about 1710 cm^{-1}. Slight differences are observed with the different anions.

In the ^1H NMR spectra (300 MHz), the main resonance of the hydride ($\delta \approx +0.7$) and of the diphosphanyl ligand resonances overlap, so that only the two external satellites of the hydrido ligand ($^1J_{H-Pt} = 984$ Hz) are observed. Their multiplicity (up to 323 K) is intermediate between the previously reported limiting spectra,[13] a quintet (fast exchange region) and a triplet of triplets (frozen), suggesting that the exchange process is slower in this case. Variable

Table 1. Relevant IR and NMR data for selected diphosphanyl platinum hydrides

Compound	^{1}H[a] Hydrido region[b]			^{31}P{^{1}H}[a]					IR	Ref.
	δ	$^{1}J_{H-Pt}$	$^{2}J_{H-P}$	δ	$^{1}J_{P-Pt}$	$^{2}J_{P-Pt}$	$^{3}J_{P,P}$	J_{Pt-Pt}	ν_{Pt-H}	
$[Pt(P\text{-}P)H]_2$										
dcype[c] [d]	0.49	512	40	92.8	2180	420	44		1965, 1937	[5a]
dippe[c][e]	0.49	516	40	105.5	2210	410	45		1939, 1926	[5a]
dtbpe[c][f]	0.05	570	42	119.9	3112	362	47		1975, 1931	[5a]
dppe[g]	0.30[h]	564	42	70.9	2201	388	44	1902	not isolated	[4c]
$[Pt(P\text{-}P)H]_2^{2+}$ [i]										
dcype	n.r.[j]	n.r.[j]	n.r.[j]	96	2758	134	26		1644	[6]
dtbpe	1.72[k]	786	[k]	119	2880	139	35	1280	1631	[6]
dtbpp	0.12	767	31	61	2861	133	20[l]	1820	1629	[6]
$[Pt_2(P\text{-}P)_2(H)_3]^+$ [m]										
dcype	−2.77	480	38	84.0	2803	150	8.1	801	1980 s,br[n]	this work
dtbpe	−3.85	443	40	108.7	2946	161	7.9	815	2000, 1650	[4a]
dtbpp	−5.89	396	38	49.4	3039	168	6.8	840	2045, 1650	[4a]
dppe	−2.8	500	41	57.2	2925	171	9.8	793	2000 w,br	[4b]
dppp	−3.7	458	40	9.0	2913	172	7.3		2020 m,br	[4b]
$[Pt_3(dppe)_3(H)_3]^+$	−1.6	387	29	57.8	2837	108	17.7		2010 s	[12]

[a] At ambient temperature unless otherwise stated; *J* in Hz. [b] always observed as quintets with satellites. [c] In C_6D_6. [d] Frozen at 237 K. [e] Frozen at 219 K. [f] Fluxional at 183 K. [g] In [D$_8$]THF. [h] At 213 K. [i] In CD_2Cl_2. [j] Not reported. [k] Triplet of triplets: $^{2}J_{H-P}trans = 73$; $^{2}J_{H-P}cis = 7$. [l] Reported as mean value. [m] In $CDCl_3$. [n] In CH_2Cl_2.

temperature ^{31}P{^{1}H} NMR spectra (121.5 MHz) show a broad singlet with satellites at 323 K, which is split at room temperature. The dynamic behaviour of compounds **7a−c** seems to be frozen at ca. 223 K, allowing the full set of coupling constants for the hydrido resonance and for the two couples of equivalent P nuclei to be evaluated.

Table 2. Selected bond lengths [Å] and angles [°] for cation **1d** (e.s.d.s in parentheses)

Pt(1)−Pt(2)	2.696(1)	Pt(1)−P(l)	2.281(1)
Pt(1)−P(2)	2.223(1)	Pt(1)−Ht(1)	1.63(2)
Pt(1)−Hb	1.69(3)	Pt(2)−P(3)	2.277(1)
Pt(2)−P(4)	2.227(1)	Pt(2)−Ht(2)	1.61(2)
Pt(2)−Hb	1.75(2)		
Pt(2)−Pt(1)−P(1)	117.2(1)	Pt(2)−Pt(1)−P(2)	149.5(1)
P(1)−Pt(1)−P(2)	88.4(1)	P(1)−Pt(1)−Ht(1)	176.7(8)
P(1)−Pt(1)−Hb	91.5(9)	P(2)−Pt(1)−Ht(1)	88.5(8)
P(2)−Pt(1)−Hb	166.5(9)	Ht(1)−Pt(1)−Hb	92(1)
Pt(1)−Pt(2)−P(3)	116.3(1)	Pt(1)−Pt(2)−P(4)	149.7(1)
P(3)−Pt(2)−P(4)	88.2(1)	P(3)−Pt(2)−Ht(2)	177.6(9)
P(3)−Pt(2)−Hb	89.7(8)	P(4)−Pt(2)−Ht(2)	90.2(8)
P(4)−Pt(2)−Hb	171(1)	Ht(2) −Pt(2)−Hb	92(1)

X-ray Crystal Structure of Compound 1d

The structure of compound **1d** consists of packing of $[Pt_2(dcype)_2(H)_3]^+$ cations and BPh_4^- anions in the molar ratio of 1:1 with normal van der Waals contacts. An ORTEP view of the cation is shown in Figure 1, while selected interatomic distances and angles are listed in Table 2. The cation consists of two five-membered rings, each made up of a Pt atom and a chelating dcype ligand, separated by a Pt-Pt distance of 2.696(1) Å, which is the shortest value observed in these trihydrido cations but similar to that reported in the case of the doubly hydrido bridged 28e$^-$ species $[Pt(dcypp)(H)]_2^{2+}$ [Pt−Pt = 2.698(1) Å].[6] The two Pt atoms are also bonded to three hydride ligands, one bridging the Pt−Pt vector, and two terminally bonded, one for each metal atom.

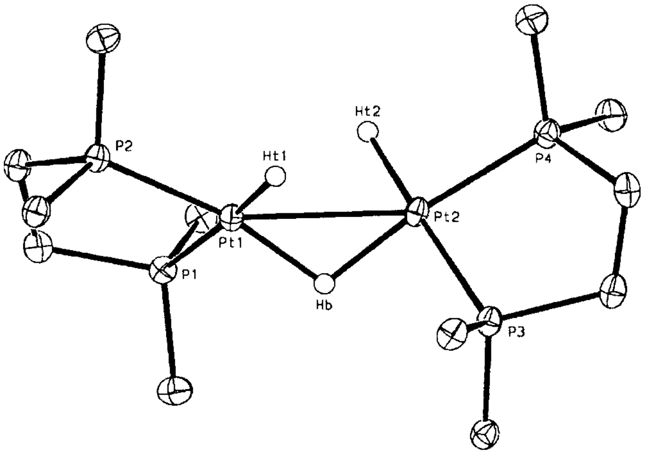


Figure 1. ORTEP view of the inner core of cation **1**, $[Pt_2(dcype)_2(H)_3]^+$; ellipsoids are drawn at 30% probability level

The dihedral angle between the Pt1−P1−P2 and Pt2−P3−P4 planes is 82.74(1)°, in agreement with the "overall conformation" detected in homologous cations. At variance with this, the same dihedral angle ranges from "90° to 180° conformations" in the reported structures of the dihydrido platinum species,[5,6] either neutral Pt^{I} complexes $[Pt(P\text{-}P)(H)]_2$ or 28 e$^-$ platinum(II) cations $[Pt(P\text{-}P)(H)]_2^{2+}$, in which the geometry around each platinum centre was assumed to be square-planar as in cation **1**. The accommodation of the third hydride in the $Pt_2(P\text{-}P)_2(H)_2$ core may be responsible for the "90° conformation" which appears as a typical feature of these platinum(II) 30 e^- cations.

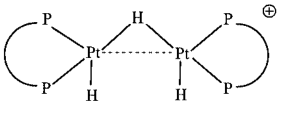
Bond lengths and angles involving the Pt atoms in the current cation can be compared with those found in cation $[Pt_2(butaphos)_2(H)_3]^+$ (**10**).[4g] Cation **10** differs from the present one only in the substitution of the two dcype ligands with two butaphos ones. In both cations the overall coordination around the Pt atom, if the Pt−Pt bond is neglected, can be described as distorted square planar, and the idealised symmetry of the two cations is C_2, with the twofold axis passing through the bridging hydride ligand and the midpoint of the Pt−Pt vector. The Pt−P distances are of two kinds: two shorter [Pt1−P2 2.223(1) vs. 2.222(3) Å in **10**, and Pt2−P4 2.227(1) vs. 2.217(3) in **10**], and two longer [Pt1−P1 2.281(1) vs. 2.324(3) Å in **10**, and Pt2−P3 2.277(1) vs. 2.309(3) Å in **10**]. The longer bonds are approximately *trans* to the terminal hydrides, displaying the expected *trans* influence. We also note that the Pt1−P1 and Pt2−P3 bonds are significantly longer in **10**, possibly due to the different steric requirements of the butaphos and dcype ligands and the formation of seven vs. five-membered metallacycles, respectively.

Whereas in **10** only two hydride atoms had been detected in the final Fourier maps, and the third was placed in its position on the basis of symmetry considerations, in the current cation the three hydrides have been found in the final Fourier maps and included in the refinement with isotropic thermal parameters, thus confirming the stereochemistry suggested for **10**.[4g] The current structure is the first X-ray determination of a complex of the type $[Pt_2(P\text{-}P)_2(H)_x]^{n+}$ ($x = 2$, $n = 0, 2$; $x = 3$, $n = 1$) in which all the hydride ligands have been experimentally located, and the resulting bond parameters are consistent with those reported in the more precise neutron diffraction structure of the cation $[Pt_2(dppe)_2(H)_3]^+$.[8,15]

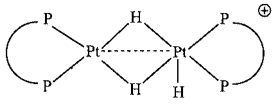
It was previously suggested that the geometry of the $Pt_2(P\text{-}P)_2(H)_3$ cores is controlled by the steric bulk of the phosphorus substituents,[4f] rather than by the bite angle of the chelating diphosphane. This view is supported by the current structure if comparison is made with the analogous cation with dppe: different structures are indeed observed with two diphosphanes with different steric bulk but similar bite angles. On the other hand, the same structure was reported for cations with diphosphanes displaying the same bite angle but different substituents (as in **10** or with dtbpp).[4b,4g] The available X-ray structure determinations therefore suggest that no conclusive statement can be made on this point, and that misleading conclusions may be drawn by use of comparison criteria focused only on these ligand features. As previously emphasised,[4c] the fluxional behaviour in solution suggests a very soft energy surface producing different core conformations, so that even apparently weak forces, such as crystal packing forces, could well be responsible for structural differences involving small energy changes. In this connection, it is worth noting the significant change, from a 90° to a 180° conformation, in the polymorphic platinum(I) hydride $[Pt(dfepe)H]_2$[5b] observed to occur at very low energy, also in the solid state.

Incoherent Inelastic Neutron Spectroscopy (INS) of 1a and 5a

As the structures of $[Pt_2(dcype)_2(H)_3][BF_4]$ (**1a**) and $[Pt_2(dppe)_2(H)_3][BF_4]$ (**5a**) have been shown by diffraction methods (X-ray and neutron for **1a** and **5a**,[4c,8] respectively) to be different, we have carried out an INS spectroscopic study of these complexes to obtain additional information on the nature of the Pt−H interactions.



1a



5a

While the vibrational modes of bridging hydrides can be investigated by optical spectroscopy,[16] this is in general rather difficult because of severe line broadening and interference from other modes. Instead, INS has the major advantage that the incoherent neutron scattering cross section for hydrogen is much larger than that for all other atomic species and that modes involving H atoms therefore dominate the INS spectra. To distinguish the vibrational modes of the hydrides from those of the hydrogens in the ligands unambiguously, however, a "sample difference"[17] technique has been used (see Exp. Sect.).

The INS difference spectra of **5a** and of **1a** are shown in Figures 2 and 3, respectively. As can be seen, the two spectra are quite different, reflecting the different coordination of the two "Pt_2H_3" moieties.

Although a complete assignment of the vibrational modes would require a normal coordinates analysis, a qualitative assignment of the main spectral features may still be carried out on the basis of published data for similar binuclear complexes[18] and other metal hydrides.[16,19] We note that the stretching frequency for a terminal "Pt−H" group is to be expected in the 1900−2100 cm^{-1} region,

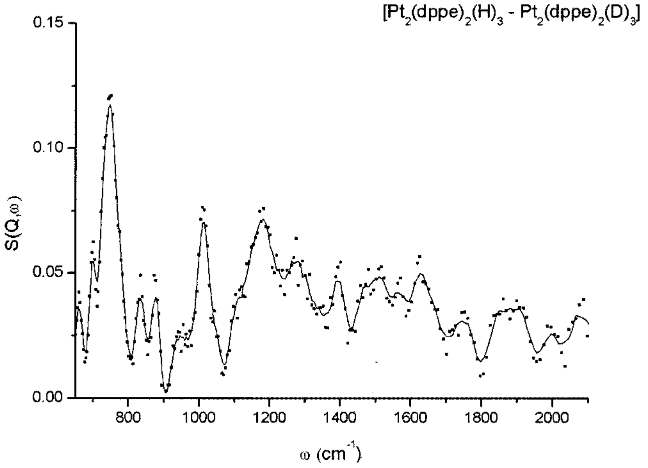


Figure 2. INS difference spectrum for compound **5a**; the line is drawn only as a guide for the eye

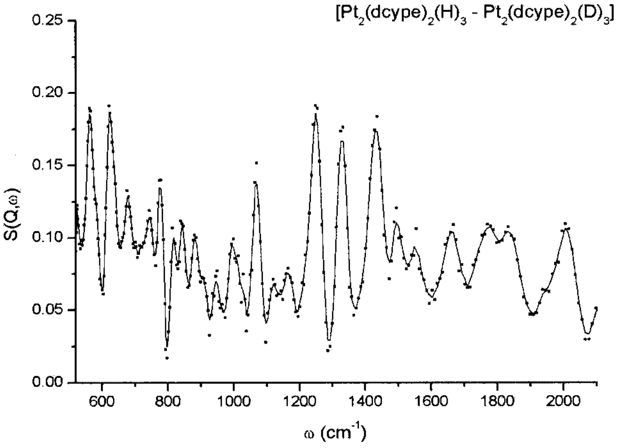


Figure 3. INS difference spectrum for compound **1a**; the line is drawn only as a guide for the eye

while the modes involving the μ-bridging H may be described in terms of a symmetric (ν_s) and anti-symmetric (ν_{as}) M−H−M stretching modes (1000−1400 cm^{-1}) as well as skeletal deformations and torsions (i.e., δ_{PMH} and δ_{MHM}) at lower frequencies.[18−20] As the intensities of the INS bands depend on the displacements of the H ligands, one would expect that the intensities of the deformation and torsional modes should be greater than those of the stretching modes, if coupling between the modes is small. These qualitative criteria allow for a relative straightforward assignment of the principal bands.

Thus, in the difference spectrum of **5a**, we assign the band at 2080 cm^{-1} to the Pt−H stretch (based on the correspondence with the IR broad band at ca. 2000 cm^{-1}), the 1170 cm^{-1} band to the ν_{as} and that at 1010 cm^{-1} to the ν_s mode of the "Pt(μ-H)Pt" moiety. The very intense bands at 750 cm^{-1} correspond to the δ_{MHM} mode of the same moiety.

It is worth noting that it is possible to obtain structural information on the M−H−M bridge from the ν_s/ν_{as} ratio. Howard and co-workers[21] have in fact shown that, if the metal framework may be regarded as rigid and the angle-bending force constant is small, then the following relation holds: $\nu_{as}/\nu_s = \tan(\theta/2)$, where θ is the M−H−M angle. We have also shown[18] that the above equation also holds accurately for compounds of the type $[PR_3LPt(\mu\text{-}H)PtLPR_3]$ (L = Ph, H; PR_3 = PMe_3, PEt_3).

From the above assignment for **5a**, a value of θ = 98° is obtained from this relationship, in very good agreement with the average value of 97° for the Pt−H−Pt angle obtained from single-crystal neutron diffraction.[8]

The difference spectrum of **1a** clearly reflects a different disposition of the H ligands around the Pt centres, as found by X-ray diffraction. The Pt−H stretch is now at 2000 cm^{-1} [1970−1950 cm^{-1} in the IR (Nujol)], while the deformation modes are at lower frequencies (560−620 cm^{-1}), possibly reflecting the different electron densities at the metal centres due to the different basicity of the phosphanes.

A more complex pattern than in **5a** is found in the 1200−1600 cm^{-1} region. The ν_s mode is at 1080 cm^{-1}, while the ν_{as} bands are at 1240 cm^{-1} and 1340 cm^{-1}. These two bands are consistent with two slightly different environments around the two Pt atoms. Moreover, the new band at 1420 cm^{-1} may be connected with the presence of a single bridging hydride and thus a less rigid metal framework. To help with this assignment we have carried out a DFT calculation[22] on the model compound $[(PMe_3)_2HPt(\mu\text{-}H)PtH(PMe_3)_2]^+$ and have found a mode at 1490 cm^{-1} corresponding to a combination of the ν_s(μ−H) and the out of plane bending of both terminal hydrides, a vibrational mode not possible when the platinum atoms are bridged by two hydrides.

These results, as also observed previously,[18] show that coupling between stretching and bending modes may be important in these bridging hydrides.

Experimental Section

Evaporation was always carried out under reduced pressure. The analytical samples were pumped to constant weight (room temperature, ca 0.1 Torr). Elemental analyses were performed by the Analytical Laboratory of the University of Milan and the Mikroanalytisches Labor Pascher (Remagen-Bandorf).

The infrared spectra were recorded on a Jasco FT/IR 420 spectrometer. NMR spectra were recorded at ambient temperature in $CDCl_3$ solutions unless otherwise stated, on a Bruker DRX 300 Avance spectrometer operating at 300 (^1H), 121.5 (^{31}P), and 64.5 MHz (^{195}Pt), respectively. The shift values are given in ppm from the usual standards; δ = ^{195}Pt is referred to $Na_2[PtCl_6]$ aqueous solution. Abbreviations used in the description of NMR spectroscopic data are as follows: br., broad; s., singlet; d., doublet; t., triplet; q., quintet; m., multiplet.

Solvents (RPE grade; Carlo Erba) were distilled prior to use. $NaBH_4$, $NaBD_4$ and KBH_4 were purchased from Merck, Aldrich and Fluka, respectively. The diphosphanyl ligands were obtained from Strem Chemicals and employed as received.

The $[Pt(P\text{-}P)Cl_2]$[4d,23] from $[Pt(COD)Cl_2]$ and the *cis*-$[Pt(P\text{-}P)(H)_2]$[7] complexes were synthesised by literature methods.

Synthesis and Characterisation. $[Pt(dcype)(\mu\text{-}OH)]_2[BF_4]_2$ (2): The products isolated by previously reported procedures[11] were mixtures of different p1atinum species with O-donors; compound **2** was always the most abundant product (NMR). Starting from $[Pt(dcype)Cl_2]$ (636 mg, 0.92 mmol) and $AgBF_4$ (360 mg, 1.9 mmol), the analytical sample was isolated as follows. After accurate elimination of the insoluble AgCl, the crude reaction product was crystallised from CH_2Cl_2/Et_2O. A first crop was precipitated by slow addition of diethyl ether to the dichloromethane solution; it was filtered off and then washed with acetone. Compound **2** was obtained as a residue (150 mg) slightly soluble in acetone. A second fraction (40 mg) of the same compound was obtained from the mother liquor by concentration in the presence of diethyl ether and of a few drops of MeOH. Yield 30%. IR (nujol, cm^{-1}): 3550 vbr. ν_{OH}, 1065 br. ν_{BF4}. $^{31}P\{^1H\}$ NMR: δ = 59.9 (s., $^1J_{P,Pt}$ = 3513 Hz) ppm. FAB MS (NBA): 1266 *m/z* $[M - 2H]^{+\cdot}$. M.p. 235 °C (dec). $C_{52}H_{98}B_2F_8O_2P_4Pt_2$ (1443.01): calcd. C 43.28, H 6.86, B 1.50, F 10.53, O 2.22, P 8.58, Pt 27.04; found C 43.32, H 7.10, F 9.93, P 8.4, Pt 26.7.

$[Pt_2(dcype)_2(H)_3][X]$ (X: BF_4, 1a, Cl 1b; OH, 1c; BPh_4, 1d): The salts **1a**, **1b**, and **1c** were obtained from compound **2** (i), from $[Pt(dcype)Cl_2]$ (ii), or from *cis*-$[Pt(dcype)(H)_2]$[5a] (iii), respectively.

(i) $[Pt_2(dcype)_2(H)_3][BF_4]$ (1a): From $[Pt(dcype)(\mu\text{-}OH)]_2[BF_4]_2$ (**2**). A suspension of KBH_4 (7.5 mg. 0.14 mmol) in methanol (20 mL) was added under dinitrogen atmosphere to a stirred solution of compound **2** (172 mg, 0.12 mmol) in the same solvent (10 mL). After ten minutes the colourless solution was evaporated to dryness and the residue was extracted with CH_2Cl_2 (ca. 7 mL). The insoluble material was filtered off, and the white product (99 mg, yield 62%) was precipitated by addition of diethyl ether (ca. 20 mL) to the clear solution. IR (nujol, cm^{-1}): $\tilde{\nu}$ = 1970 s,br ν_{PtH}, 1050 s,br ν_{BF4}. FAB MS: 1237 *m/z* $[M]^+$. M.p. 218 °C (dec.). $C_{52}H_{99}BF_4P_4Pt_2$ (1325.22): calcd. C 47.14, H 7.54; found C 47.18, H 7.44.

(ii) $[Pt_2(dcype)_2(H)_3][Cl]$ (1b): From *cis*-$[Pt(dcype)Cl_2]$. A solution of $NaBH_4$ (120.0 mg, 3.17 mmol) in ethanol (50 mL) was added dropwise under dinitrogen atmosphere to a stirred solution of $[Pt(dcype)Cl_2]$ (1.00 g, 1.45 mmol) in dichloromethane (70 mL). After ten minutes, the turbid solution was evaporated to dryness and the white solid residue was extracted with few millilitres (ca. 5) of CH_2Cl_2. The crude product (830 mg) was precipitated by addition of diethyl ether to the clear, filtered solution. The analytical sample was obtained by crystallisation from CH_2Cl_2/Et_2O (790 mg; yield 85.6%). IR (nujol, cm^{-1}): 1970−1950 s,br (1980 s,br in CH_2Cl_2) ν_{PtH}. ^1H NMR (ppm): δ = 1.6−1.9 and 1.3−1.1 (m. unresolved, CH_2), δ = −2.77 (q. with satellites, H, $^1J_{H-Pt}$ = 480, $^2J_{H-P}$ = 38 Hz). $^{31}P\{^1H\}$ (ppm): δ = 84.0 (s., $^1J_{P,Pt}$ = 2803, $^2J_{P,Pt}$ = 150, $^3J_{P,P}$ = 8.1, $^1J_{Pt-Pt}$ = 801 Hz); $^{195}Pt\{^1H\}$ and $^{195}Pt\{^{31}P\}$ $[(CD_3)_2CO$, ppm]: δ = −5141 tt. ($^1J_{Pt-P}$ = 2795; $^2J_{Pt-P}$ = 148 Hz) or quadruplet ($^1J_{Pt-H}$ ≈ 480 Hz), respectively. M.p. 185 °C (dec.). $C_{52}H_{99}ClP_4Pt_2$ (1273.87): calcd. C 49.04, H 7.85, Cl 2.79, P 9.74, Pt 30.65; found C 48.82, H 7.87, Cl 2.90, P 9.52, Pt 31.0.

[Depending on the $NaBH_4$ stock, indefinable salts of the binuclear cation (NMR data), possibly with B_xH_y type anions (IR suggestion), were isolated as white powders. By addition of a large excess (400%) of a methanolic solution of NH_4Cl to the reaction crude, it is converted to **1b** in few minutes (15′). This procedure is near quantitative (yield 80% after crystallisation). Take care that working with NaCl in acetone solution the major product was a yellow oily, in which 4-hydroxy-4-methyl-2-pentanone was identified by GC.MS and ^1H NMR data as the most abundant product.]

(iii) $[Pt_2(dcype)_2(H)_3][OH]$ (1c): From *cis*-$[Pt(dcype)(H)_2]$. A solution of *cis*-$[Pt(dcype)(H)_2]$ in methanol was stirred overnight under dinitrogen atmosphere, and was then evaporated to dryness. The white solid residue was dissolved in the minimum amount of CH_2Cl_2, and compound **1c** was precipitated by slow addition of diethyl ether (yield 95%). IR (nujol, cm^{-1}): 3400−3200 vs,br ν_{OH}, 1968 s,br ν_{PtH}. $C_{52}H_{100}OP_4Pt_2$ (1255.42): calcd. C 49.75, H 8.04; found C 49.31, H 7.90.

The tetraphenylborate salt **1d** was obtained variously from **1a**, **1b**, or **1c** by exchange reactions carried out in methanol solution with a large excess of $NaBPh_4$. The yields referred to analytica1ly pure samples were: 80% from **1a**, 90% from **1b**, and 84% from **1c**. IR (nujol, cm^{-1}): $\tilde{\nu}$ = 1966br. s ν_{PtH}, 1580 m (BPh_4^-). M.p. 240 °C (dec). $C_{76}H_{119}BP_4Pt_2$ (1557.68): ca1cd. C 58.62, H 7.72; found C 58.71, H 7.68.

$[Pt_2(dcype)_2(D)_3][Cl]$ (1b-d_3): The deuteride was obtained by procedure (ii), but with use of $NaBD_4$ and deuterated solvents. The crude material was crystallised twice (yield 36%). $^{31}P\{^1H\}$ NMR (ppm): δ = 83.9 (br. s, $^1J_{P,Pt}$ = 2788, $^2J_{P,Pt}$ = 149, $^3J_{P,P}$ = not detectable, J_{Pt-Pt} = 802 Hz).

Reactions of $Pt(P\text{-}P)Cl_2$ (P-P = dppe, dppp, dppb) with BH_4^-: These reactions were attempted by procedure (ii) as reported above for **1b**, but under various experimental conditions [i.e., with or without H_2 atmosphere, with $NaBH_4$ or KBH_4, with use of different BH_4/Pt ratios (from 1:1 to 4:1), and at different temperatures (from −15 °C to room temperature]. Even though the formation of the $[Pt_2(P\text{-}P)_2(H)_3]^+$ cations was always observed, only the compounds $[Pt_2(dppp)_2(H)_3][Cl]$ (**3a**) and $[Pt_3(dppe)_3(H)_3][Cl]$ (**6**) were isolated as analytical samples.

The former product (**3a**) was isolated (yield 40%) by crystallisation from acetone/diethyl ether of reaction products obtained by procedure (ii), but with use of a BH_4/Pt ratio of 1:1.

With dppe ligand, under dihydrogen atmosphere but independently of temperature and BH_4/Pt ratio, the isolated powders were found to be mixtures of unchanged $Pt(dppe)Cl_2$ and variable amounts of the binuclear (**5**) and trinuclear (**6**) hydrides. Compound **6** was isolated as a pale yellow powder by slow addition of diethyl ether to clear solutions of these mixtures in a few millilitres (4−5) of dichloromethane. The best results (yield 63%) were obtained by carrying out the reactions in ethanol/dichloromethane mixtures (1:1), with use of a BH_4/Pt ratio of 4:1, either at −15 °C or at room temperature. The reaction times were 2 hours and 30 minutes, respectively.

Reaction of 1 with CO and KCN. $[Pt_2(dcype)_2(\mu\text{-}CO)(\mu\text{-}H)][X]$ (X: Cl, 7a; BF_4, 7b; BPh_4, 7c): The compounds were synthesised by bubbling CO through acetone solutions of the appropriate hydrido salt at room temperature. The colourless solutions quickly turned blue. The compounds were isolated by addition of diethyl ether to the concentrated solutions at different reaction times: 30 minutes (**7a**) or 4 hours (**7b** and **7c**). Compounds **7b** and **7c** were isolated as analytical samples (yields: 83% and 95%, respectively), while **7a** was crystallised from acetone/diethyl ether (yield 68%). IR (nujol, cm^{-1}): $\tilde{\nu}$ = 1710s ν_{CO} (1053 s,br, ν_{BF4}, **7b**; 1579 m, BPh_4, **7c**). $^{31}P\{^1H\}$ NMR $[(CD_3)_2CO$, under CO atmosphere, ppm]: δ = 64.3 (br, $^1J_{P,Pt}$ = 2260 Hz, $P_{trans\text{-}C}$), δ = 64.1 (br, $^1J_{P,Pt}$ = 4390, $^2J_{P,Pt}$ = 460 Hz, $P_{trans\cdot H}$). ^1H NMR $[(CD_3)_2CO$, under CO atmosphere, at 243 K, ppm]: δ = +0.72 (hydrido resonance; external satellites observed as triplets of triplets: $^1J_{H-Pt}$ = 454, $J_{H-Ptrans}$ = 76, J_{H-Pcis} = 10 Hz). $^{31}P\{^1H\}$ NMR $[(CD_3)_2CO$, under CO atmosphere, at 223 K, ppm]: δ = 65.8 (d, $^1J_{P,Pt}$ = 2240, $^2J_{P,P}$ = 26 Hz, $P_{trans-C}$), δ = 65.0 (d, $^1J_{P,Pt}$ = 4370, $^2J_{P,Pt}$ = 470, $^2J_{P,P}$ = 26 Hz, $P_{trans-H}$). M.p. (dec) 200 °C, **7a**; 215 °C, **7b**; 190 °C, **7c**. $C_{53}H_{97}BF_4OP_4Pt_2$ (1351.21), **7b**: ca1cd. C 47.14, H 7.25, found C 47.42, H 7.22.

***cis*-Pt(dcype)(H)(CN) (8):** A suspension of KCN (100 mg; 1.54 mmol) in methanol (20 mL) was added to a vigorously stirred solution of **1b** (400 mg, 0.314 mmol) in the same solvent (25 mL). The solution immediately fizzed and a white precipitate was formed. After ten minutes the suspension was evaporated to dryness, the white residue was dissolved in CH_2Cl_2, and the insoluble material was filtered off; this was repeated twice. The analytical sample (300 mg; yield 75.3%) was obtained by addition of a large excess of diethyl ether to few millilitres of a dichloromethane solution of the crude product. IR (nujol, cm^{-1}) 2118 vs ν_{CN}, 1992 vs ν_{PtH}. ^1H NMR (hydrido region, ppm): δ = −2.01 (dd, $^2J_{H-Ptrans}$ = 178.4, $^2J_{H-Pcis}$ = 15; $^1J_{H-Pt}$ = 986 Hz). $^{31}P\{^1H\}$ NMR (ppm): δ = 71.8 (s, $^1J_{P(transCN)-Pt}$ = 2706 Hz), δ = 69.0 (s, $^1J_{P(transH)-Pt}$ = 1714 Hz). $^{195}Pt\{^1H\}$ NMR $[(CD_3)_2CO$, ppm]: δ = −5244 (dd). FAB MS (NBA): 644 *m/z* $[M]^{+\cdot}$. M.p.: 180 °C (dec). $C_{27}H_{49}NP_2Pt$ (644.72): calcd. C 50.30, H 7.68, N 2.17; found C 49.93, H 7.70,

Table 3. Crystallographic data

Compound	**1d**
Formula	$C_{76}H_{119}BP_4Pt_2$
M	1557.68
Colour	Colourless
Crystal system	Monoclinic
Space group	$P2_1/n$ (no.14)
a [Å]	23.637(2)
b [Å]	13.328(1)
c [Å]	24.351(2)
α [°]	90
β [°]	109.17(1)
γ [°]	90
U [Å^3]	7246.0(11)
Z	4
F(000)	3184
Dc [g cm^{-3}]	1.43
T [K]	200
Crystal dimensions [mm]	0.25 × 0.25 × 0.40
μ (Mo-$K\alpha$) [cm^{-1}]	40.23
Min. and max. transmission factors	0.76−1.00
Scan mode	ω
Frame width [°]	0.30
Time per frame [s]	20
No. of frames	2450
Detector−sample distance [cm]	5.00
θ-range [°]	3−25
Reciprocal space explored	full sphere
No. of reflections (total; independent)	63529; 12751
R_{int}	0.038
Final R_2 and R_{2w} indices[a] (F^2, all reflections)	0.029, 0.043
Conventional R_1 index [$I > 2\sigma(I)$]	0.018
Reflections with $I > 2\sigma(I)$	10901
No. of variables	760
Goodness of fit[b]	0.93

[a] $R_2 = [\Sigma(F_o^2 - kF_c^2)/\Sigma F_o^2]$, $R_{2w} = [\Sigma w(F_o^2 - kF_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. [b] $[\Sigma w(F_o^2 - kF_c^2)^2/(N_o - N_v)]^{1/2}$, where $w = 4F_o^2/\sigma(F_o^2)^2$, $\sigma(F_o^2) = [\sigma^2(F_o^2) + (0.02F_o^2)^2]^{1/2}$, N_o is the number of observations and N_v the number of variables.

N 2.16. During the ^{195}Pt{^{1}H} NMR spectrum ($CDCl_3$ solution) acquisition, compound **8** was converted into [Pt(dcype)Cl_2] and *cis*-[Pt(dcype)(Cl)(CN)] (**9**): ^{31}P{^{1}H} NMR (ppm): $\delta = 65.4$ (s, $^1J_{\mathrm{P}(trans\mathrm{Cl})-\mathrm{Pt}} = 3337$ Hz), $\delta = 63.0$ (s, $^1J_{\mathrm{P}(trans\mathrm{CN})-\mathrm{Pt}} = 2568$ Hz). ^{195}Pt{^{1}H} NMR (ppm): $\delta = -4839$ (dd).

X-ray Data Collection and Structure Determination: Crystal data and other experimental details are summarised in Table 3. The diffraction experiment was carried out on a Bruker SMART CCD area-detector diffractometer at 200 K by use of Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å) with a graphite crystal monochromator in the incident beam. Cell parameters and orientation matrix were obtained from least-squares refinement of 123 reflections each measured in three different sets of 15 frames, in the range $3 < \theta < 23°$. At the end of data collection the first 50 frames, containing 235 reflections, were recollected to monitor crystal decay. No correction was necessary. The collected frames were processed with the SAINT software package,[24] and an absorption correction was applied (SADABS)[25] to the 63529 collected reflections, 12751 of which are unique with $R_{\mathrm{int}} = 0.0378$ ($R_{\mathrm{int}} = \Sigma|F_o^2 - F_{\mathrm{mean}}^2|/\Sigma F_o^2$).

The calculations were performed on a Pentium III Pc by use of the Personal Structure Determination Package[26] and the physical constants tabulated therein. Scattering factors and anomalous dispersion corrections were taken from ref. 27. The structure was solved by direct methods (SHELXS 86)[28] and refined by full-matrix, least-squares, by using all reflections and minimising the function $\Sigma w(F_o^2 - kF_c^2)^2$. Anisotropic displacement factors were refined for all the non-hydrogen atoms. The three hydrides were found in the final Fourier maps and refined isotropically. The other hydrogen atoms were placed in their ideal positions (C−H = 0.97 Å, B 1.10 times that of the carbon atom to which they are attached) and not refined. In the final difference Fourier map the maximum residual was 1.06(14) Å^{-3} at 0.78 Å from Pt(2). CCDC-208551 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44−1223/336-033; E-mail: deposit@ccdc.cam.ac.uk.

Inelastic Incoherent Neutron Scattering (INS) Measurements: The INS experiments were carried out on TOSCA-I, a crystal-analyser inverse-geometry spectrometer[29] operating at the ISIS pulsed-neutron source. The incident neutron beam spans a broad energy (E_0) range and energy selection is carried out on the secondary neutron flight-path by use of the (002) Bragg reflection of a graphite analyser placed in back-scattering position (≈ 136°). The resolving power of TOSCA-I is fairly good ($2\% < \Delta\hbar\omega/E_0 < 3.5\%$) in the accessible energy transfer range (24 cm^{-1} < $\hbar\omega$ < 8065 cm^{-1}) making this instrument a neutron equivalent of a Raman optical spectrometer. All the intramolecular vibrations can in principle be easily observed by INS spectroscopy, but it should be also pointed out that, due to molecular recoil, the neutron-measured frequencies might be slightly different from those observed on a conventional Raman spectrometer.

The measurements were carried out on samples of [Pt_2(dppe)$_2$(H)$_3$][BF_4] (**5a**) and [Pt_2(dcype)$_2$(H)$_3$][BF_4] (**1b**) and their deuterium analogues (approximately 1 g each), all contained in individual thin Al-film bags. During the data collection, the samples were maintained at ca. 12 K and the spectra were recorded up to an integrated proton current of 1967 μA/h (roughly 10 hours of beam time).

In order to distinguish the M−H vibrational modes from all other vibrations involving hydrogen atoms of the ligands, a "sample difference" technique[17] was used. The method is based on the fact that the incoherent neutron scattering cross sections of hydrogen and deuterium are very different [79.91(4) and 2.94(3) barn, respectively),[30] making vibrational modes involving D atoms difficult to detect by INS in the presence of many hydrogen atoms. The difference between two experimental INS spectra (i.e., those containing the "Pt−D" and "Pt−H" moieties) should thus only leave the peaks involving the motion of the hydrides (bridging or terminal), provided that any possible coupling of the hydride modes to other molecular modes is negligible (on the scale of the resolution of the INS experiment). Therefore, as the contribution from the ligand modes is subtracted out, it is unnecessary to prepare samples with fully deuterated ligands.

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