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Synthesis and characterization of the neutral dinuclear hydrido complexes of platinum with bridging phosphides *cis*-$Pt_2(H)_2(PHBu^t_2)_2(\mu\text{-}H)(\mu\text{-}PBu^t_2)$ (Pt–Pt) and *trans*-$[Pt(H)(PHBu^t_2)(\mu\text{-}PBu^t_2)]_2$ (Pt–Pt)

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trans-$PtCl_2(PHBu^t_2)_2$ **1** reacts with $NaBH_4$ in THF affording the dinuclear platinum(II) complexes *cis*-$Pt_2(H)_2(PHBu^t_2)_2(\mu\text{-}H)(\mu\text{-}PBu^t_2)$ (Pt–Pt) **2** and *trans*-$[Pt(H)(PHBu^t_2)(\mu\text{-}PBu^t_2)]_2$ (Pt–Pt) **3** along with the boron adduct $BH_3{\cdot}PHBu^t_2$ **4**. Pure **2** can be obtained in 85% yield in the reaction carried out in the presence of two equivalents of di-*tert*-butylphosphine.

Introduction

We have recently described the spectroscopic and XRD characterization of *trans*-$PtCl_2(PHBu^t_2)_2$ **1** that exists as a mixture of rotational conformers.[1,2] Aiming at preparing new, low-valent platinum complexes a sodium reduction of **1** was carried out, leading to a mixture of compounds among which the presence of $[Pt(\mu\text{-}PBu^t_2)(PHBu^t_2)]_2$ could be detected.[1]

Reductants commonly employed to access low-valent transition metal complexes such as sodium naphthalenide,[3] zinc dust[4] and sodium methoxide[5] were used unsuccessfully since no reaction with **1** took place.

The reactivity of sodium borohydride towards transition metal complexes has been long studied, both for the preparation of zero-valent phosphino- and arsino- complexes,[6] and for the synthesis of hydrido species. In particular, $NaBH_4$ reaction with Pt(II) dichloride diphosphine complexes, either in the presence or absence of molecular hydrogen, resulted nearly always in the substitution of one or both the chlorine atoms with co-ordinated hydrides.[7] Such hydrides, depending on the bulkiness of the phosphorus ligands, can vary from being very unstable (unhindered phosphines) in air to thermally very stable (bulky phosphines). The only case of a $PtCl_2P_2$–$NaBH_4$ reaction that does not give rise to chloro/hydrogen exchange is that reported by Brown and co-workers[8] on $PtCl_2$(dppm) [dppm = bis(diphenylphosphino)methane]. Such a reaction led to the binuclear cation $[Pt_2H_2(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$.

The reaction of $NaBH_4$ with **1** carried out in refluxing THF resulted in the synthesis of two neutral dimeric hydrido complexes: *cis*-$Pt_2(H)_2(PHBu^t_2)_2(\mu\text{-}H)(\mu\text{-}PBu^t_2)$ (Pt–Pt) **2** and *trans*-$[Pt(H)(PHBu^t_2)(\mu\text{-}PBu^t_2)]_2$ (Pt–Pt) **3**. The concomitant formation of **3** was prevented by carrying out the reaction in the presence of free di-*tert*-butylphosphine ($PHBu^t_2$).

Results and discussion

When a suspension of *trans*-$PtCl_2(PHBu^t_2)_2$ **1** was reacted for 12 h with $NaBH_4$ in THF at reflux, hydrogen evolution was detected and a black suspension was obtained. After filtering off the excess $NaBH_4$ and the NaCl and platinum metal formed during the reaction, the $^{31}P\{^1H\}$ NMR spectrum of the solution showed three sets of signals which could be assigned to three different species. A quartet (four 1:1:1:1 lines) without ^{195}Pt satellites centered at δ 48.84 with a coupling constant of 46.5 Hz, which split into a doublet of quartets [J(PH) 349 Hz] in the proton coupled spectrum, could be easily assigned to the BH_3–$PHBu^t_2$ Lewis adduct **4**. Such a species is characterised by the observed $^{11}B^{31}P$ 46.5 Hz coupling constant. Moreover ^1H, ^{31}P, ^{13}C and ^{11}B NMR data of compound **4** are identical with those of a pure sample of the adduct synthesised by condensation of $PHBu^t_2$ with $BH_3{\cdot}Me_2S$ (at −20 °C)[9] or $BH_3{\cdot}Et_2O$ (at room temperature).

The other two sets of signals observed in the $^{31}P\{^1H\}$ NMR spectrum of the filtrate reaction solution are both ^{195}Pt coupled and can be assigned to a mixture (*ca.* 1:1) of *cis*-$Pt_2(H)_2(PHBu^t_2)_2(\mu\text{-}H)(\mu\text{-}PBu^t_2)$ (Pt–Pt) **2** and *trans*-$[Pt(H)(PHBu^t_2)(\mu\text{-}PBu^t_2)]_2$ (Pt–Pt) **3** on the basis of their multinuclear NMR features. Ethanol extraction of the crude product obtained after solvent evaporation from the filtrate allowed the removal of adduct **4** from the mixture of the two Pt complexes. The lower solubility of **2** with respect to **3** in a 1:1 C_6H_6–MeCN solution allowed selective enrichment of **3** in the mixture, whereas pure complex **2** could be synthesised by an alternative route as described below.

The $^{31}P\{^1H\}$ NMR spectrum of complex **2** consists of two signals coupled with each other [J(PP) 271 Hz], both flanked by ^{195}Pt satellites and centred at δ 188.0 (triplet) and 53.3 (doublet), respectively (Fig. 1).

In the proton coupled spectrum the doublet split into a doublet of doublets [J(PH) 323 Hz], and the triplet gave rise only to negligible splitting. These findings, along with the observation that low field ^{31}P NMR resonances are characteristic for bridging phosphides involved in three-membered rings,[10] support a dimeric structure in which two platinum atoms, each carrying one terminal $PHBu^t_2$, are bridged by a PBu^t_2 group. The large value of the phosphorus–phosphorus coupling constant suggests that both of the terminally co-ordinated phosphines are *trans* to the bridging phosphide.

The ^1H NMR spectrum of **2** shows (i) a broad doublet centered at δ 5.02, (ii) two doublets in a 1:2 ratio at δ 1.55 and

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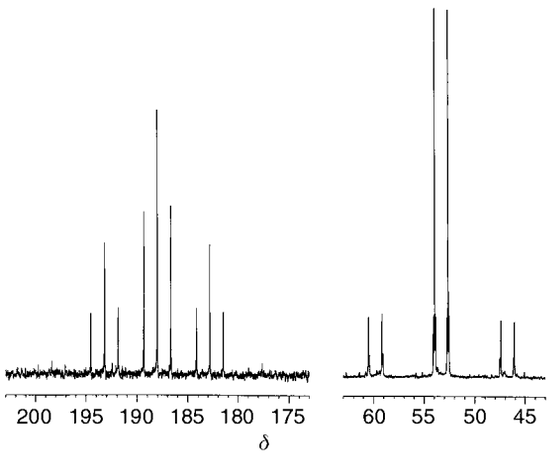


Fig. 1 $^{31}P\{^{1}H\}$ NMR spectrum of **2** (C_6D_6).

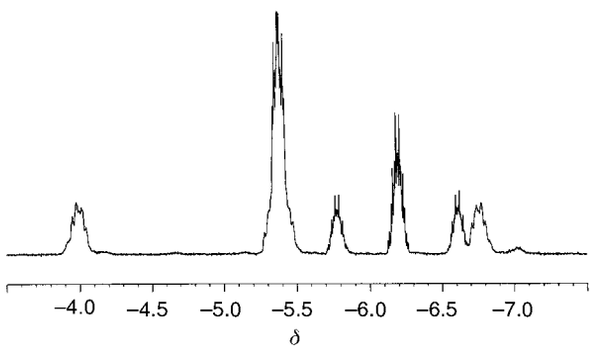


Fig. 2 Hydride region in the ^{1}H NMR spectrum of **2** (C_6D_6).

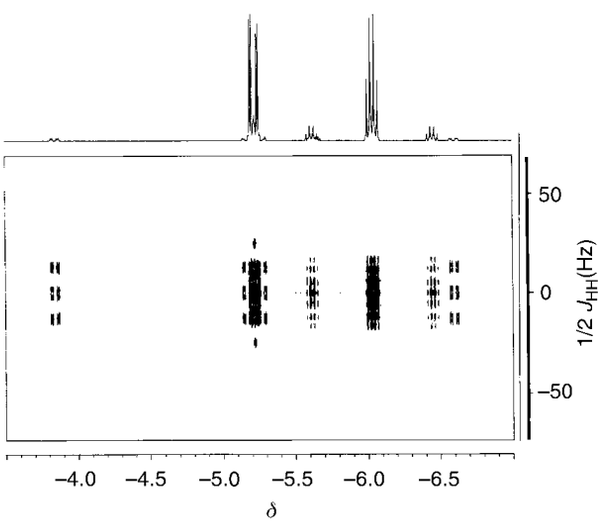


Fig. 3 Contour plot of the 2D ^{1}H *J*-resolved NMR spectrum of **2** (hydride region). The top trace refers to the projection on the ^{1}H chemical shift axis.

1.32, and (iii) two further multiplets in a 2:1 ratio, both ^{195}Pt coupled, and centered at δ −5.39 and −6.22 (Fig. 2). These signals can be ascribed to: (i) the hydrogen directly bound to the phosphorus atom for the co-ordinated $PBu^{t}_{2}H$ [^{1}J(PH) 323 Hz], (ii) the *tert*-butyl groups of the phosphines and of the phosphide [^{3}J(PH) 14.2 and 13.8 Hz, respectively], and (iii) two different kinds of co-ordinated hydrides.

^{195}Pt coupling of the upfield signals at δ −5.39 [^{1}J(PtH) 1378 Hz] and −6.22 [*J*(PtH) 411 Hz] are typical for terminal and bridging hydrides respectively.[8b,11] These experimental data suggest the dimeric structure proposed for **2** characterised by two terminal hydrides *cis* to the bridging phosphide and one bridging hydride. The ^{195}Pt satellite pattern of the δ −6.22 signal, which consists of two sets of resonances due to H–Pt

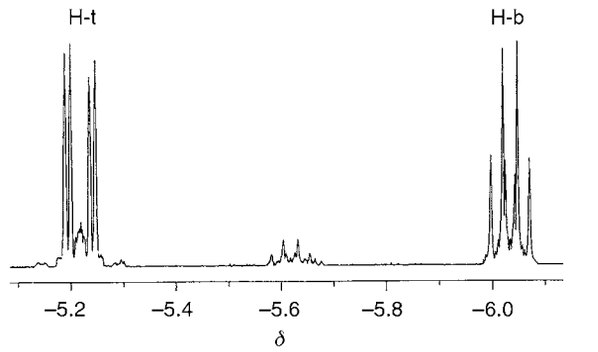


Fig. 4 F2 projection of the 2D ^{1}H *J*-resolved NMR spectrum of **2** in the hydride region.

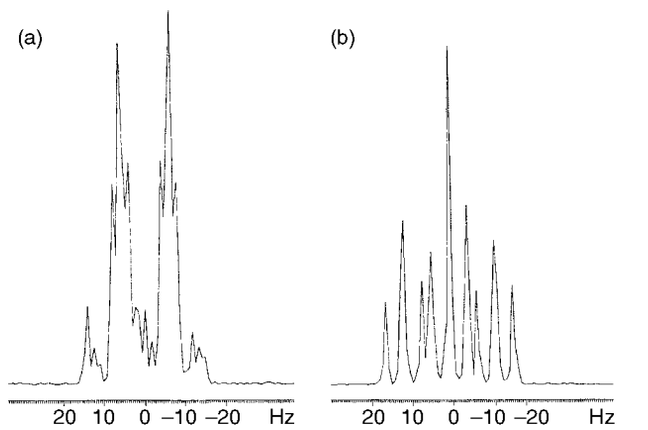


Fig. 5 F1 slices of the δ −5.39 and −6.22 proton signals from the 2D ^{1}H *J*-resolved spectrum of **2**: (a) terminal hydrides; (b) bridging hydride.

coupling in molecules containing one or two NMR active Pt atoms, is also in accord with the presence of one bridging hydride.

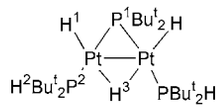
In order to extract the values for the coupling constants between the terminal and bridging hydrides as well as between the hydrides and the phosphorus atoms, a *J*-resolved 2D-NMR experiment on a benzene-d_6 solution of **2** was carried out (Fig. 3). In such an experiment the multiplets due to H–H coupling are tilted in the second dimension (F1) and the residual pattern, easily detected as the projection in the first dimension (F2 projection), only contains the couplings between hydrogens and heteroatoms.

The F2 projection of the terminal hydride signals consists of a sharp doublet of doublets due to the isotopomer containing no NMR active Pt atoms, in addition to lower signals due to the H–Pt couplings in the isotopomers containing one or two NMR active Pt atoms. In F2, the bridging hydride gives a doublet of triplets due to couplings with the bridging phosphide [^{2}J(HP) 14 Hz] and terminal phosphines [^{2}J(HP) 11 Hz], respectively (Fig. 4).

In the F1 dimension the signal of the terminal hydrides results in a doublet of multiplets deriving from the overlapping of two spin systems: an AA′MXX′, due to the isotopomer containing no or both NMR active Pt atoms, and an ABMXY, due to the isotopomer containing only one NMR active Pt atom. From this pattern it was possible to extract only the ^{2}J(HH) 12 Hz with the bridging hydride (Fig. 5).

The signal of the bridging hydride in the F1 dimension consists of a sharp triplet of triplets due to the couplings with the terminal hydrides [^{2}J(HH) 12 Hz] and with the hydrogens directly bound to the phosphorus atoms in the terminal phosphines [^{3}J(HH) 5.5 Hz].

The $^{195}Pt\{^{1}H\}$ NMR spectrum (Fig. 6) consists of a doublet of doublets of doublets centered at δ −5995 due to the



2

Table 1 NMR parameters for **2**[a]

	P^1	P^2	H^1	H^2	H^3	Pt
P^1	**188.0**	271	5.5		14	2105
P^2	271	**53.3**	23.4	323	11	2643
H^1	5.5	23.4	**−5.39**	1.5	12	1378
H^2		323	1.5	**5.02**	5.5	
H^3	14	11	12	5.5	**−6.22**	411
Pt	2105	2643	1378		411	**−5995**

[a] Solvent C_6D_6; chemical shifts (bold typeface) are in ppm; coupling constants (normal type) are in Hz.

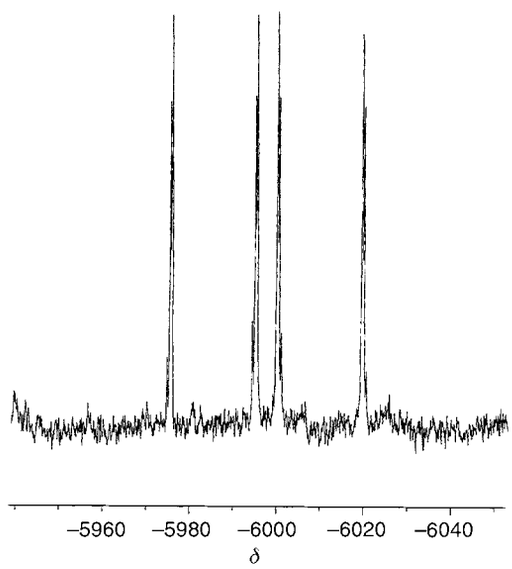


Fig. 6 $^{195}Pt\{^1H\}$ NMR spectrum of **2** (C_6D_6).

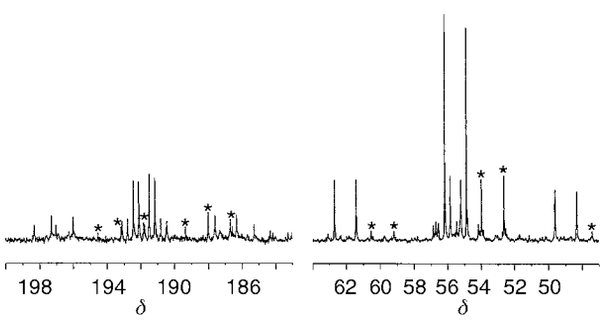
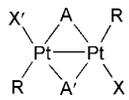


Fig. 7 $^{31}P\{^1H\}$ NMR spectrum of **3** (C_6D_6). Asterisked peaks refer to residual **2**.

isotopomer containing only one NMR active platinum atom [$^1J(PtP_t)$ 2643 Hz, $^1J(PtP_\mu)$ 2105 Hz and $^2J(PtP_t)$ 43 Hz], together with minor signals originated by the X part of an AA′MXX′ spin system (A and M are phosphorus atoms) due to the isotopomer containing both NMR active platinum atoms. The main multinuclear NMR features for **2** are collected in Table 1.

The other platinum complex present in the reaction mixture showed the $^{31}P\{^1H\}$ NMR spectrum reported in Fig. 7. The spectrum mainly consists of two sextets centered at δ 191.8 and 55.5, typical for two chemically equivalent bridging phosphides and two chemically equivalent terminal phosphines {further splitting [J(PH) 318 Hz] is observed in the proton coupled spectrum}, respectively, of a AA′XX′ spin system of the type



in which $J(XX') = 0$.[12] Computer simulation of the spectrum, using as starting chemical shifts and coupling constants those extractable directly from the experimental spectrum,[13] gave the following parameters: $\delta(P_b) = 191.8$, $\delta(P_t) = 55.5$ ppm, $^2J(AX) = {}^2J(A'X') = 264$ Hz, $^2J(AX') = {}^2J(A'X) = -1.5$ Hz, $^2J(AA') = 210$ Hz.

Minor signals due to ^{195}Pt satellites for the isotopomers containing one or two magnetically active platinum atoms allowed the calculation of $^1J(PtP_t)$ 2643 Hz (separation of the terminal phosphine satellites) and of the mean of the two $^1J(PtP_\mu)$ coupling constants (1963 Hz, separation of the bridging phosphide satellites).[13]

The ^1H spectrum shows, besides the resonances ascribed to *tert*-butyl methyls and the PH signals [δ_H 5.25, ^1J(PH) 318 Hz] a multiplet centred at δ −5.40 flanked by two satellites [^1J(HPt) 1505 Hz] in the hydride region. The value of ^1J(HPt) is again in agreement with the proposed terminal co-ordination of the hydrides. The satellites are doublets of pseudotriplets, owing to the coupling with the phosphorus atoms.

The $^{195}Pt\{^1H\}$ NMR spectrum of **3** allowed assignment of the chemical shift of the platinum atoms (δ_{Pt} −5914), to confirm the $^1J(PtP_t)$ (2643 Hz) and to extract the ^2J(PPt) (64 Hz) between the magnetically active platinum and the terminal phosphine co-ordinated to the other platinum atom.

The main IR features of **3** could be obtained recording the spectrum of the solid enriched in **3** (**3**:**2** = 3.7:1). P–H and Pt–H stretching were found respectively at 2294 and 2085 cm^{-1}.

Complex **3** has been proposed by Leoni *et al.* as the result of the reaction of $CpPt(\eta^3\text{-}C_3H_5)$ with $PHBu^t_2$ on the basis of its reactivity.[14] However, the authors describe the complex as sparingly soluble in all common organic solvents. The discrepancy between these results and ours can be explained by admitting that the complex prepared by Leoni's group is an oligomer of **3**. This could account for both its reactivity and its lack of solubility.

When $NaBH_4$ reduction of **1** was carried out in the presence of free $PHBu^t_2$ (2:1 P:Pt ratio) the reaction resulted in the selective synthesis in high yield (85%) of complex **2**. Pure **2** is a white microcrystalline powder soluble in aromatic solvents and THF, scarcely soluble in ethanol, methanol and diethyl ether and insoluble in acetone and acetonitrile. Its IR spectrum recorded in Nujol mull shows two strong sharp bands at 2067 and 2293 cm^{-1}. The 2293 cm^{-1} band is ascribable to the P–H stretching of the co-ordinated di-*tert*-butylphosphines, whereas the 2067 cm^{-1} band is ascribable to the Pt–H stretching of the terminal hydrides. Similar resonances have been found for the hydrido binuclear complexes $[Pt_2(\mu\text{-}PBu^t_2)_2(H)(PHBu^t_2)_2]C_3(CN)_5$ [2289 cm^{-1} (ν_{PH}), 2031 cm^{-1} (ν_{PtH})],[15] $[Pt_2(\mu\text{-}H)(H)(PCy_3)_2]_2$ [2090 cm^{-1} ($\nu_{PtH\text{-}t}$), 1550 cm^{-1} ($\nu_{PtH\text{-}b}$)],[16] $[Pt_2[P–P^*]_2(H)_3][BF_4]$ [P–P* = (*S*)-prolophos: 2015 cm^{-1} (ν_{PtH}); P–P* = (*S*)-butaphos: 2000 cm^{-1} (ν_{PtH})],[17] $[Pt_2[P–P]_2(H)_3][BF_4]$ [P–P = chelating diphosphine; 1975–2060 cm^{-1} (ν_{PtH})][18] and $[Pt_2H_3\{R(Bu^t)P(CH_2)_nPR(Bu^t)\}_2]X$ [R = Bu^t, Ph; n = 2, 3; X = BPh_4, OMe; 2000–2045 cm^{-1} ($\nu_{PtH\text{-}t}$), 1650 cm^{-1} ($\nu_{PtH\text{-}b}$)].[19] A band centred at 1630 cm^{-1} was also present in the IR spectrum of **2** ascribable to Pt–H–Pt stretching.[20]

The suggested mechanism for the formation of **2** is depicted in Chart 1. The first step is the expected substitution of one chloro ligand with a hydride leading to species **A** (all species labeled with capital letters are supposed to be transient in solution). Such a species could in turn undergo HCl elimination (responsible for the observed H_2 evolution in the presence of $NaBH_4$) with formation of the terminal phosphido–hydrido co-ordinatively unsaturated Pt(II) intermediate **B**. This intermediate could either give dimerisation with formation of **3** or react

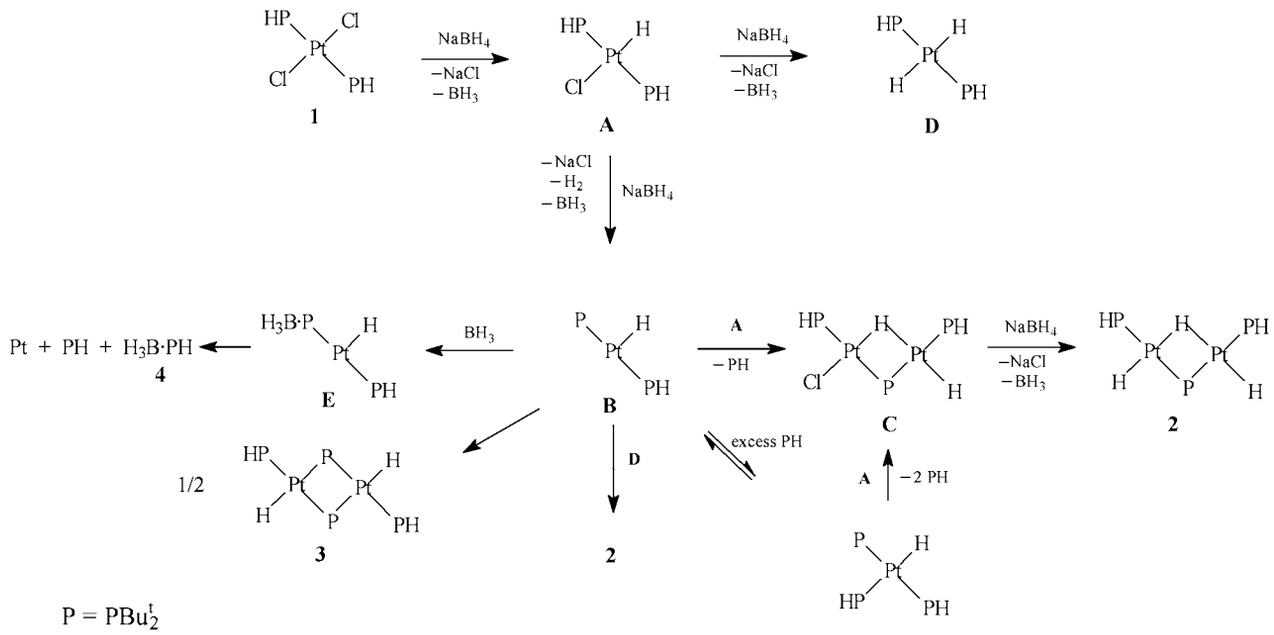


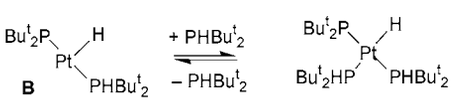
Chart 1

with **A** to give the dimeric species **C** *via* nucleophilic attack of the electron-rich terminal phosphido ligand on the electrophilic Pt centre of **A** which, in turn, undergoes displacement of one phosphine and transformation of the terminal into bridging hydride. Species **C** could generate **2** by further substitution of the chloride with a hydride owing to the presence of excess $NaBH_4$.

It cannot be excluded that substitution of both chlorides with hydrides could also take place by reaction of BH_4^- with **1** with formation of the *trans*-dihydride **D**. In this case the formation of **2** could be derived by nucleophilic attack of the phosphido species **B** on **D**.

The key step of the proposed mechanism, *e.g.* the formation of HCl from the moiety *cis*-M(Cl)(PR_2H) (M = metal) has been already observed for the synthesis of complexes of type $[M_2X_2(\mu\text{-}PR'_2)_2(PR_3)_2]$ (M = Pd,[21] Pt[13]).

The observation that, in the presence of excess phosphine, only **2** is formed in high yield and no platinum metal forms could be explained invoking two main effects. The free phosphine could sequestrate the BH_3 as it forms, giving the adduct $PHBu^t_2{\cdot}BH_3$ **4**, and stabilise the intermediate **B** by occupying the free co-ordination site according to the following equilibrium.



The presence of such an equilibrium lowers the concentration of **B** in solution and renders its dimerisation to **3** unlikely. As to the formation of platinum metal it may be due to decomposition of species **E** formed by reaction between BH_3 and **B**.

In order to verify this hypothesis we carried out an experiment reacting **1** with excess $NaBH_4$ in the presence of one equivalent of $BH_3{\cdot}Et_2O$. This reaction led to the formation of only platinum metal, hydrogen, the adduct **4** and NaCl according to the stoichiometry:

$$PtCl_2(PHBu^t_2)_2 + 2\ NaBH_4 \longrightarrow 2\ NaCl + Pt + H_2 + 2\ BH_3{\cdot}PHBu^t_2$$

Although the attempts to isolate **C** were unsuccessful, the $^{31}P\{^1H\}$ NMR spectrum of the crude product obtained after filtration of excess $NaBH_4$ showed, apart from the signals of **2**, **3** and **4**, a weak doublet of doublets centered at δ 186 with *trans* J(PP) 263 and 228 Hz ascribable to the bridging phosphide of **C**. Unfortunately, the crowding of peaks due to the presence of **2**, **3** and **4** did not allow the corresponding signals in the PH region to be exactly located.

Experimental

All manipulations were carried out under a pure dinitrogen atmosphere, using freshly distilled and oxygen-free solvents. Di-*tert*-butylphosphine was purchased from Aldrich and used as received. *trans*-$PtCl_2(PHBu^t_2)_2$ was prepared as previously described.[1]

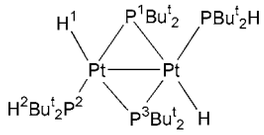
Infrared spectra were recorded on a Perkin-Elmer Spectrum One spectrometer. Elemental analyses were carried out by using a Carlo Erba model EA 1108 elemental analyser. NMR spectra were recorded on a Bruker Avance DRX500 spectrometer (CARSO); frequencies are referenced to Me_4Si (^1H, ^{13}C), 85% H_3PO_4 (^{31}P), $BF_3{\cdot}Et_2O$ (^{11}B) and H_2PtCl_6 (^{195}Pt). Simulated spectra were calculated with the program MestRe-C 2.0 assuming the ^3J(PP) between the two terminal phosphorus atoms to be equal to zero.

Reaction of 1 with sodium borohydride

$NaBH_4$ (0.200 g, 5.3 mmol) was added to a THF solution of *trans*-$PtCl_2(PHBu^t_2)_2$ (0.651 g, 1.17 mmol in 20 cm^3). The resulting suspension was stirred at reflux for 12 h. Filtration of the suspension and evaporation of the solvent from the filtrate afforded a dark residue that was washed three times with ethanol (3 × 7 cm^3). A pale yellow solid (0.155 g) was so obtained, the spectroscopic features of which indicate as a mixture of **2** and **3** in a 1:1 ratio. Treating this mixture with C_6H_6–MeCN 1:1 followed by filtration afforded a solution that contained **2** and **3** in a 1:3.7 ratio as revealed by ^1H and ^{31}P NMR. Main NMR features of **3** are collected in Table 2. NMR data other than those collected in Table 2 are, δ_H (C_6D_6): 1.55 [36H, d, $^3J(Bu^tP_\mu)$ 13.9 Hz, 4 Bu^tP_μ], 1.35 [36H, d, $^3J(Bu^tP_t)$ 13.9 Hz, 4 Bu^tP_t]. IR (Nujol, ν_{max}/cm^{-1}): (PH) 2294s, (PtH) 2085vs.

Synthesis of [*cis*-dihydride-bis(di-*tert*-butylphosphine)-(μ-hydride)(μ-di-*tert*-butylphosphide)diplatinum(II)] 2

$PHBu^t_2$ (0.297 g, 2.03 mmol) was added to a solution of **1** in THF (0.567 g, 1.015 mmol in 20 cm^3). $NaBH_4$ (0.179 g,



3

Table 2 NMR parameters for **3**[a]

	P^1	P^2	P^3	H^1	H^2	Pt
P^1	**191.8**	264	210	7		[b]
P^2	264	**55.5**	−1.5	7	318	2643
P^3	210	−1.5	**191.8**	23		[b]
H^1	7	7	23	**−5.40**	1.5	1505
H^2		318		1.5	**5.25**	
Pt	[b]	2643	[b]	1505		**−5914**

[a] Solvent C_6D_6; chemical shifts (bold typeface) are in ppm; coupling constants (normal type) are in Hz. [b] $[^1J(PtP^1) + {}^1J(PtP^3)]/2 = 1963$ Hz.

5.1 mmol) was then added to the yellow solution and stirred at reflux for 20 h. The resulting white suspension was filtered off and a colourless solution of *cis*-$Pt_2(H)_2(PHBu^t_2)_2(\mu$-H)-($\mu$-$PBu^t_2$) **2** and $BH_3{\cdot}PHBu^t_2$ **4** was obtained. Evaporation of the solvent followed by extraction of **4** with ethanol (3×7 cm^3) yielded pure **2** as a white microcrystalline powder (0.361 g, 85%). mp (C_6H_6–MeCN) 200 °C decomp. (Found: C, 34.41; H, 7.12; P, 11.08. $C_{24}H_{59}P_3Pt_2$ requires C, 34.70; H, 7.16; P, 11.18%). IR (Nujol, ν_{max}/cm^{-1}): (PH) 2293s, (PtH_t) 2067vs, (PtH_b) 1630m, 1261m, 1180m, 941w, 905m, 853s, 814vs, 682s, 620w, 588m, 468s, 390w. NMR data other than those collected in Table 1 are, δ_H (C_6D_6) 1.55 [18H, d, $^3J(Bu^tP)$ 14.2 Hz, 2 Bu^tP^1], 1.32 [36H, d, $^3J(Bu^tP)$ 13.8 Hz, 4 Bu^tP^2]; $^2J(PtH_t)$ 38 Hz; $^2J(PtP_t)$ 43 Hz. UV/VIS [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})] in toluene (5.8×10^{-4} mol dm^{-3}): 287 (5280), 280 (2000).

Synthesis of di-*tert*-butylphosphineborane 4

PBu^t_2H (0.386 g, 2.65 mmol) was dissolved in 1.5 cm^3 of THF and 2.8 ml of a 1.0 mol dm^{-3} BH_3 solution in THF was added, dropwise, and the system stirred for 45 min. The solution was evaporated *in vacuo* obtaining pure **4** as a white solid (416 mg, 98%). Mp 64.8 °C (Found: C, 60.11; H, 13.79; P, 19.22. Calc. for $C_8H_{22}BP$: C, 60.04; H, 13.86; P, 19.35%). IR (Nujol, ν_{max}/cm^{-1}): 2384vs, (B–H) 2351vs, 2276m, (P–H) 2258m, 2125w, 1467vs, 1393m, (B–P) 1369vs, 1196s, 1137s, 1066vs, 1025vs, 906vs, 819vs, 692s, 625s, 543m. NMR, δ_H ($CDCl_3$): 3.74 [dq, $^1J(PH)$ 349, $^3J(HH)$ 6.8], 1.25 [qm, $^1J(HB)$ 100], 1.033 [d, $^3J(HP)$ 13.2]; δ_C ($CDCl_3$): 28.92 [d, $^2J(CP)$ 1.7], 30.35 [d, $^1J(CP)$ 27.0]; $^{31}P\{^1H\}$ ($CDCl_3$): 48.84 [q, $^1J(PB)$ 46.5]; δ_B ($CDCl_3$): −42.69 [dq, $^1J(BP)$ 46.8, $^1J(BH)$ 98.5].

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