Synthesis of New Neutral and Cationic Phosphido-Bridged Dinuclear Platinum(II) Hydrides

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Introduction

A certain number of homodinuclear platinum hydrides have been reported.[1−7] In a former subclass the dinuclear unit is ensured only by the presence of hydride bridges. One[1] or two[1a,2] hydride bridges hold together the complexes which consist either of two interlocked square planes, with different dihedral angles between the two planes [(μ-H) derivatives],[1] or of one square plane interlocked with one trigonal bipyramid [(μ-H)$_2$ derivatives].[2] All of them complete the coordination around the platinum metals with tertiary phosphine and terminal hydride (or phenyl) ligands and are represented by the formulas $[(R_3P)_2(R')Pt(\mu\text{-}H)Pt(H)(PR_3)_2]^+X^-$ (R′ = H,[1] R′ = Ph[1b]) and $[(R_3P)_2Pt(\mu\text{-}H)_2Pt(H)(PR_3)_2]^+X^-$.[1a,2] Singly- and doubly-H-bridged derivatives can easily interconvert, provided terminal and bridging hydrides are in pseudo-*cis* orientation.[1a] Moreover, a common feature of these compounds seems to be the lability of the binuclear structure, and in the presence of coordinating anions they are in equilibrium with their neutral monomeric precursors.[1a,b,2b,d,7c] Other doubly-H-bridged binuclear complexes are $[Pt(\mu\text{-}H)(R)(PCy_3)]_2$ (R = H, SiR'_3, GeR'_3),[3] but their stability toward monomerization reactions was not investigated. The second broad subclass of homodinuclear platinum hydrides contains bridging and/or terminal hydrides in the presence of other bridges, the latter contributing to the reinforcement of the dinuclear unit. The most representative compounds of this last class are the numerous bis(diphenylphosphino)methane-bridged complexes.[4] Other derivatives contain bridging CO,[1c,2c,5] CN,[6] or phosphido[7] ligands.

We recently investigated the synthesis and reactivity of new phosphido-bridged binuclear complexes of palladium(I).[8] The key compound was obtained by reacting $CpPd(\eta^3\text{-}C_3H_5)$ with PBu^t_2H.[8b,j] The reaction was shown[8j] to proceed through the intermediate formation of $Pd(PBu^t_2H)_3$, which was then supposed to react as in Scheme 1.[8b]

Although, on the basis of our experimental observations and of the known aspects of the reactivity of palladium complexes, the intermediacy[8b] of $[Pd(\mu\text{-}PBu^t_2)(H)(PBu^t_2H)]_2$ (**1**) sounded reasonable, our attempts to detect it in the early steps of the reaction were unsuccessful. The final product[8b] of the reaction was $[Pd(\mu\text{-}PBu^t_2)(PBu^t_2H)]_2$ (**2**), which was then protonated[8c,d] with strong acids to yield $[Pd_2(\mu\text{-}PBu^t_2)(\mu\text{-}PBu^t_2H)(PBu^t_2H)_2]^+X^-$ (**3a**, X = BF_4; **3b**, X = CF_3SO_3), with a labile bridging secondary phosphine.[8c−i]

Stimulated by the relevance of the results obtained in the investigation on the palladium systems, we attempted to extend our studies to the analogues of platinum, keeping in mind that identical behavior could not necessarily be expected, due either to the higher kinetic inertness of platinum or to its known ability to form stronger bonds, with respect to palladium.[9]

We report here the synthesis and the characterization of two new phosphido-bridged bimetallic hydrides of platinum(II), which were prepared in this study.

Results and Discussion

$CpPt(\eta^3\text{-}C_3H_5)$[10] was reacted with PBu^t_2H in toluene solution. The colorless solid, only sparingly soluble in all common organic solvents, which was isolated after workup, analyzed nicely for the composition $[Pt(PBu^t_2H)_2]_n$. We assign to this complex the structure $[Pt(\mu\text{-}PBu^t_2)(H)(PBu^t_2H)]_2$ (**4**), the platinum analogue of complex **1**. The IR spectrum of complex **4** is nearly superimposable on that of complex **2**, except for a sharp strong signal at 2032 cm^{-1}, in agreement with the presence of terminal Pt−H ligands (ν_{PtH} stretching modes for terminal

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(1) (a) Paonessa, R. S.; Trogler, W. C. *Inorg. Chem.* **1983**, *22*, 1038−1048. (b) Bracher, G.; Grove, D. M.; Venanzi, L. M.; Bachechi, F.; Mura, P.; Zambonelli, L. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 778−779. (c) Bracher, G.; Kellenberger, B.; Venanzi, L. M.; Bachechi, F.; Zambonelli, L. *Helv. Chim. Acta* **1988**, *71*, 1442−1457. (d) Carmona, D.; Thouvenot, R.; Venanzi, L. M.; Bachechi, F.; Zambonelli, L. *J. Organomet. Chem.* **1983**, *250*, 589−608.

(2) (a) Bachechi, F.; Bracher, G.; Grove, D. M.; Kellenberger, B.; Pregosin, P. S.; Venanzi, L. M.; Zambonelli, L. *Inorg. Chem.* **1983**, *22*, 1031−1037. (b) Tulip, T. H.; Yamagata, T.; Yoshida, T.; Wilson, R. D.; Ibers, J. A.; Otsuka, S. *Inorg. Chem.* **1979**, *18*, 2239−2250. (c) Knobler, C. B.; Kaesz, H. D.; Minghetti, G.; Bandini, A. L.; Banditelli, G.; Bonati, F. *Inorg. Chem.* **1983**, *22*, 2324−2331. (d) Paonessa, R. S.; Trogler, W. C. *J. Am. Chem. Soc.* **1982**, *104*, 3529−3530.

(3) (a) Ciriano, M.; Green, M.; Howard, J. A. K.; Proud, J.; Spencer, J. L.; Stone, F. G. A.; Tsipis, C. A. *J. Chem. Soc., Dalton Trans.* **1978**, 801−808. (b) Green, M.; Howard, J. A. K.; Proud, J.; Spencer, J. L.; Stone, F. G. A.; Tsipis, C. A. *J. Chem. Soc., Chem. Commun.* **1976**, 671−672.

(4) (a) Hadj-Bagheri, H.; Puddephatt, R. J.; Manoijlovic-Muir, L.; Stefanovic, A. *J. Chem. Soc., Dalton Trans.* **1990**, 535−539. (b) Brown, M. P.; Fisher, J. R.; Hill, R. H.; Puddephatt, R. J.; Seddon, K. R. *Inorg. Chem.* **1981**, *20*, 3516−3521. (c) McLennan, A. J.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 811−813. (d) Foley, H. C.; Morris, R. H.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 7337−7339. (e) Brown, M. P.; Fisher, J. R.; Mills, A. J.; Puddephatt, R. J.; Thomson, M. *Inorg. Chim. Acta* **1980**, *44*, L271−L272. (f) Brown, M. P.; Puddephatt, R. J.; Rashidi, M.; Seddon, K. R. *J. Chem. Soc., Dalton Trans.* **1978**, 516−522. (g) Brown, M. P.; Fisher, J. R.; Puddephatt, R. J.; Seddon, K. R. *Inorg. Chem.* **1979**, *18*, 2808−2813. (h) Brown, M. P.; Cooper, S. J.; Frew, A. A.; Manoijlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J.; Thomson, M. A. *J. Chem. Soc., Dalton Trans.* **1982**, 299−305.

(5) Bandini, A. L.; Banditelli, G.; Cinellu, M. A.; Sanna, G.; Minghetti, G.; Demartin, F.; Manassero, M. *Inorg. Chem.* **1989**, *28*, 404−410.

(6) Manzer, L. E.; Parshall, G. W. *Inorg. Chem.* **1976**, *15*, 3114−3116.

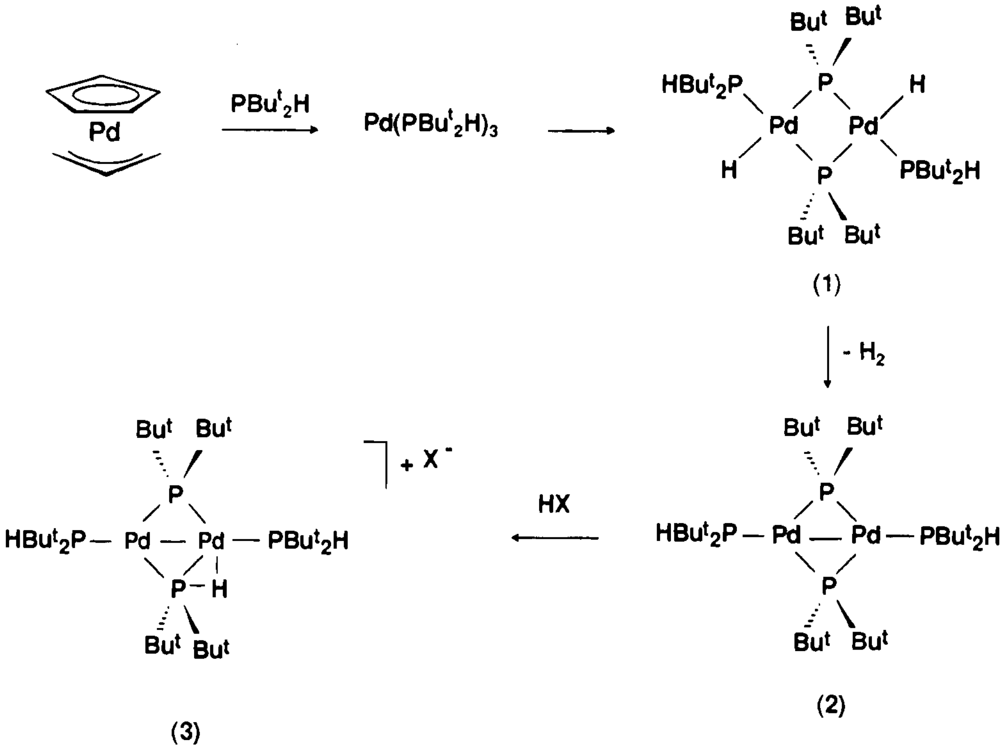
(7) (a) Ebsworth, E. A. V.; Ferrier, H. M.; Henner, B. J. L.; Rankin, D. W. H.; Reed, F. J. S.; Robertson, H. E.; Whitelock, J. D. *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 482−484. (b) Chatt, J.; Davidson, J. M. *J. Chem. Soc. (A)* **1964**, 2433−2445. (c) Siedle, A. R.; Newmark, R. A.; Gleason, W. B. *J. Am. Chem. Soc.* **1986**, *108*, 767−773. (d) Jans, J.; Naegeli, R.; Venanzi, L. M.; Albinati, A. *J. Organomet. Chem.* **1983**, *247*, C37−C41. (e) van Leeuwen, P. W. N. M.; Roobeek, C. F.; Frijns, J. H. G.; Orpen, A. G. *Organometallics* **1990**, *9*, 1211−1222.

(8) (a) Sommovigo, M.; Pasquali, M.; Leoni, P.; Braga, D.; Sabatino, P. *Chem. Ber.* **1991**, *124*, 97−99. (b) Leoni, P.; Sommovigo, M.; Pasquali, M.; Sabatino, P.; Braga, D. *J. Organomet. Chem.* **1992**, *423*, 263−270. (c) Albinati, A.; Lianza, F.; Pasquali, M.; Sommovigo, M.; Leoni, P.; Pregosin, P. S.; Ruegger, H. *Inorg. Chem.* **1991**, *30*, 4690−4692. (d) Leoni, P.; Pasquali, M.; Sommovigo, M.; Laschi, F.; Zanello, P.; Albinati, A.; Lianza, F.; Pregosin, P. S.; Ruegger, H. *Organometallics* **1993**, *12*, 1702−1713. (e) Pasquali, M.; Marchetti, F.; Leoni, P.; Beringhelli, T.; D'Alfonso, G. *Gazz. Chim. Ital.* **1993**, *11*, 659−664. (f) Leoni, P.; Marchetti, F.; Pasquali, M. *J. Organomet. Chem.* **1993**, *451*, C25−C27. (g) Leoni, P.; Pasquali, M.; Sommovigo, M.; Albinati, A.; Lianza, F.; Pregosin, P. S.; Ruegger, H. *Organometallics* **1993**, *12*, 4503. (h) Sommovigo, M.; Pasquali, M.; Marchetti, F.; Leoni, P.; Beringhelli, T. *Inorg. Chem.* **1994**, *33*, 2651−2656. (i) Sommovigo, M.; Pasquali, M.; Leoni, P.; Englert, U. *Inorg. Chem.* **1994**, *33*, 2686−2688. (l) Leoni, P. *Organometallics* **1993**, *12*, 2432−2434.

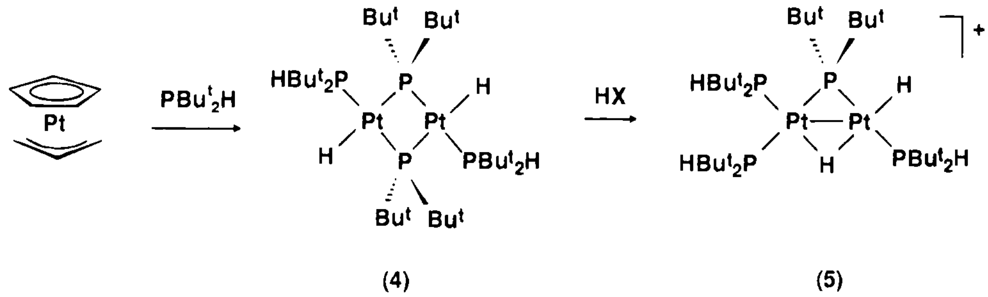
(9) (a) Sakaki, S.; Ogawa, M.; Musashi, Y.; Arai, T. *Inorg. Chem.* **1994**, *33*, 1660−1665. (b) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41−49.

(10) Mann, B. E.; Shaw, B. L.; Shaw, G. *J. Chem. Soc. A* **1971**, 3536−3544.

Scheme 1



Scheme 2



hydrides in dinuclear derivatives are reported in the range 1970–2250 cm^{-1});[1a,2a–c,4a,b,d,f,5,6] the signal due to the P–H bond stretching of the secondary phosphines was observed at 2289 cm^{-1} as a medium-intensity sharp signal (2280 cm^{-1} for complex **2**).

The low solubility of complex **4** prevented a complete multinuclear NMR characterization. It was however possible to observe the resonances of its ^{1}H NMR spectrum at 80 °C. The spectra exhibited *tert*-butyl resonances as doublets at 1.81 and 1.53 ppm ($^3J_{PH}$ = 11.5 and 13.0 Hz, respectively). The hydride resonances were observed at −7.08 ppm; the central stronger multiplets, assigned to the isotopomer which does not contain ^{195}Pt, consist of a doublet of broadened triplets, the large doublet splitting (145 Hz) being reasonably due mainly to the phosphorus atom of the phosphide group *trans* to the hydride ligands. ^{195}Pt satellites, arising from the isotopomers with one ^{195}Pt nucleus, were observed and suggest that the hydrides are terminally bonded. A direct coupling, $^1J_{PtH}$, of 835 Hz was in fact observed. In the known diplatinum complexes, bridging hydrides give ^{1}H NMR signals with $^1J_{PtH}$ in the range 300–600 Hz,[1a,b,2a,d,4f,h,7c–e] while terminal hydrides give signals with $^1J_{PtH}$ = 800–1400 Hz and $^2J_{PtH}$ from unobserved to *ca.* 300 Hz.[1a,b,2a,d,4c,d,f,6] The long-range $^2J_{PtH}$ (or $^3J_{PtH}$ depending on the presence or not of a metal–metal bond) could not be precisely evaluated from the spectra of complex **4**, due to partial overlapping with the central signal and to line broadeness. Resonances due to the P–H protons of the secondary phosphines were observed at 4.87 ppm as a doublet of broad multiplets, with the usual[8] large $^1J_{PH}$ (*ca.* 300 Hz).

Complex **4** reacted cleanly with strong acids (HBF$_4$·Et$_2$O or CF$_3$SO$_3$H) giving, in 81% yield, a yellow crystalline solid, well soluble in polar solvents. This allowed a full spectroscopic characterization of the compound to which the structure [(Bu$^t_2$PH)$_2$Pt(μ-PBu$^t_2$)(μ-H)Pt(H)(PBu$^t_2$H)]X (**5**) (scheme 2) can be assigned with confidence (see next paragraph). The structure of **5** confirms indirectly the reasonableness of the structure suggested for **4**. We are reminded in fact that strong acids protonate one of the phosphido ligands of the palladium derivative **2** forming **3**, with a new bridging secondary phosphine. The reaction with acids of **4**, which differs from **2** only in the presence of the hydride ligands, can again be seen as the protonation of one of the phosphido ligands. The new secondary phosphine remains in this case terminally bonded, with one of the hydride ligands, initially present in **4**, going to bridge the two platinum metals in **5** (Scheme 2).

Characterization of Complex 5. Significant signals in the IR spectrum of **5** were a medium-intensity, slightly broadened signal at 2359 cm^{-1}, in the region where the P–H stretching frequencies of metal-coordinated secondary phosphines[8] are always observed, and a medium-intensity sharp band at 2124 cm^{-1}, diagnostic of the presence of terminal Pt–H bonds. The presence of a bridging hydride could only be suggested by a

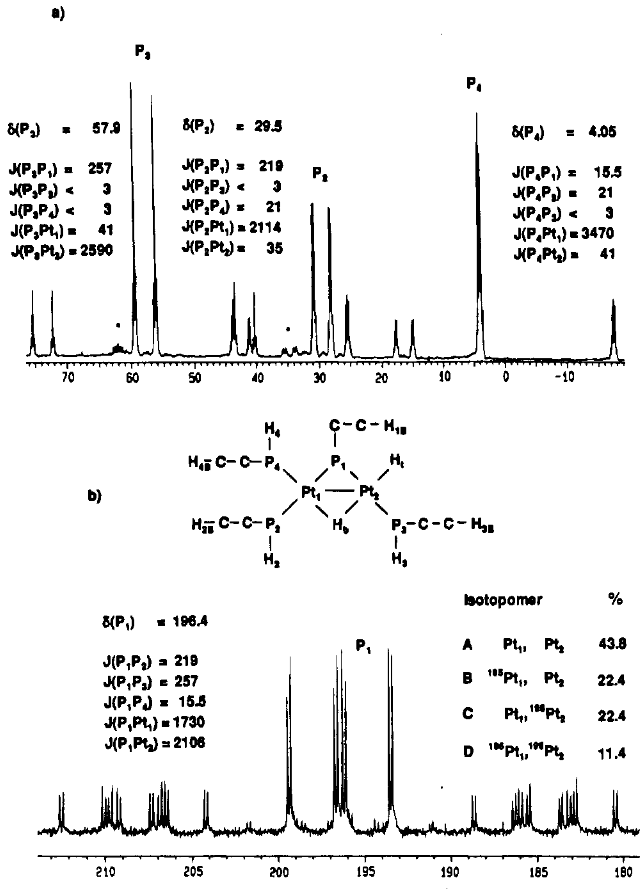


Figure 1. $^{31}P\{^1H\}$ NMR spectrum of complex **5** (CD_2Cl_2, 298 K). Peaks marked with an asterisk are due to an impurity.

broad weak band around 1600 cm^{-1} but was better ascertained by ^1H NMR spectra. Other signals were observed at 1274 vs, 1142 s, 1034 s, and 637 s cm^{-1}, a pattern characteristic of the uncoordinated triflate anion.[11]

The complex $^{31}P\{^1H\}$ NMR spectrum (Figure 1) exhibited signals for four types of magnetically inequivalent phosphorus atoms. A low-field resonance was observed at 196.4 ppm, a region diagnostic of metal–metal-bonded bridging phosphido ligands.[8,12] The signal consists of a central doublet of doublets of doublets (due to the isotopomer **A**, which does not contain ^{195}Pt, 43.8%), with $^2J_{PP}$ = 257, 219, and 15.5 Hz, indicating that this phosphorus atom (P_1) is coupled to other two pseudo-*trans* and one pseudo-*cis* oriented phosphorus nuclei (*trans* $^2J_{PP}$ are generally 1 order of magnitude greater than *cis* $^2J_{PP}$).[13]

Two different sets of satellites arising from isotopomers **B** and **C** (22.4% each), which contain only one ^{195}Pt nucleus ($I = ^1/_2$, isotopic abundance 33.8%), were observed. Each of them is a doublet of the central ddd and is therefore composed of 16 lines; the coupling of P_1 with the two inequivalent platinum atoms is $^1J_{Pt_2P_1} = 2106$ and $^1J_{Pt_1P_1} = 1730$ Hz. A third subset of signals is due to isotopomer **D** (11.4%), containing two ^{195}Pt nuclei, and can again be discussed using a "first-order" approximation. The two different $^1J_{PtH_b}$ split the central ddd in a ddddd, for a total of 32 weak lines (all observable, 0.356% of the total area each line). The signal, on the whole, has roughly the appearance of a 1:8:18:8:1 quintet of multiplets, as reported for diplatinum systems bridged by $I = ^1/_2$ nuclei.[4f]

The remaining three phosphorus nuclei show resonances at 57.9, 29.5, and 4.05 ppm; this region of the spectrum is typical of metal-coordinated Bu^t_2PH molecules,[8] and the proton-coupled ^{31}P NMR spectrum exhibited, accordingly, the expected large $^1J_{PH}$ (*ca.* 320, 340, and 360 Hz, respectively; more precisely estimated from ^1H NMR spectra). The first two were assigned to two phosphine ligands (P_3 and P_2, respectively) lying *trans* and the third was assigned to a phosphine (P_4) *cis* to the phosphido ligand (P_1). Assignment is facilitated by the shape of the central lines of each signal, due to isotopomer **A**, which appear as a doublet ($^2J_{P_3P_1} = 257$ Hz), a doublet of doublets ($^2J_{P_2P_1} = 219$, $^2J_{P_2P_4} = 21$ Hz) and another doublet of doublets ($^2J_{P_4P_1} = 15.5$, $^2J_{P_4P_2} = 21$ Hz), respectively. The two phosphine ligands *trans* to P_1 are easily recognized from the large $^2J_{PP}$; which of them (P_2) lies *cis* to P_4 was inferred by the presence (or absence) of a second, small *cis* coupling ($^2J_{P_4P_2}$). In agreement with a terminal bonding situation, each of these signals shows, for the isotopomers **B** and **C**, satellites with a large $^1J_{PtP}$ (2590, 2114, and 3470 Hz, respectively) and a small, long-range coupling ($^2J_{Pt_1P_3} = 41$, $^2J_{Pt_2P_2} = 35$, and $^2J_{Pt_2P_4} = 41$ Hz).

As described earlier for Pt_2 systems terminally bonded by H or P spins,[1,2,4f] each complete signal due to the secondary phosphine ligands appears as five multiplets in a 1:1:4:1:1 integral ratio, with a small separation (or overlapment) within the central three groups and a large separation of the outer two groups.

The whole $^{31}P\{^1H\}$ NMR spectrum is highly reminiscent of the spectrum reported for $[(Ph_3P)_2Pt(\mu\text{-}PPh_2)(\mu\text{-}H)Pt(Ph)(PPh_3)]^+X^-$ (**6**), whose structure, confirmed by X-ray crystal structure determinations,[7c,d] is nearly identical to the one we suggest for complex **5**, except for the presence of a terminal phenyl in place of a terminal hydride ligand. The strict similarity of the coupling constant patterns of the two systems is reasonably due to the similar σ-donation exerted by a terminal hydride and a phenyl ligand.

The ^1H NMR spectrum of **5** (Figure 2) shows four different doublets for the *tert*-butyl protons [δ, ppm ($^3J_{P_xH_xB}$, $x = 1-4$, in Hz in parentheses): 1.32 (14.7), 1.45 (15.4), 1.48 (14.8), 1.54 (15.2)], in keeping with the presence of one phosphido and three inequivalent phosphines. Three different P–H resonances were observed for the secondary phosphines as doublets of multiplets at [δ, ppm ($^1J_{PH}$ in Hz in parentheses): 6.43 ($^1J_{P_4H_4} = 357.2$), 5.31 ($^1J_{P_2H_2} = 335.0$) and 4.59 ($^1J_{P_3H_3} = 318.5$)]. Each signal was assigned to the proper phosphine by comparing ^1H and ^{31}P proton coupled spectra. Moreover, the spectrum exhibits high-field resonances which unequivocally demonstrate the presence of one terminally bonded and one bridging hydride ligand. The terminal hydride, absorbing at −5.12 ppm, exhibits $^1J_{PtH_t} = 1590$ Hz and $^2J_{PtH_t} = 114$ Hz, with the satellites due to the smaller coupling partially overlapping the central multiplet. The latter appear as a broad triplet due to minor HH and/or HP couplings (J_{app} = *ca.* 30 Hz). Bridging hydrides are generally found at slightly lower fields than their terminal counterparts in platinum dinuclear derivatives,[1-7] in contradiction to the general trend observed for other classes of transition metal hydrides;[14] in this case, however, the bridging hydride was observed at slightly higher fields, at −7.34 ppm, with two sets of $^1J_{PtH_b}$ satellites ($^1J_{PtH_b} = 356$, $^1J_{Pt'H_b} = 584$ Hz); the central signal, due to isotopomer **A**, is a broad doublet of doublets ($J_1 = 92$, $J_2 = 27$ Hz). The larger coupling can be attributed to the phosphorus

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(11) Johnstone, D. H.; Shriver, D. F. *Inorg. Chem.* **1993**, *32*, 1045.

(12) (a) Carty, A. J.; Mac Laughlin, S. A.; Nucciarone, D. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis: Organic Compounds and Metal Complexes;* Verkade, J. B., Quin, L. D., Eds.; VCH: Deerfield Beach, FL, 1987; p 559. (b) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229–266.

(13) Pregosin, P. S.; Kunz, R. W. *NMR: Basic Princ. Prog.* **1979**, *16*.

(14) (a) Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1972**, *72*, 231–281. (b) Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* **1979**, *25*, 145–222. (c) Moore, D. S.; Robinson, S. D. *Chem. Soc. Rev.* **1983**, *12*, 415–452.

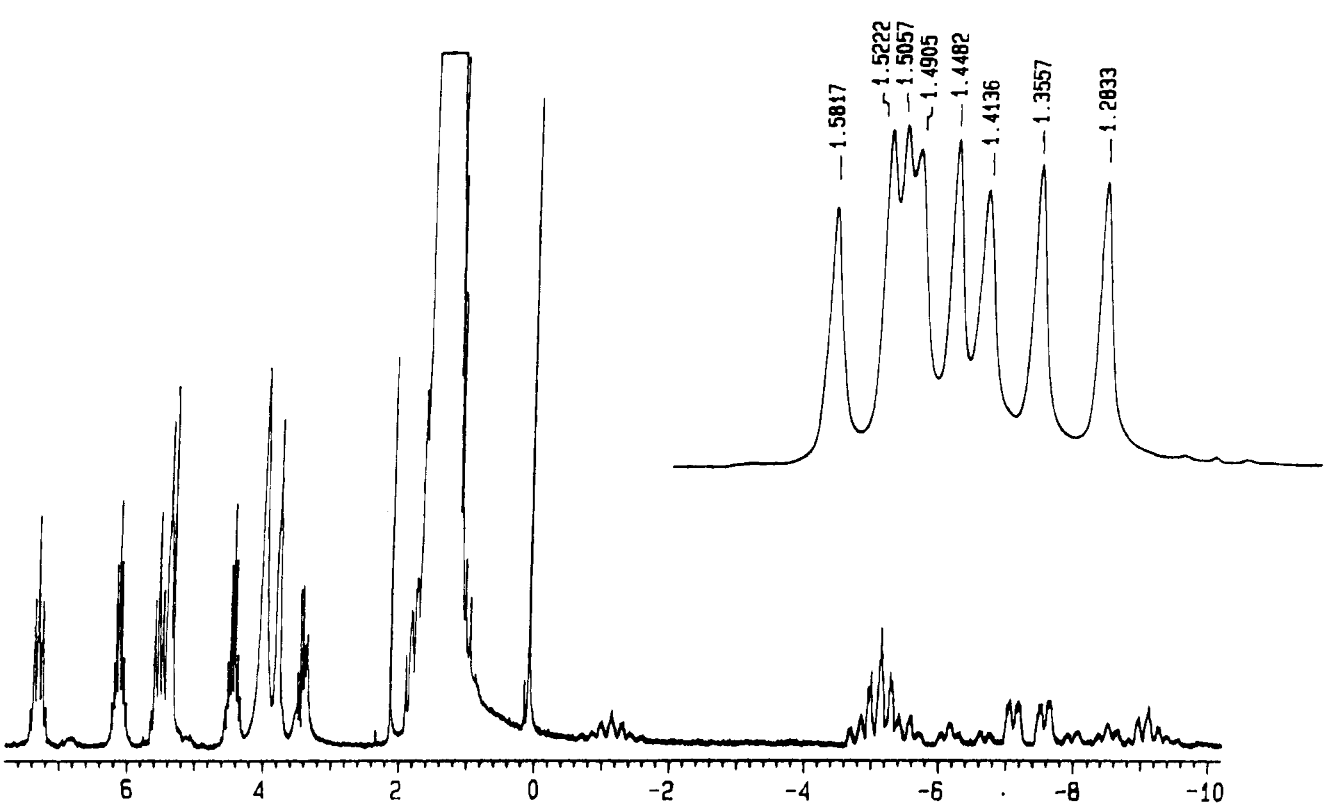

Figure 2. ^1H NMR spectrum of complex **5** (CD_2Cl_2, 298 K; *tert*-butyl region in the inset).

trans (P_4) to the bridging hydride (the corresponding coupling in complex **6** is 96 Hz).

Concluding Remarks. Two new platinum(II) dihydride complexes have been prepared and characterized. The first one, complex **4**, is a neutral, symmetrical derivative bearing a terminal hydride ligand on each metal. Complex **5** is a cationic binuclear complex with a terminal and a bridging hydride and contains two platinum atoms in a different coordinative environment. Both compounds were isolated in good yields and purity, which will permit their utilization as precursors of new platinum compounds. In this respect, the presence of bridging phosphido ligands, which should preserve the dinuclear structure in a broad range of experimental conditions, could be of particular value. The structures of the complexes make them interesting substrates for the study of reactions of insertion of unsaturated ligands in the Pt−H bonds. The dissociation of a phosphine molecule through chemical or photochemical reactions and/or the removal of one of the hydride ligands could give access to useful unsaturated Pt derivatives, while the removal from each complex of both hydrides as molecular hydrogen would produce new Pt(I) binuclear derivatives. Finally, catalytic applications of the complexes are worth investigating, considering that platinum hydrides were found to be active catalysts in reactions of alkene hydrogenation,[15] isomerization,[16] hydroformylation,[17] and (also of dienes and alkynes) hydrosilylation[3,18] and of decomposition of formic acid to hydrogen and carbon dioxide.[1a,2d,19]

Experimental Section

General Data. All manipulation were carried out under a nitrogen atmosphere using standard Schlenck techniques. $CpPt(\eta^3\text{-}C_3H_5)$ was prepared as previously described.[10] Solvents were dried by conventional procedures and distilled prior to use. IR spectra (Nujol mull, KBr plates) were recorded on a Perkin-Elmer FT-IR 1725X spectometer. Proton and phosphorus NMR spectra were recorded at 199.975 and 80.95 MHz, respectively, on a Varian Gemini 200 BB spectrometer; chemical shifts are referred to Me_4Si (^1H) or 85% H_3PO_4 (^{31}P, with downfield shifts as positive).

Preparation of $[Pt(\mu\text{-}PBu^t_2)(H)(PBu^t_2H)]_2$ (4). PBu^t_2H (0.45 mL, 2.28 mmol) was added to a solution of $CpPt(\eta^3\text{-}C_3H_5)$ (320 mg, 1.06 mmol) in toluene (20 mL). The yellow solution was heated 5 h at 70 °C, and the pale yellow solid which precipitated was filtered off, washed with small portions of pentane, and vacuum-dried (310 mg, 60% yield). Anal. Calcd for $C_{32}H_{76}P_4Pt_2$: C, 39.4; H, 7.86. Found: C, 38.9; H, 7.74.

Preparation of $[Pt_2(\mu\text{-}PBu^t_2)(\mu\text{-}H)(H)(PBu^t_2H)_3](CF_3SO_3)$ (5). CF_3SO_3H (0.115 mL, 1.3 mmol) was added to a suspension of complex **4** (421 mg, 0.432 mmol) in DME (30 mL). The suspension was heated at 60 °C with progressive dissolution of the solid. The solvent was evaporated from the yellow clear solution obtained after 1 h, and the residue was taken up with Et_2O (20 mL). The suspension was kept overnight at −30 °C, and the yellow microcrystalline solid was filtered off and vacuum-dried (393 mg, 81% yield). Anal. Calcd for $C_{33}H_{77}F_3O_3P_4Pt_2S$: C, 35.2; H, 6.90. Found: C, 35.0; H, 7.05.

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(15) (a) Bailar, J. C.; Itatani, H. *J. Am. Chem. Soc.* **1967**, *89*, 1592−1599. (b) Clark, H. C.; Billard, C.; Wong, C. S. *J. Organomet. Chem.* **1979**, *173*, 341−347.

(16) (a) Eaborn, C.; Farrel, N.; Pidcock, A. *J. Chem. Soc., Chem. Commun.* **1973**, 766−767. (b) Clark, H. C.; Kurosawa, H. *Inorg. Chem.* **1973**, *12*, 1566−1570. (c) Mc Munn, D.; Moyes, R. B.; Wells, P. B. *J. Catal.* **1978**, *52*, 472. (d) Kanai, H.; Hirako, O. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 953−954.

(17) (a) Paumard, E.; Mortreux, A.; Petit, F. *J. Chem. Soc., Chem. Commun.* **1989**, 1380−1383. (b) van Leeuwen, P. W. N. M.; Roobeck, C. F.; Wife, R. L.; Frijns, J. H. G. *J. Chem. Soc., Chem. Commun.* **1986**, 31−33. (c) Hsu, C. Y.; Orchin, M. *J. Am. Chem. Soc.* **1975**, *97*, 3553.

(18) (a) Tsipsis, C. A. *J. Organomet. Chem.* **1980**, *187*, 427−446. (b) Tsipsis, C. A. *J. Organomet. Chem.* **1980**, *188*, 53−61. (c) Green, M.; Spencer, J. L.; Stone, F. G. A.; Tsipsis, C. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1519−1525, 1525−1529.

(19) Yoshida, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3941−3942.