

Inorganica Chimica Acta 259 (1997) 305-316



## Synthetic, structural and inelastic neutron scattering studies of the hydridobridged cationic complexes $[(PMe_3)_2(Y)Pt(\mu-H)Pt(Y)(PMe_3)_2]^+$ $(Y = Ph, C_6F_5, C_6Cl_5)$ and of $[(PEt_3)_2(H)Pt(\mu-H)Pt(Ph)(PEt_3)_2]^+$

Alberto Albinati<sup>a</sup>, Stanislav Chaloupka<sup>b</sup>, Jürgen Eckert<sup>c</sup>, Luigi M. Venanzi<sup>b,\*</sup>, Martin K. Wolfer<sup>b</sup>

> \* Istiuto di Chimica Farmaceutica, Università di Milano, I-20131 Milan, Italy b Laboratorium für Anorganische Chemie, ETH-Z, CH-8092 Zurich, Switzerland c LANSCE, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

> Received 25 October 1996; revised 23 December 1996; accepted 22 January 1997

#### Abstract

The mono-hydrido-bridged diplatinum complexes  $[(PMe_3)_2(C_6X_5)Pt(\mu-H)Pt(C_6X_5)(PMe_3)_2](CF_3SO_3)$  (X = H, F, C]) were prepared from the corresponding mononuclear species trans- $[PHt(C_6X_5)(PMe_3)_2]$  and trans- $[P(X_CX_5)(S)(PMe_3)_2](CF_3SO_3)$  (X = H, F, C]) were prepared from the corresponding mononuclear species trans- $[PHt(C_6X_5)(PMe_3)_2]$  and trans- $[P(X_CX_5)(S)(PMe_3)_2](CF_3SO_3)$  (X = wakly coordinating solvent). The X-ray crystal structures of  $[(PMe_3)_2(Pht(\mu-H)Ph(\mu)PMe_3)_2]$  [BPha\_1, prepared from the corresponding triflate (space group  $P\overline{1}$ , a = 13.731(5), b = 16.192(2), c = 23.425(8) Å, a = 96.46(2),  $\beta = 100.54(3)$ ,  $\gamma = 95.05(2)^\circ$ , Z = 4, R = 0.043,  $R_{=} = 0.056$  for 6914 observed reflections) and of  $[(PMe_3)_2(C_6Y_5)Pt(\mu-H)Pt(C_6Y_5)(PMe_3)_2](CF_3SO_3) \cdot CH_2Cl_2$  (space group  $P\overline{2}_1/n$ , a = 11.762(2), b = 19.500(3), c = 19.112(3),  $\beta = 105.64(1)$ , Z = 4, R = 0.038,  $R_{=} = 0.049$  for 2528 observed reflections) were determined. Both cations contain the two planar [Pt(C\_6X\_5)(PMe\_3)\_2] (CF\_5XO\_3) + 0.049 for 2528 observed to 3.064(17) and 3.0969(9) Å for X = H and 3.009(1) Å for X = F. Inelastic incoherent neutron scattering studies were carried out on  $[(PMe_3)_2(CF_5SO_5), and (PF(5_3)_2((PF_5)C_5)_2)] (CF_5SO_5), and (PE(5_3)_2(Ph)P((\mu-H)Pt(Ph)(PE(5_3)_2)] (CF_5SO_5), and (PE(5_3)_2(Ph)P((\mu-H)Pt(Ph)(PE(5_3)_2)] (CF_5SO_5), and proximate values of the Pt-H-Pt bord angles in compounds of this type.$ 

Keywords: Diplatinum complexes; Mono-hydrido-bridged compounds; Phosphine complexes; Crystal structures; Inelastic incoherent neutron scattering spectroscopy

#### 1. Introduction

Hydrido-bridged dimetallic complexes have been very actively investigated in recent years [1]. One of the most interesting aspects of these studies has been the search for a relationship between molecular arc.'utecture and bonding within the M-H<sub>x</sub>-M' fragments [2].

While many sets of dimetallic compounds containing up to four bridging hydrides have been described [3], monohydrido-bridged species have received particular attention as recent developments have made their syntheses more controllable [1a] and their theoretical modeling simpler [4]. Furthermore, some of the structural features of compounds of this type [5] show that they are worthy of a detailed study as they might provide a basic insight into the nature of the bonding within the M-H-M fragments.

The orbital interactions in these fragments have been qualitatively described in terms of three-center-two-electron bonds and classified on the basis of their M-H-M' bond angles, the latter being used as measures of the extent of the direct M-M' overlap. Furthermore, it has been established by neutron diffraction studies that when the M-M interaction is weak the bridging hydride ligand is placed below the intersect of the vectors defining the M-E, bonds of the donors E in *trans*-positions to H. The converse is true for strong interactions. Schematic representations of (a) 'weak' and (b) 'strong' interactions of the latter type are presented in Scheme 1 [2c].

The M-H-M' fragments in mono-hydrido-bridged complexes can be easily deformed and one well documented case

<sup>\*</sup> Corresponding author. Tel.: 41 1 632 2851; fax: 41 1 632 1090.

<sup>0020-1693/97/\$17.00 © 1997</sup> Elsevier Science S.A. All rights reserved PII S0020-1693 (97) 05509-6



Scheme 1. (a) 'Weak' M-M interaction. (b) 'Strong' M-M interaction.

is that of the set of compounds containing the anions  $[(CO)_{M}(\mu-H)M(CO)_{5}]^{-}$  (M=Cr, Mo, W) [5] where the M-M distances and M-H-M angles are strongly influenced by the nature of the counterions.

It would be interesting to establish how widespread this phenomenon might be, and to relate its extent to the relative contributions of electronic and steric factors on the structures of cations of the type  $[L_m M(\mu-H)M'L'_n]^{z+}$ . For this purpose it is necessary to carry out structural and spectroscopic studies on a related series of compounds for which systematic variations of the ligands L and L' can easily be made.

One class of complexes suitable for this purpose, of the type  $[L_2YPt(\mu-H)PtYL_2]^+$  ( $L=PR_3$  or AsR\_3; Y and Y'=H and/or alkyl and aryl) (1) is shown below. These cations are well known and numerous analogs can be readily prepared by reacting the hydrido complexes *trans*-[PtHYL\_2] (2) with the corresponding solvento cations *trans*-[PtY'(S)L\_2]^- (3) (S=weakly coordinated solvent), as shown in Eq. (1) [1a].



The best known group of compounds of this type is those where L is PEt<sub>3</sub>, e.g. those with Y - Y' = H (4a); Y = H, Y' = Ph (4b); Y = Y' = Ph (4c); Y = H,  $Y' = C_6F_5$  (4d).



X-ray structural studies, carried out on salts containing the cations 4a-c, showed that the Pt-Pt distances span a wide range: 3.028(1) Å for 4a [6a], 3.093(1) Å for 4b [6b], and 3.238(1) Å for 4c [6c].

Interestingly, if  $L = PEt_3$  and both Y and Y' are heavily substituted aryl groups such as mesityl and pentafluoro- or pentachlorophenyl, compounds of type 1 are formed extremely slowly [7]. These observations raise the question whether the stability of cations of type 1 is also significantly affected by the size of the phosphines. Thus, salts of  $PMe_{3-2}$ containing cations [( $PMe_{3}$ )<sub>2</sub> $YPt(\mu-H)PtY(PMe_{3})_2$ ]<sup>-</sup>,  $(Y = Ph, C_6F_5, C_6Cl_5 (6a-c, respectively))$  were prepared and studied.



This paper reports: (i) the preparation and full characterization of the  $CF_3SO_3$  salts of the cations 6a-c;, (ii) the X-ray crystal structures of  $[6a][BPh_a]$  and  $[6b]-(CF_3SO_3) \cdot CH_2Cl_2;$  (iii) inelastic incoherent neutron scattering (IINS) spectroscopic studies of the Pt-H-Pt vibrations in 4b, 4c and 6a.

## 2. Results and discussion

## 2.1. Preparative studies

The compounds  $[(PMe_3)_2YPt(\mu-H)PtY(PMe_3)_2]-(CF_3SO_3)$  (Y =Ph (**6a**); C<sub>6</sub>F<sub>5</sub> (**6b**); C<sub>6</sub>Cl<sub>5</sub> (**5c**)) were prepared by reacting the hydrido complexes *trans*-[PtHY(PMe\_3)\_2] (Y =Ph (**7a**); C<sub>6</sub>F<sub>5</sub> (**7b**); C<sub>6</sub>Cl<sub>5</sub> (**7c**)) (PMe\_3)](CF\_3SO\_3) (Y =Ph, S=THF (**8a**); Y = C<sub>6</sub>F<sub>5</sub>, S = Et<sub>2</sub>O (**8b**); Y = C<sub>6</sub>Cl<sub>5</sub>, S = Et<sub>2</sub>O (**8c**)) (see Eq. (1)). It was found that the rates of formation of compounds **6a**-c are considerably faster that those of the corresponding compounds containing PEt<sub>3</sub> (**4**), showing that the phosphines in these compounds do exert a significant steric effect. It is noteworthy that for Y = C<sub>6</sub>Cl<sub>5</sub>, wen when L = PMe<sub>3</sub>, reaction (1), i.e. that between **7c** and **8c**, was quite slow, being only 90% complete after two days at room temperature.

The IR and NMR spectroscopic data of the new mononuclear and the dinuclear complexes (see Section 5) are typical for compounds of this type and require no comment.

## 2.2. X-ray crystal structures

The crystals of  $[(PMe_3)_2(Ph)Pt(\mu-H)Pt(Ph)(PMe_3)_2]-[BPh_4]$  (**[6a][BPh\_4]**) contain discrete cations and anions separated by normal van der Waals distances. There are two independent molecules in the asymmetric unit. A selection of bond distances and angles for the two cations **A** and **B** is given in Table 1.

#### A. Albinati et al. / Inorganica Chimica Acta 259 (1997) 305-316

Table 1

Compound	ба		<del>ര</del> ം	4c
	Cation A	Cation B		
Pt1-Pt2	3.0641(7)	3.0969(9)	3.009(1)	3.238(1)
Pt1–P1	2.302(4)	2.315(4)	2.309(6)	2.306(6)
Pt1-P2	2.294(4)	2.292(4)	2.298(6)	2.312(6)
Pt2-P3	2.282(4)	2.282(4)	2.301(6)	2.303(7)
Pt2-P4	2.310(4)	2.311(4)	2.325(6)	2.318(7)
Pt1-C1	2.06(3)	2.07(1)	2.04(2)	2.05(2)
Pt2-C7	2.04(1)	2.02(2)	2.02(2)	2.05(2)
Pt1-H	1.79(8)		1.6(1)	
Pt2-H	1.73(7)		1.7(1)	
Pt1-H-Pt2	121(5)		126(9)	
P1-Pt1-P2	170.3(1)	172.4(2)	171.9(2)	167.6(2)
P3-Pt2-P4	170.0(1)	171.6(2)	173.7(2)	165.9(2)
C1-Pt1-Pt2	164.3(3)	165.1(4)	167.4(5)	162.4(6)
C7-Pt2-Pt1	167.7(4)	167.0(5)	168.8(5)	162.9(6)
C1-Pt1-P1	87.6(4)	87.5(4)	88.1(5)	87.3(6)
C1-Pt1-P2	89.3(4)	86.8(4)	89.9(5)	83.3(6)
C7-Pt2-P3	87.3(4)	87.8(5)	89.0(6)	85.5(7)
C7-Pt2-P4	85.1(4)	86.6(4)	84.8(6)	86.4(7)
P1-Pt1-Pt2	88.78(9)	87.9(1)	91.781)	105.6(2)
P2-Pt1-Pt2	96.62(9)	98.8(1)	91.9(2)	85.4(2)
P3-Pt2-Pt1	103.8(1)	102.9(1)	101.9(1)	88.6(2)
P4Pt2Pt1	84.4(1)	83.4(1)	84.4(1)	102.3(2)
Angle between the lines through the atoms (C1,Pt1) and (Pt2,C7)	152.1	152.3	156.8	
Angle between the planes defined by (C1,Pt1,P1,P2) and (C7,Pt2,P3,P4)	83.6(3)	85.8(4)	89.8(3)	

Selected bond lengths (Å) and bond angles (°) for the cations  $[^{PMe_3}_2(Ph)Pt(\mu-H)Pt(Ph)(PMe_3)_2]^+$  (6a).  $[[(PMe_3)_2(C_0F_5)Pt(\mu-H)Pt(C_0F_5)-(PMe_3)_2]^+$  (6b) and  $[(PEt_3)_2(Ph)Pt(\mu-H)Pt(Ph)(PEt_3)_2]^+$  (4c)



Fig. 1. An ORTEP view of the cation 6a(A) in [(PMe<sub>3</sub>)<sub>2</sub>(Ph)Pt(µ-H)Pt(Ph)(PMe<sub>3</sub>)<sub>2</sub>][BPh<sub>4</sub>] ([6a][BPh<sub>4</sub>]).

(iii) the P3-Pt2-P4 angles  $(170.0(1)^{\circ} \text{ and } 171.6(2)^{\circ}, \text{ respectively}).$ 

Different M-M distances in chemically identical molecules, in the same asymmetric unit, in mono-hydrido-bridged dinuclear complexes, have been previously observed, e.g. in  $[(CO)_5W(\mu-H)W(CO)_5]^-$  [8], and  $[(\eta^5C_5H_5)_2HW-(\mu-H)W(Ph)(PEt_5)_2]^+$  [9]. Significantly, also in these species the M-M distances are longer than 3 Å. The different Pt-Pt distances in the **6a** cations indicate that the potential for the deformation of the 'Pt-H-Pt' moiety in this cation is very soft. Thus, as postulated, in the above tungsten complexes [8,9], the different Pt-Pt distances in **6a(A)** and **6a(B)** can be attributed to packing forces. It is also expected that a shorter distance between the {Pt(Ph)(PMe\_3)\_2} fragments

will, in turn, cause shorter contacts between the phosphine ligands across the Pt-H-Pt bridge and, therefore, in a decrease of the P-Pt-P angles, as observed.

The briging hydride ligand in cation **6a(A)** was localized on a difference Fourier map (see Section 5) and refined. A Pt-H-Pt angle of 121(5)° was obtained. As the two C-Pt vectors define at an angle of ~152°, the bridging hydride must be located above the intersection of these two vectors, as unambiguously established by neutron diffraction, e.g. in [(PEt<sub>3</sub>)<sub>2</sub>HPt( $\mu$ -H)Pt(Ph)(PEt<sub>3</sub>)<sub>2</sub>][BPh<sub>4</sub>] [10],  $\beta$ -[(CO)<sub>5</sub>W( $\mu$ -H)W(CO)<sub>4</sub>(NO)] and [P(OMe)<sub>3</sub>](CO)<sub>4</sub>-W( $\mu$ -H)W(CO)<sub>4</sub>(NO)] [11].

The changes in bonding parameters caused by replacing PMe<sub>3</sub> by PEt<sub>3</sub> can be assessed by comparing the data for 6a and 4c; the numerical values for 6a(A) will be used for this purpose. The only significant differences between them are: (i) the Pt-Pt distances which increase from 3.0641(7) Å in 6a(A) to 3.328(1) Å in 4c; (ii) the P1-Pt1-P2 angles which decrease with the increasing size of the phosphine (170.3(1) and 167.6(2)° for 6a(A) and 4c, respectively); (iii) the P3-Pt2-P4 angles which show a similar decrease, i.e. from 170.0(1) to 165.9(2)°. As Tolman's cone angle value for PMe<sub>3</sub> (118°) is significantly smaller than that of PEt<sub>3</sub> (132°), the geometries of the central Pt-H-Pt moieties in these complexes appear to be mainly affected by intramolecular van der Waals contacts and, once again, the most severe interactions are those occurring across the Pt-H-Pt bridges. The bonding within the bridging unit is likely to be significantly stronger in 6a than in 4c as the Pi-Pt distance is ~0.17 Å longer in the latter compound.

The crystals of  $[(PMe_3)_2(C_6F_5)Pt(\mu-H)Pt(C_6F_5)-(PMe_3)_2](CF_3SO_3)$  (**[6b]**(CF\_3SO\_3)), also contain discrete cations and anions separated by normal van der Waals contacts. A selection of bond distances and angles is given in Table 1. An ORTEP view of the cation **6b** is shown in Fig. 2. The structural features of this cation are fully analogous to those of closely related complexes, e.g. **4a**–c and **6a** (see Table 1). Therefore, only differences between these compounds will be discussed.

The major effect of replacing a  $C_6H_5$  by a  $C_6F_5$  group, as deduced by comparing the geometrical features of the cations

**6a** and **6b**, is the change in the Pt-Pt distance which increases from 3.009(1) Å in **6b** to 3.0641(7) Å in **6a(A)** and to 3.0969(9) Å in **6a(B)**.

The similar values of the P-Pt-P bond angles in cations **6a** and **6b** indicate that the replacement of the C<sub>6</sub>H<sub>5</sub> by the C<sub>6</sub>F<sub>5</sub> ligand does not significantly change the size of the [PtY(PMe<sub>5</sub>)<sub>2</sub>] moiety. Thus, the shorter Pt-Pt distance in **6b** must be mainly due to electronic effects. As it is expected that the platinum atoms in **6b** will be less electron-rich than in **6a**, the shorter Pt-Pt distance in the former cation is indicative of stronger interactions within its central Pt-H-Pt unit.

The bridging hydride in **6b**, as found in **6a**, is placed above the intercept of the two C-Pt vectors as the angle they define is ~157° while the Pt-H-Pt angle is 126(9)°. Although obtained from X-ray data, this and the corresponding value for **6a(A)** (121(5)°) are comparable with the Pt-H-Pt angle in [(PEt<sub>3</sub>)<sub>2</sub>(H)Pt( $\mu$ -H)Pt(Ph)(PEt<sub>3</sub>)<sub>2</sub>]<sup>+</sup> (**4b**) (128(2)°), obtained by neutron diffraction (see Table 1) [10]. Thus, the above values found in **6a(A)** and **6b** can be taken as being reliable, at least within their standard deviations.

It can then be concluded that in all the compounds of the type  $[L_2YPt(\mu-H)PtY'L_2]^+$  the hydride ligands are located above the intersection of the two Pt-Y (or Y') vectors.

## 3. Inelastic incoherent neutron scattering spectroscopic (IINS) studies

These studies were carried out on the  $CF_3SO_3^-$  salts of the cations  $[(PBe_3)_2(C_6F_3)Pt(\mu-H)Pt(C_6F_3)(PMe_3)_2]^+$ (**6b**),  $[(PEt_3)_2(H)Pt(\mu-H)Pt(Ph)(PEt_3)_2]^+$  (**4b**) and  $[(PEt_3)_2(Ph)Pt(\mu-H)Pt(Ph)(PEt_3)_2]^+$  (**4c**) in order to obtain additional information about the nature of the Pt-H-Pt interactions.

While the vibrational modes of bridging hydrides can be assigned using optical techniques [12], in general this is rather difficult because of severe line-broadening and interference from other modes. Instead, IINS has the major advantage that the neutron scattering cross section of hydrogen is larger than that of all other atoms and, therefore, the modes involving hydrogen atoms in a molecule dominate the spec-



Fig. 2. An ORTEP view of the cation 6b in [(PMe<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)Pt(µ-H)Pt(C<sub>6</sub>F<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>](CF<sub>3</sub>SO<sub>3</sub>) ([6b](CF<sub>3</sub>SO<sub>3</sub>)).

The vibrational modes of the  $\mu_2$ -bridging hydride may be described [13] in terms of a symmetric ( $\nu_{sym}$ ) and an antisymmetric ( $\nu_{asym}$ ) M-H stretching mode, as well as deformations of the complex, such as  $\delta_{(PMH)}$ , which include some displacement of the bridging hydride. Since the IiNS band intensities are largely governed by the displacements of hydrogen atoms and these, in turn, are smaller for modes of higher frequency, one expects the intensities of the M-H stretching modes to be lower than those of the deformation modes. These qualitative criteria allow a relatively straightforward mode assignment.

The 'sample difference' spectrum of  $[(PMe_3)_2(C_6F_5)-Pt(\mu-H)Pt(C_6F_5)(PMe_{31})_2]^+$  (**6b**) is shown in Fig. 3. The IINS data for **[6b](CF\_3SO\_3)**,  $[(PEt_3)_2(H)Pt(\mu-H)-Pt(Ph)(PMe_{31})_2](CF_3SO_3), [($ **4b](CF\_3SO\_3)** $) and <math>[(PEt_3)_2-(Ph)Pt(\mu-H)Pt(Ph)(PMe_{31})_2](CF_3SO_3), [($ **4c](CF\_3SO\_3)**) are collected in Table 2. These assignments are in good agreement with published data for analogous complexes [13,14].

Howard et al. [14] have shown that, in favorable cases, one can use the ratio  $\nu_{asym}/\nu_{sym}$  to derive structural information on the M-H-M bridge. They showed that if (i) the metal framework can be considered as being rigid and (ii) the angle-bending force constant (in a valence force field) is negligible, one obtains the relationship shown in Eq. (2), where  $\theta$  is the M-H-M bond angle.

$$\nu_{\rm asym}/\nu_{\rm sym} = \tan(\theta/2) \tag{2}$$

They also showed that, if there are weak interactions between the two stretching modes, Eq. (2) should be modified by adding a multiplicative factor, A, to  $\tan(\theta/2)$ . The equation then becomes:





Fig. 3. 'Sample difference' IINS spectrum (12 K) of  $[(PMe_3)_2(C_6F_3)Pt-(\mu-H)Pt(C_6F_5)(PMe_3)_2](CF_3SO_3)$  ([6b](CF\_3SO\_3)).

able 2	
--------	--

Pt-Pt distances (Å), frequencies  $\nu$  (cm<sup>-1</sup>) and Pt-H-Pt angles (\*) in [(PMe<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>F<sub>3</sub>)Pt( $\mu$ -H)Pt(C<sub>6</sub>F<sub>3</sub>)(PMe<sub>3</sub>)<sub>2</sub>]<sup>+</sup> (6b), [(PEt<sub>3</sub>)<sub>2</sub>(H)Pt( $\mu$ -H)-Pt(Ph)(PEt<sub>3</sub>)<sub>2</sub>]<sup>+</sup> (4b) and [(PEt<sub>3</sub>)<sub>2</sub>(Ph)Pt( $\mu$ -H)Pt(Ph)(PEt<sub>3</sub>)<sub>2</sub>]<sup>+</sup> (4c)

Compound	Pt-H-Pt	₽ <sub>asym</sub>	P <sub>sym</sub>	ν <sub>ssym</sub> /ν <sub>sym</sub>	Pt-H-Pt *
6Ъ	3.009(1)	1260	1020	1.24	116
4b	3.093(1)	1280	990	1.29	116
4c	3.238(1)	1415	925	1.53	125 *

\* Values calculated from the IINS data.

<sup>b</sup> Value from X-ray diffraction: 126(9)°.

As the value of  $\theta$  approaches 180°, i.e. for a nearly linear M–H–M fragment, the coupling with angle-bending forces becomes important and the above relation no longer holds.

One can test whether the correlation of Howard et al. can be used for the present class of compounds as the value of the  $\theta$  angle in the cation [(PEt<sub>3</sub>)<sub>2</sub>(H)Pt( $\mu$ -H)Pt(Ph)-(PEt<sub>3</sub>)<sub>2</sub>]<sup>+</sup> (4b) is know from neutron diffraction studies and the ratio  $v_{asym}/v_{sym}$  was obtained in this study (see Table 2). Thus, one can add a new point to the plot constructed using the data of Howard et al. [14], for the regime where interactions between different modes cannot be neglected, i.e, Eq. (3). As can be seen in Fig. 4, the new point falls close to the line giving the best fit for the other compounds. Therefore, the above IINS spectroscopic data were used to obtain approximate M-H-M angles in compounds for which structural data are not available, i.e. for  $[(PEt_3)_2(C_6H_5)Pt(\mu-H)Pt(C_6H_5)(PEt_3)_2]^+$  (4c) and  $[(PMe_3)_2(C_6F_5)Pt(\mu-H)(C_6F_5)(PMe_3)_2]^+$  (6b) (see Table 2). The 'spectroscopic' Pt-H-Pt angles thus obtained



Fig. 4. A plot of  $\nu_{m,m} \nu_{sym}$ , st. tan( $\theta/2$ ) (see text); solid circles represent the following compounds (see Ref. [15]):  $1 = [Os_{3}(H_{2}(OO)_{10}]; 2 = [Os_{3}(H_{2}(OO)_{10}(CH:CH_{2})]; 3 = [Os_{3}(H_{2}(OO)_{10}(CH:CH_{2})]; 1 = [Os_{3}(H_{2}(OO)_{10}(CH:CH_{2})]; 3 = [Os_{3}(H_{2}(OO)_{10}(CH:CH_{2})]; 3 = [Os_{3}(H_{2}(OO)_{10}(CH:CH_{2})]; 3 = [Os_{3}(H_{2}(OO)_{10}(CH:CH_{2})]; (CF_{3}SO_{3}); 5 = [Ph_{3}(W_{2}(H_{2}(H_{1}(OO)_{10})(CH_{3}(OO)_{2})]; (CF_{3}SO_{3}); 5 = [Ph_{3}(W_{2}(H_{2}(H_{1}(OO)_{10})(CH_{3}(OO)_{2})]; (CF_{3}SO_{3}); 7 = [Ms_{3}(H_{3}(OO)_{12}]; 8 = [NE_{4}][W_{2} - (\mu+H_{1}(OO)_{10})]. Open squares are drawn on the straight line using the <math>\nu_{m,m}/\nu_{p_{m}}$  studes for cations et and 6 et and 6b.

were then compared with the values obtained from the X-ray diffraction studies. The ratio  $v_{ayym}/v_{sym}$  for **6b** and the correlation of Fig. 4 gave a Pt-H-Pt angle of ~116° in this compound, a value which is in acceptable agreement with that of 126(9)° found by X-ray diffraction in this cation. On the same basis, one obtained a value of ~126° for the Pt-H-Pt angle in [(PEt<sub>3</sub>)<sub>2</sub>(Ph)Pt( $\mu$ +H)Pt(Ph)(PEt<sub>3</sub>)<sub>2</sub>]<sup>+</sup> (**4c**). These results show that the coupling between stretching and bending modes is important also in the series of monohydrido-bridged complexes described here.

## 4. Conclusions

These results, taken in conjunction with other published data, allow the definition of the following limiting situations for the M-H-M angles in dinuclear mono-hydrido-bridged complexes:

(i) they are larger than  $120^{\circ}$  in compounds with very long M-M distances, > 3.2 Å, as in 4c;

(ii) they are close to 115° for M-M distances around 3.0 Å, as in **6b** and **4c**;

(iii) they are ~105°, or even smaller when the M-M distances are quite short, i.e. 2.8 Å, as in  $[(PEt_3)_2(H)Pt-(\mu-H)Pt(Ph)(PEt_3)_2]^+$  (4b).

As it can be presumed that smaller Pt–H–Pt angles are associated with stronger direct Pt–Pt overlap, the data presented above are indicative that this interaction is strengthened by a decrease in electron density at the metal atom of the  $\{PtYL_{2}\}$  moiety.

## 5. Experimental

#### 5.1. Equipment

C, H and P microanalyses were performed by the Microanalytical Laboratory of the Swiss Federal Institute of Technology in Zurich. The IR spectra were recorded in KBr pellets or Nujol mulls on Perkin-Eimer model 883 or 1430 spectrophotometers. The NMR spectra were recorded as follows: <sup>1</sup>H at 250.13 and 500.13 MHz, <sup>13</sup>C at 62.9 and 125.7 MHz, <sup>31</sup>P at 101.15 and 202.5 MHz, <sup>159</sup>Pi at 53.7 and 107.5 MHz, on Bruker WM-250 and AMX-500 instruments. They are referenced as follows: external Me<sub>4</sub>Si for <sup>1</sup>H and <sup>13</sup>C; external 85% H<sub>2</sub>PO<sub>4</sub> for <sup>31</sup>P; external Na<sub>2</sub>[PICl<sub>6</sub>] for <sup>195</sup>Pt.

## 5.2. Materials

The compounds PMe<sub>3</sub>, C<sub>6</sub>H<sub>3</sub>Br, C<sub>6</sub>F<sub>5</sub>Br and C<sub>6</sub>Cl<sub>5</sub>Br were obtained from Fluka AG and used without further purification, while the required platinum salts were purchased from Johnson Matthey & Brandenberg AG. The complex *cis*-[PtCl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>] was prepared as described by Evans et al. [15], while [Pt(PMe<sub>3</sub>)<sub>4</sub>] [16]a was obtained as reported by Wolfer [16b].

### 5.3. Syntheses

Unless otherwise stated these were carried out under an stmosphere of dry, oxygen-free nitrogen or argon. The solvents were used as received from Fluka AG but deoxygenated by bubbling inert gas through the solution for 10 min before use.

#### 5.3.1. Trans-[PtCl(Ph)(PMe3)2]

A solution of 'PhMgBr', prepared from PhBr (0.50 g, 3.11 mmol) and magnesium turnings (0.080 g, 3.29 mmol) in THF (5 ml) was added dropwise to a stirred suspension of cis-[PtCl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>] (1.30 g, 3.11 mmol) in THF (5 ml). The mixture was stirred overnight, hydrolyzed with water (10 ml), and repeatedly extracted with CH2Cl2. Evaporation of the organic solvent left 1.19 g of residue. This consisted of a mixture of approximately equal amounts of trans- $[PtCl(Ph)(PMe_3)_2]$  and trans- $[PtBr(Ph)(PMe_3)_2]$ . A small amount of trans-[PtCl(Ph)(PMe<sub>3</sub>)<sub>2</sub>] was obtained by reacting an acetone solution of pure trans-[PtBr(Ph)-(PMe<sub>3</sub>)<sub>2</sub>] (see below) with an equivalent amount of AgNO<sub>3</sub>, filtering off the AgBr precipitate and adding LiCl to the solution. After filtration and evaporation of the solvent, the residue was recrystallized from CH2Cl2/MeOH. Decomp. 197°C. Anal. Calc. for C12H23ClP2Pt: C, 31.35; H, 5.04; P, 13.47. Found: C, 31.20; H, 4.40; P, 13.20%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ=7.50-6.81 (5H, aromatic), 1.25 (18H, CH<sub>3</sub>,  $|^{2}J(P,H) + {}^{4}J(P,H)| = 7.5, {}^{3}J(Pt,H) = 30.1 \text{ Hz}.$ NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = -13.78$  (<sup>1</sup>J(Pt,P) = 2751 Hz).

#### 5.3.2. Trans-[PtBr(Ph)(PMe3)2]

The above mixture (1.10 g) in CH<sub>2</sub>Cl<sub>2</sub>/EtOH (1:1, 5 ml) to which AgNO<sub>3</sub> (0.44 g, 2.60 mmol) had been added, was stirred for 3 h at r.t., and filtered through Celite. The solution was evaporated to dryness under reduced pressure, the residue dissolved in acetone (10 ml), the solution treated with KBr (0.50 g, 4.20 mmol), stirred for 3 h, and the solvent evaporated to dryness under reduced pressure. The product, after extraction with CH<sub>2</sub>Cl<sub>2</sub>/MeOH. Yield: 1.15 g, 96%. Decomp. 205°C. *Anal.* Calc. for C<sub>12</sub>H<sub>23</sub>BrP<sub>2</sub>Pt: C, 28.58; H, 4.60; P, 12.28. Found: C, 28.32; H, 4.39; P, 12.01%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 7.49-6.82$  (5H, aromatic), 1.28 (18H, CH<sub>3</sub>, <sup>1</sup>J/(P,H) + <sup>4</sup>J(P,H)| = 7.5, <sup>3</sup>J(Pt,H) = 30.8 Hz). <sup>31</sup>P(<sup>1</sup>H) NMR (CDC):  $\delta = -16.02$  (<sup>1</sup>J(Pt,P) = 2721 Hz).

## 5.3.3. Trans-[PtBr( $C_6F_5$ )(PMe<sub>3</sub>)<sub>2</sub>]

Neat  $C_6F_8Br$  (2.00 g, 8.1 mmol) was added dropwise to a stirred solution of [Pt(PMe<sub>3</sub>)<sub>4</sub>] (3.07 g, 6.15 mmol) in E<sub>2</sub>O (20 ml) which had been precooled to  $-80^{\circ}C$ . A white precipitate formed immediately. The mixture was allowed to warm up to room temperature, and after stirring for a further 1 h, the liquid phase was completely evaporated under reduced pressure. The residue was extracted with Et O and, after evaporation of the solvent, the crude product was recrystallized from Et<sub>2</sub>O. Yield: 3.0 g, 85%. Decomp. 199°C. Anal. Calc. for  $C_{12}H_{18}Brf_{5}P_{2}Pt$ : C, 24.26; H, 3.05; Br, 13.45. Found: C, 24.72; H, 3.12; Br, 14.13%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 1.37$  (18H, CH<sub>3</sub>, |<sup>2</sup>/(P,H) + <sup>4</sup>/(P,H)| = 7.4, <sup>3</sup>/(Pt,H) = 27.9 Hz). <sup>31</sup>P(<sup>1</sup>H) NMR (CDCl<sub>3</sub>):  $\delta = -18.30$  (<sup>1</sup>/(Pt,P) = 2388 Hz). <sup>195</sup>P(<sup>1</sup>H) NMR (CDCl<sub>3</sub>):  $\delta = -4549$  (<sup>1</sup>/(Pt,P) = 2388, <sup>3</sup>/(Pt,F) = 405.0, <sup>4</sup>/(Pt,F) = 101.4, <sup>5</sup>/(Pt,F) = 20.5 Hz).

## 5.3.4. Trans-[PtBr(C6Cl5)(PMe3)2]

A solution of C<sub>6</sub>Cl<sub>5</sub>MgBr, prepared from C<sub>6</sub>Cl<sub>6</sub>Br (0.20 g, 0.61 mmol) and Mg turnings (0.061 g. 0.66 mmcl) in THF (5 ml), was added dropwise to a stirred suspension of cis-[PtCl<sub>2</sub>(PMc<sub>3</sub>)<sub>2</sub>] (0.24 g, 0.58 mmol) in THF (3 mi). Stirring was continued overnight and the mixture was hydrolyzed by addition of water (10 ml). The product was extracted using several aliquots of CH<sub>2</sub>Cl<sub>2</sub>, these extracts were evaporated under reduced pressure and the residue dissolved in CH<sub>2</sub>Cl<sub>2</sub>/EtOH (1:1, 10 ml), Solid AgNO<sub>3</sub> (0.12 g. 0.68 mmol) was then added to this solution and the suspension stirred for 4 h. The silver halide precipitate was filtered off over Celite and the solution evaporated to dryness under reduced pressure. The residue was dissolved in acetone. KBr (0.12 g, 1.00 mmol) was added and the solution, after stirring for 5 h, was evaporated to dryness under reduced pressure. The crude product was dissolved in CH-Cl-, the solution filtered over Celite and evanorated to dryness under reduced pressure. The pure product was obtained by recrystallization from CH2Cl2/MeOH. Yield: 0.25 g, 63%. Decomp. 205°C. Anal. Calc. for C12H10BrCl6P2Pt; C. 21.30; H, 2.680; P, 9.16. Found: C, 21.12; H, 2.41; P, 9.02%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 1.38 (18H, CH<sub>3</sub>,  $|^{2}J(P,H) + {}^{4}J(P,H)|$ =7.6 Hz).  ${}^{31}P{}^{1}H$  NMR (acetone-d<sup>6</sup>):  $\delta = -19.34$  $(^{1}J(Pt.P) = 2549 \text{ Hz}).$ 

#### 5.3.5. Trans-[PtH(Ph)(PMe3)2] (2a)

A suspension of *trans*-[PtBr(Ph) (PMe<sub>3</sub>)<sub>2</sub>] (0.70 g, 1.39 mmol), in EtOH/H<sub>2</sub>O (5:1, 10 ml), at 0°C, was treated with solid Na[BH<sub>4</sub>] (0.25 g, 6.6 mmol) and stirred for 3 h at r.t. Water (10 ml) was then added and the resulting solid filtered off. It was recrystallized from acctetone/MeOH. Yield: 0.52 g, 88%. Decomp. 105°C. *Anal.* Calc. for C<sub>12</sub>H<sub>24</sub>P<sub>2</sub>Pt: C, 33.85; H, 5.69; P, 14.56. Found: C, 33.55; H, 5.52; P, 14.30%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 7.46–6.79 (5H, aromatic), 1.41 (18H, CH<sub>3</sub>, <sup>1</sup>Z<sup>1</sup>/(P,H) + <sup>4</sup>J(P,H) = 6.9, <sup>3</sup>J(P,H) = 3.4 Hz), -6.20 (hydride, <sup>1</sup>J(Pt,H) = 683 Hz, <sup>2</sup>J(P,H) = 19.8 Hz). <sup>31</sup>P(<sup>1</sup>H; NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = -21.05 (s+d, <sup>1</sup>J(Pt,P) = 2710 Hz). IR (CDCl<sub>3</sub>):  $\nu$  (Pt-H) 1917 (m) cm<sup>-1</sup>.

#### 5.3.6. Trans-[PtH(C6F5)(PMe3)2] (2b)

To a stirred suspension of trans-[PtBr( $C_6F_3$ )(PMe<sub>3</sub>)<sub>2</sub>] (1.81 g, 3.05 mmol) in EtOH/H<sub>2</sub>O (5:1, 20 ml), precooled to  $0^{\circ}C_1$ , solid Na[BH<sub>4</sub>] (0.50 g, 13 mmol) was added. Stirring was continued for 1 h after the gas evolution had stopped. Water was then added to precipitate the product. This was filtered off, extracted with CH<sub>2</sub>Cl<sub>2</sub> and the organic solvent evaporated to dryness under reduced pressure. The pure product was obtained by recrystallization from acetone. Yield: 1.35 g, 86%. Decomp. 150°C. Anal. Calc. for C<sub>12</sub>H<sub>19</sub>F<sub>2</sub>P<sub>2</sub>Pt: C, 27.97; H, 3.72. Found: C, 28.11; H, 3.59%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 1.47 (18H, CH<sub>3</sub>, 1<sup>2</sup>J(P,H) + <sup>4</sup>J(P,H) | = 7.0, <sup>3</sup>J(Pt,P) = 33.8 Hz), -7.20 (hydride, <sup>1</sup>J(Pt,H) = 833, <sup>2</sup>J(P,H) = 18.9, <sup>4</sup>J(F,H) = 14.0, <sup>5</sup>J(F,H) = 14.0 Hz). <sup>31</sup>P[<sup>1</sup>H) NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = -19.92 (<sup>1</sup>J(Pt,P) = 2558 Hz). <sup>19</sup>Pt(<sup>1</sup>H) NMR:  $\delta$  = -4524. IR (CHCl<sub>3</sub>):  $\nu$  (Pt-H) 2000 (m) cm<sup>-1</sup>.

### 5.3.7. Trans-[PtH(C6Cl5)(PMe3)2] (2c)

A solution of [Pt(PMe<sub>1</sub>)<sub>4</sub>] (0.88 g, 1.77 mmol) in THF (5 ml) was added dropwise to a suspension of C.Cl.Br (0.72 g. 2.19 mmol) in THF (8 ml) which had been pre-cooled to - 80°C. Another solid formed immediately. The mixture was allowed to warm up to room temperature and stirring was continued for 5 h. The solid intermediate, which proved to be  $[Pt(C_6Cl_3)(PMe_3)_3]Br^1$ , was filtered off and extracted with MeOH (~5 ml) to remove unreacted C<sub>s</sub>Cl<sub>s</sub>Br. The above intermediate was precipitated by addition of Et<sub>2</sub>O. filtered off and used directly for the next stage. It was dissolved in EtOH/H<sub>2</sub>O (10:1, 10 ml), the solution cooled to 0°C, and treated with solid Na[BH\_] (0.50 mg, 13 mmol). The resulting suspension was stirred for 5 h, the solid filtered off and recrystallized from acetone. Yield: 0.41 g. 58%. Decomp. 210°C. Anal. Calc. for C12H19Cl5P2Pt: C, 24.12; H, 3.20. Found: C. 24.26; H. 3.12%. H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 1.46$  (18H, CH<sub>3</sub>,  $|^{2}J(P,H) + {}^{4}J(P,H)| = 7.2$ ,  ${}^{3}J(Pt,H)$ = 33.9 Hz), -9.04 (<sup>1</sup>J(Pt,H) = 776 Hz, <sup>2</sup>J(P,H) = 19.7 Hz).  ${}^{31}P{}^{1}H{}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = -22.74$  $({}^{1}J(Pt,P) = 2653 \text{ Hz})$ . IR (CHCl<sub>3</sub>):  $\nu(Pt-H)$  2010 (m) cm<sup>-1</sup>.

## 5.3.8. $[(PMe_3)_2(Ph)Pt(\mu-H)Pt(Ph)(PMe_3)_2](CF_3SO_3)$ ([6a](CF\_3SO\_3))

A solution of *trans*-[Pt(Ph) (THF) (PMe<sub>3</sub>)<sub>2</sub>] (CF<sub>3</sub>SO<sub>3</sub>) was prepared in situ by reacting *trans*-[PtBr(Ph)(PMe<sub>3</sub>)<sub>2</sub>] (0.101 mg, 0.20 mmol), dissolved in THF (5 ml), with AgCF<sub>3</sub>SO<sub>3</sub> (52 mg, 0.20 mmol). The mixture was stirred, at room temperature, in the absence of light, for 4 h and then filtered through Celite. The resulting solution was added dropwise to a solution of *trans*-[PtH(Ph)(PMe<sub>3</sub>)<sub>2</sub>] (85 mg, 0.20 mmol) in THF (3 ml). A white precipitate formed over 4 h. This was filtered off and recrystallized from acetone<sup>4</sup> pentane. Yield: 148 mg, 74%. Decomp. 155°C. Anal. Caic. for C<sub>23</sub>H<sub>47</sub>F<sub>3</sub>O<sub>3</sub>P<sub>4</sub>SPt<sub>2</sub>: C, 30.06; H, 4.74; P, 12.40. Found: C, 30.09; H, 4.93; P 12.29%. <sup>1</sup>H NMR (acetone-d<sup>5</sup>):  $\delta$ = 7.50–7.05 (SH, aromatic), 1.53 (36H, CH<sub>3</sub>, [<sup>2</sup>/(P,H)] +<sup>4</sup>/(P,H)] = 7.2 Hz, <sup>3</sup>/(Pt,H) = 31.3 Hz), -11.486

<sup>&</sup>lt;sup>1</sup> This compound is characterized by the following NMR parameters:  $\delta^{31}P(trans \text{ to } C) = -26.4 ({}^{1}J({}^{195}Pt,{}^{31}P) = 2395 \text{ Hz}; \delta^{-31}P(trans \text{ to } P)$  $= -33.3 ({}^{1}J({}^{195}Pt,{}^{31}P) = 2098 \text{ Hz} [17].$ 

 ${}^{1}J(Pt,H) = 453 \text{ Hz}, {}^{2}J(P,H) = 10.7 \text{ Hz}). {}^{31}P{}^{1}H} \text{ NMR}$ (acetone-d<sup>6</sup>):  $\delta = -19.97 \text{ (m, hydride, } {}^{1}J(Pt,P) = 2595 \text{ Hz}, {}^{3}J(Pt,P) = 21.0 \text{ Hz}). {}^{195}Pt{}^{1}H} \text{ NMR}: \delta = -4673 (}^{1+2}(Pt,Pt) = 220 \text{ Hz}).$ 

## 5.3.9. $[(PMe_3)_2(Ph)Pt(\mu-H)Pt(Ph)(PMe_3)_2][BPh_4]$ ([6a][BPh\_4])

This salt was prepared by adding a stoichiometric amount of Na[BPh<sub>4</sub>], in EtOH, to a CH<sub>2</sub>Cl<sub>2</sub> solution of [6a]-(CF<sub>3</sub>SO<sub>3</sub>). The mixture was stirred for 2 h, the solvent evaporated under reduced pressure and the residue extracted with CH<sub>2</sub>Cl<sub>2</sub>. Crystals suitable for X-ray diffraction were obtained by placing a layer of EtOH over the filtered extract and leaving the vessel at room temperature.

## 5.3.10. $[(PMe_3)_2(C_6F_5)Pt(\mu-H)Pt(C_6F_5)(PMe_3)_2](CF_3SO_3)$ ([6b](CF\_3SO\_3))

A solution of trans-[PtBr(C<sub>6</sub>F<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>] (91.8 mg, 0.154 mmol) in anhydrous Et<sub>2</sub>O (5 ml) was treated with AgCF<sub>3</sub>SO<sub>3</sub> (39.7 mg, 0.154 mmol) and stirred for 1 h in the absence of light. The AgBr precipitate was filtered off over Celite and the resulting solution added to trans-[PtH(C<sub>6</sub>F<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>] (79.6 mg, 0.154 mMol) in anhydrous Et<sub>2</sub>O (~5 ml). A fine, white precipitate formed over several hours. The solvent was evaporated to ~5 ml under reduced pressure and the suspension stirred overnight. The solvent was then evaporated under reduced pressure and the residue extracted with a small amount of CH2Cl2. The pure product was obtained from the filtrate by placing a layer of pentane over the CH<sub>2</sub>Cl<sub>2</sub> solution and leaving the mixture overnight in a refrigerator, Yield: 125 mg, 69%. Decomp. 165°C. Anal. Calc. for C25H37F13O3P4Pt2S: C, 30.06; H, 4.74; P, 12.40. Found: C, 30.09; H, 4.93; P, 12.29%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 1.60$  (36H, CH<sub>3</sub>,  $|^{2}J(P,H) + {}^{4}J(P,H)| = 7.2$  Hz,  ${}^{3}J(Pt,H) = 28.8$ , -11.60 (hydride,  ${}^{1}J(Pt,H) = 512$  Hz,  $^{2}J(P,H) = 22.3 \text{ Hz}, \,^{4}J(F,H) = 4.9 \text{ Hz}, \,^{5}J(F,H) = 1.4 \text{ Hz}).$ <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = -21.9$  (<sup>1</sup>J(Pt,P) = 2257 Hz,  ${}^{3}J(Pt,P) = 37 \text{ Hz}, {}^{1+2}J(Pt,Pt) = 870 \text{ Hz}?). {}^{195}Pt{}^{1}H} \text{ NMR}$  $(CD_2Cl_2): \delta = -4758 ({}^{3}J((Pt,F) = 326 \text{ Hz}, {}^{4}J(Pt,F^m) =$ 80 Hz).

Crystals suitable for X-ray diffraction of this compound were obtained using the recrystallization procedure described above.

## 5.3.11. $[(PMe_3)_2(C_6Cl_5)Pt(\mu-H)Pt(C_6Cl_5)(PMe_3)_2] - (CF_3SO_3) ([6c](CF_3SO_3))$

A suspension of *trans*-[PtBr( $C_6Cl_5$ )(PMe\_3)<sub>2</sub>] (84.2 mg, 0.124 mmol) and AgCF<sub>3</sub>SO<sub>3</sub> (32.0 mg, 0.124 mmol) in anhydrous Et<sub>2</sub>O (5 ml) was stirred for 3 h under exclusion of light. The AgBr precipitate was filtered off over Celite and the solution added to another of *trans*-[PtH( $C_6Cl_5$ )-(PMe<sub>3</sub>)<sub>2</sub>] (74.4 mg, 0.124 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml). The volume of the resulting solution was reduced to ~3 ml under reduced pressure and placed in a 10 mm NMR tube. The course of the reaction was monitored by <sup>31</sup>P NMR. Although after two weeks the reaction was only 90% complete, the solution was evaporated to dryness under reduced pressure, the residue dissolved in the minimum amount of CH<sub>2</sub>Cl<sub>2</sub>, the solution filtered over Celite and a layer of pentane placed over it. On standing in a refrigerator for several days the product crystallized out. Yield: 97 mg, 58%. Decomp. 180°C. *Anal.* Calc. for C<sub>23</sub>H<sub>27</sub>Cl<sub>13</sub>O<sub>4</sub>P<sub>4</sub>P<sub>5</sub>S: C. 22.35; H. 2.78. Found: C, 23.16; H, 2.94%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 1.80 (36H, CH<sub>3</sub>, 1<sup>2</sup>J(P,H) + <sup>4</sup>J(P,H) |= 1.80 Hz, <sup>3</sup>J(P,H) = 22.8 Hz), -15.76 (hydride, <sup>1</sup>J(Pt,H) = 452.8 Hz, <sup>2</sup>J(P,H) = 10.1 Hz). <sup>31</sup>P[<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = -25.10 (hydride, <sup>1</sup>J(Pt,P) = 260 Hz).

#### 5.4. Crystallography

Crystals of **6a** and **6b**, covered with acrylic resin for protection, were mounted on glass fibers at a random orientation on an Enraf-Nonius CAD4 diffractometer for the unit cell and space group determinations and for the data collection. Unit cell dimensions were obtained by least-squares fit of the  $2\theta$  values of 25 high order reflections using the CAD4 centering routines. Selected crystallographic and other relevant data are listed in Table 3.

Data were measured with variable scan speed to ensure constant statistical precision on the collected intensities. Three standard reflections were used to check the stability of the crystals and of the experimental conditions and measured every hour. The orientations of the crystals were checked by measuring three reflections every 300 measurements. Data were corrected for Lorentz and polarization factors and for decay (compound [6a][DPh\_a]) using the data reduction programs of the MolEN package [18]. Empirical adsorption corrections were applied by using azimuthal ( $\Psi$ ) scans of three 'high- $\chi$ ' angle reflections to both sets of data. The standard deviations on intensities were calculated in terms of statistics alone, while those on  $F_0$  were calculated as shown in Table 3.

The structures were solved by a combination of Patterson and Fourier methods and refined by full-matrix least-squares [18] (the function minimized being  $\sum [w(F_o - 1/kF_o)]^2$ ). No extinction correction was found to be necessary. The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature [19]. All calculations were carried out using the Enraf-Nonius MolEN crystallographic package [18].

#### 5.4.1. Structural study of [6a][BPh\_]

A total of 11 536 data was collected. After averaging, a set of 11 464 independent reflections was obtained, of which 6914 were considered as observed and used for the refinement. Anisotropic displacement parameters were used for the platinum and phosphorus and for the carbon atoms of the phosphines; isotropic temperature factors were used for the remaining atoms. A model in which all the atoms of the cation were refined anisotropically did not produce a significantly

Compound	[6a][BPh4]	[6b](CF <sub>3</sub> SO <sub>3</sub> )·CH <sub>2</sub> Cl <sub>2</sub>	
Formula	C48H67BP4Pt2	$C_{25}H_{39}Cl_2F_{13}O_3P_4Pt_2S$	
Molecular weight	1168.96	1263.62	
Crystal dimensions (mm)	0.30×0.45×0.25	0.25×0.20×0.18	
Data collection T (°C)	23	23	
Crystal system	triclinic	monoclinic	
Space group	PĪ	$P2_1/n$	
a (Å)	13.731(5)	11.762(2)	
b(Å)	16.192(2)	19.500(3)	
c (Å)	23.425(8)	19.112(3)	
α (°)	96.46(2)	90.	
β(°)	100.54(3)	105.64(1)	
γ(°)	95.05(2)	90.	
V (Å <sup>3</sup> )	5056(2)	4221(1)	
Z	4	4	
$\rho$ (calc.) (g cm <sup>-3</sup> )	1.535	1.988	
$\mu$ (cm <sup>-1</sup> )	57.385	70.980	
Radiation, λ (Å)	Mo K $\alpha$ (graphite monochromate	d), 0.71073	
Measured reflections	$\pm h, \pm k, \pm l$	$\pm h, +k, +l$	
θRange (°)	2.5< <del>0</del> <21.2	2.5<θ<21.0	
Scan type	ω/2θ	ω/2θ	
Background time (s)	0.5 × scan-time	0.5 × scan-time	
Max. scan speed (° min <sup>-1</sup> )	21.5	21.5	
Prescan rejection limit	0.60 (1.67 σ)	0.50 (2.00 σ)	
Prescan acceptance limit	0.02 (50.00 σ)	0.03 (33.3 σ)	
No. data collected (total)	11536		
No. data collected (ind.)	11464	4404	
No. observed reflections $(n_0)$	6914	2528	
	$( F_0 ^2 > 4.0\sigma( F ^2))$	$( F_0 ^2 > 2.5\sigma( F ^2))$	
Transmission coefficient	0.9986-0.8313	0.9198-0.8250	
Decay correction	0.9954-1.3695		
No. parameters refined (n.)	595	340	
Fudge factor, f	0.060	0.060	
$\Delta p/\sigma(p)$ (at conv.)	< 0.2	<0.2	
Ray	0.028		
R	0.043	0.038	
R <sub>w</sub>	0.056	0.049	
GOF	1.566	1.300	

Table 3 Experimental data for the X-ray diffraction study of compounds [6a][BPh.] and [6b](CF-SO-)-CH-CI-

 $R_{\rm av} = \sum i |F_{\rm o,av} - F_{\rm o,i}| / \sum i |F_{\rm o,av}|; R = \sum (|F_{\rm o}| - (1/k)|F_{\rm c}|) / \sum |F_{\rm o}|.$ 

$$\begin{split} & \int_{\mathbb{R}^{n}} = [\Sigma w(|F_{0}| - (1/k)|F_{0}|)^{2} \Sigma w|F_{0}|^{2}]^{1/2} where w = [\sigma^{2}(F_{0})]^{-1}; \ \sigma(F_{0}) = [\sigma^{2}(F_{0}^{2}) + f^{4}(F_{0}^{2})]^{1/2} / 2F_{0}. \\ & \text{GOF} = [\Sigma w(|F_{0}| - (1/k)|F_{0}|)^{2} / (n_{0} - n_{v})]^{1/2}. \end{split}$$

better fit [20]. Thus, the previous model, with a better observations/parameters fit was retained.

## 5.4.2. Structural study of [6b](CF<sub>3</sub>SO<sub>3</sub>)

Toward the end of the refinement a strong peak ( $\equiv 1.2 \text{ e}$  Å<sup>-3</sup>) was found between the Pt atoms of one of the two independent molecules of the cell A, in a position suggestive of the presence of a bridging hydride. Therefore, Fourier difference maps were calculated using several cut-offs [2b] (sin  $\theta/\lambda_{max} \leq 0.35$ ) confirming the presence of the bridging hydride. This was, subsequently, included in the refinement, with an isotropic temperature factor. It was, however, impossible to locate the hydride in the other independent molecule. The contribution of the hydrogen atoms of the ligands, in calculated positions (C-H=0.95 (Å),  $B(H)=1.3 \times B(C_{bonded})$  (Å<sup>2</sup>)), was taken into account but not refined. Final atomic coordinates and isotropic equivalent displacement parameters are given in Table 4.

A total of 4404 independent reflections was collected of which 2528 were considered as observed and used in the solution and refinement of the structure. During refinement the platinum, phosphorus and fluorine atoms and the carbon atoms of the phosphines were treated anisotropically. The atoms of the triflate anion were refined isotropically. A chlathrated CH<sub>2</sub>Cl<sub>2</sub> molecule was found from a Fourier difference map and was included and refined isotropically. As for [**6a**(A)][**BPh**<sub>4</sub>], the bridging hydride was located from the final Fourier map. After the procedure described above, the hydride was included in the refinement. The contribution of the hydrogen atoms of the ligands, in idealized positions, was taken into account but not refined. Final atomic coordinates and isotropic displacement parameters are given in Table 5.

Table 4 Final positional and isotropic equivalent displacement parameters for [6a][BPh4] (e.s.d.s are given in parentheses)

## Table 4 (continued)

Atom	x	у	z	B (Å <sup>2</sup> )
Pt1	0.26317(4)	0.38256(3)	0.02564(2)	3.30(1)
Pt2	0.22915(4)	0.22880(3)	-0.06762(3)	3.81(1)
Pl	0.2174(3)	0.4632(2)	-0.0476(2)	4.33(9)
P2	0.3331(3)	0.3173(2)	0.1027(2)	4.6(1)
P3	0.3815(3)	0.2204(3)	-0.0923(2)	7.0(1)
P4	0.0723(3)	0.2122(3)	-0.0450(2)	4.9(1)
CI	0.2440(9)	0.4815(7)	0.0843(6)	3.5(3)*
C2	0.3161(9)	0.5484(8)	0.1049(6)	4.1(3)*
C3	0.300(1)	0.6141(9)	0.1452(7)	5.5(4)*
C4	0.214(1)	0.6155(9)	0.1635(7)	5.7(4)*
C5	0.140(1)	0.5500(9)	0.1459(7)	5.8(4)*
C6	0.157(1)	0.4833(8)	0.1058(6)	4.2(3)*
C7	0.175(1)	0.1321(9)	-0.1330(7)	5.0(3)*
C8	0.127(1)	0.150(1)	-0.1877(9)	8.5(5)*
C9	0.091(2)	0.084(2)	-0.234(1)	12.0(7)*
C'	0.110(2)	0.005(1)	-0.225(1)	9.9(6)*
κ	0.155(1)	-0.014(1)	-0.1774(9)	8.5(5)*
C12	0.189(1)	0.052(1)	-0.1262(7)	6.1(4)*
C13	0.323(1)	0.533(1)	-0.0525(8)	6.9(5)
C14	0.123(1)	0.532(1)	-0.0380(7)	6.4(4)
C15	0.171(1)	0.414(1)	-0.1234(8)	6.8(5)
C16	0.467(1)	0.342(1)	0.118(1)	9.2(6)
C17	0.298(2)	0.346(1)	0.1727(9)	8.8(6)
C18	0.312(1)	0.203(1)	0.0885(8)	7.5(5)
C19	0.470(1)	0.312(1)	-0.0709(8)	7.3(5)
C20	0.447(1)	0.142(1)	-0.058(1)	12.5(8)
C21	0.385(2)	0.195(2)	-0.169(1)	19(1)
C22	-0.028(1)	0.217(1)	-0.104(1)	10.8(7)
C23	0.039(1)	0.276(1)	0.017(1)	10.3(6)
C24	0.043(1)	0.109(1)	~0.0258(9)	8.5(5)
Hvd	0.309(6)	0.307(5)	-0.022(4)	6(2)*
в́	0.322(1)	-0.022(1)	0.1672(8)	4.5(4)*
CIB	0.293(1)	-0.0830(8)	0.1034(6)	4.3(3)*
C2B	0.292(1)	-0.1691(8)	0.0991(6)	4.4(3)*
C3B	0.270(1)	-0.2198(9)	0.0438(7)	5.5(4)*
C4B	0.250(1)	-0.186(1)	-0.0056(8)	6.7(4)*
C5B	0.249(1)	-0.100(1)	-0.0049(9)	7.8(5)*
C6B	0.271(1)	-0.050(1)	0.0496(8)	6.6(4)*
C7B	0.2375(9)	0.0430(8)	0.1746(6)	3.9(3)*
C8B	0.251(1)	0.104(1)	0.2219(8)	6.1(4)*
C9B	0.183(1)	0.158(1)	0.2304(8)	7.2(4)*
C10B	0.096(1)	0.156(1)	0.1940(8)	6.3(4)*
CIIB	0.076(1)	0.096(1)	0.1441(8)	6.7(4)*
C12B	0.147(1)	0.0395(9)	0.1344(7)	5.9(4)*
C13B	0.318(1)	- 0.0839(9)	0.2178(7)	5.2(3)*
C14B	0.228(1)	-0.1142(9)	0.2322(7)	5.3(3)*
C15B	0.222(1)	-0.175(1)	0.2699(8)	7.2(4)*
C16B	0.306(1)	-0.205(1)	0.2932(9)	7.9(5)*
C17B	0.393(1)	-0.181(1)	0.2814(9)	8.2(5)*
C18B	0.404(1)	-0.119(1)	0.2443(8)	6.8(4)*
C19B	0.432(1)	0.0330(9)	0.1740(7)	5.0(3)*
C20B	0.481(1)	0.072(1)	0.2282(8)	6.8(4)*
C21B	0.574(1)	0.128(1)	0.2365(9)	8.8(5)*
C22B	0.613(1)	0.137(1)	0.1907(9)	8.9(5)*
C23B	0.570(1)	0.100(1)	0.1365(9)	7.8(5)*
C24B	0.477(1)	0.0465(9)	0.1285(7)	5.9(4)*
Pt1'	0.27888(4)	0.28135(3)	0.41502(3)	3.89(1)
Pt2'	0.28232(4)	0.13922(3)	0.49323(3)	4.41(1)
P1′	0.1100(3)	0.2794(2)	0.4147(2)	4.8(1)
P2'	0.4416(3)	0.2896(2)	0.4036(2)	5.3(1)
P3'	0.2480(4)	0.0214(3)	0.4266(3)	6.7(1)
P4'	0.3342(4)	0.2481(3)	0.5684(2)	7.0(1)
Cl'	0.2723(9)	0.3950(8)	0.3824(6)	4.1(3)*
				(continued
				,

Atom	x	у	z	B (Å <sup>2</sup> )
C2′	0.238(1)	0.3969(9)	0.3221(7)	4.9(3)*
C3′	0.230(1)	0.4730(9)	0.3006(7)	5.9(4)*
C4'	0.255(1)	0.5475(9)	0.3369(7)	5.5(4)*
C5'	0.288(1)	0.5468(9)	0.3969(7)	5.6(4)*
C6'	0.296(1)	0.4713(9)	0.4187(7)	5.4(3)*
C7'	0.271(1)	0.065(1)	0.5561(8)	6.2(4)*
C8′	0.183(2)	0.047(1)	0.574(1)	9.2(6)*
C9′	0.174(2)	-0.002(1)	0.619(1)	10.8(7)*
C10′	0.262(2)	-0.028(1)	0.649(1)	10.6(6)*
C11′	0.349(2)	-0.008(1)	0.634(1)	9.7(6)*
C12'	0.357(1)	0.036(1)	0.5888(9)	8.0(5)*
C13′	0.035(1)	0.248(1)	0.3425(9)	8.3(6)
C14'	0.051(1)	0.210(1)	0.4576(9)	7.9(5)
C15'	0.069(1)	0.381(9)	0.4357(9)	7.5(5)
C16'	0.523(1)	0.382(1)	0.4416(8)	6.3(4)
C17'	0.454(1)	0.291(1)	0.3279(9)	7.4(5)
C18′	0.510(1)	0.205(1)	0.426(1)	10.3(7)
C19'	0.347(3)	0.003(2)	0.389(2)	20(1)*
C20′	0.153(3)	0.024(2)	0.363(2)	19(1)*
C21'	0.232(3)	-0.074(2)	0.450(2)	23(1)*
C22'	0.314(2)	0.236(1)	0.642(1)	11.4(7)*
C23'	0.468(2)	0.271(1)	0.582(1)	11.2(7)*
C24′	0.285(2)	0.347(2)	0.561(1)	11.8(7)*
B'	0.203(1)	0.525(1)	0.6949(8)	4.2(3)*
CIB'	0.2034(9)	0.5843(8)	0.6440(6)	4.0(3)*
C2B'	0.219(1)	0.6716(8)	0.6544(6)	4.5(3)*
C3B'	0.222(1)	0.7251(9)	0.6105(7)	5.5(3)*
C4B'	0.211(1)	0.6910(9)	0.5538(7)	5.9(4)*
C5B'	0.197(1)	0.6049(9)	0.5395(7)	5.6(4)*
C6B'	0.193(1)	0.5532(8)	0.5843(7)	4.8(3)*
C7B′	0.3183(9)	0.5017(8)	0.7127(6)	4.1(3)*
C8B'	0.3904(9)	0.5076(8)	0.6800(6)	4.0(3)*
C9B'	0.484(1)	0.4838(9)	0.6938(7)	5.4(3)*
C10B'	0.514(1)	0.448(1)	0.7434(8)	6.1(4)*
CI1B'	0.449(1)	0.439(1)	0.7800(8)	7.3(4)*
C12B'	0.351(1)	0.468(1)	0.7648(8)	6.3(4)*
C13B'	0.1699(9)	0.5757(8)	0.7509(6)	4.1(3)*
C14B'	0.071(1)	0.5742(9)	0.7580(7)	4.9(3)*
C15B'	0.040(1)	0.625(1)	0.8018(8)	6.2(4)*
C16B'	0.107(1)	0.678(1)	0.8411(8)	6.2(4)*
CI7B'	0.206(1)	0.681(1)	0.8375(8)	6.6(4)*
C18B'	0.238(1)	0.6298(9)	0.7933(7)	5.2(3)*
C19B'	0.126(1)	0.4387(8)	0.6730(6)	4.5(3)*
C20B'	0.043(1)	0.433(1)	0.6286(8)	6.0(4)*
C21B'	-0.029(1)	0.363(1)	0.6115(9)	7.9(5)*
C22B'	-0.013(1)	0.292(1)	0.6387(9)	8.5(5)*
C23B'	0.0/1(2)	0.292(1)	0.681(1)	10.3(6)*
C24B'	0.138(1)	0.366(1)	0.6986(9)	8.0(5)*

Starred atoms were refined isotropically. Primed atoms are those of the second independent molecule in the unit cell. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:  $(4/3) \{a^2 \beta_{1,2} + b^2 \beta_{2,2} + c^2 \beta_{3,3} + ab(\cos \gamma)\beta_{1,2} + ac(\cos \beta)\beta_{1,3} + bc(\cos \alpha \beta)\beta_{2,3}\}$ .

# 5.5. Inelastic incoherent neutron scattering experiments (IINS)

All the IINS data were collected at the Manuel Lujan Jr. Neutron Scattering Center (MLNSC). The FDS spectrometer covers the energy range 250-4000 cm<sup>-1</sup> with a resolution of 2-10% of the incident neutron energy.

Approximately 1 g of each compound, i.e.  $[(PMe_3)_2-(C_6F_5)Pt(\mu-H)Pt(C_6F_5)(PMe_3)_2](CF_3SO_3)$  ([6b](CF<sub>3</sub>-

Table 5 Final positional and isotropic equivalent displacement parameters for [6b][CF<sub>3</sub>SO<sub>3</sub>]-CH<sub>2</sub>Cl<sub>2</sub> (e.s.d.s are given in parentheses)

Atom	x	у	z	B (Å <sup>2</sup> )
Pt	-0.20944(6)	-0.01396(4)	0.21938(4)	3.10(2)
Pt2	0.02058(6)	0.05835(4)	0.22992(4)	3.25(2)
P1	0.1640(5)	-0.0993(3)	0.1476(3)	4.1(1)
P2	-0.2542(5)	0.0590(3)	0.3026(3)	4.6(1)
P3	0.1470(5)	0.0017(3)	0.3253(3)	4.7(2)
P4	-0.0897(5)	0.1231(3)	0.1331(3)	4.3(1)
F2	-0.345(1)	-0.1189(6)	0.2978(6)	6.2(3)
F3	-0.569(1)	-0.1624(7)	0.2671(7)	7.6(3)
F4	-0.728(1)	-0.1225(7)	0.1401(7)	7.2(4)
F5	-0.657(1)	-0.0353(7)	0.0504(6)	5.9(3)
F6	-0.4393(9)	0.0115(6)	0.0817(6)	5.0(3)
F8	0.140(1)	0.1953(6)	0.3079(6)	6.0(3)
F9	0.319(1)	0.2715(7)	0.2901(7)	7.2(4)
F10	0.440(1)	0.2346(7)	0.1926(8)	8.0(4)
F11	0.381(1)	0.1188(8)	0.1147(6)	7.2(4)
F12	0.199(1)	0.0398(6)	0.1321(6)	5.8(3)
Cl	-0.379(1)	-0.0501(9)	0.1923(9)	3.2(4)*
C2	-0.418(2)	-0.097(1)	0.236(1)	4.5(5)*
C3	-0.534(2)	-0.122(1)	0.219(1)	5.2(5)*
C4	-0.614(2)	-0.098(1)	0.157(1)	5.1(5)*
C5	-0.580(2)	-0.054(1)	0.113(1)	3.8(4)*
C6	-0.467(2)	-0.0322(9)	0.1296(9)	3.4(4)*
C7	0.159(2)	0.114(1)	0.2177(9)	3.7(4)*
C8	0.197(2)	0.174(1)	0.259(1)	4.4(5)*
C9	0.288(2)	0.215(1)	0.251(1)	4.5(5)*
C10	0.347(2)	0.196(1)	0.202(1)	5.3(5)*
CII	0.317(2)	0.138(1)	0.161(1)	4.7(5)*
C12	0.225(2)	0.097(1)	0.172(1)	4.2(4)*
C13	-0.018(2)	-0.102(1)	0.135(1)	8.2(7)
C14	-0.255(2)	-0.102(1)	0.058(1)	7.5(7)
CIS	-0.174(2)	-0.179(1)	0.186(1)	74(7)
CIG	-0230(3)	0.021(2)	0.391(1)	no
C17	-0.402(2)	0.089(2)	0.283(1)	9.2(8)
C18	-0.174(2)	0.137(1)	0.321(1)	8.5(7)
C19	0.294(2)	-0.015(2)	0.313(1)	11.6(9)
C20	0.097(3)	-0.076(2)	0.349(2)	12(1)
C21	0.184(4)	0.052(2)	0.405(1)	13(1)
C22	-0.063(2)	0.099(2)	0.047(1)	8.1(8)
C23	-0.245(2)	0.124(1)	0.110(1)	64(7)
C24	-0.058(2)	0.212(1)	0.139(1)	7.8(8)
Hvd	-0.08(1)	0.012(8)	0.265(8)	5(4)*
CII	-0.391(1)	0.3146(6)	0.0786(6)	14.4(3)*
CI2	-0.4713(8)	0.2370(5)	-0.0504(5)	11.9(3)*
Cs	-0.503(3)	0.268(2)	0.028(1)	9.0(8)*
S	0.1423(6)	0.3041(4)	0.0036(4)	7.5(2)*
01	0 109(3)	0.235(2)	0.002(2)	19(1)*
02	0.212(3)	0.322(2)	-0.035(2)	19(1)*
õŝ	0.185(3)	0.308(2)	0.079(2)	19(1)*
Čŕ	-0.017(5)	0.348(3)	-0.005(3)	21(2)*
Fif	-0.085(2)	0.328(2)	0.028(1)	20.0(9)*
F2f	-0.035(2)	0.350(2)	-0.082(1)	19.1(9)*
F3f	0.042(3)	0.412(2)	-0.014(2)	21(1)*
-				

Starred atoms were refined isotropically. C s, Cl1 and Cl2 are the atoms of the chlathrated solvent molecule, the following atoms those of the counterion. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:  $(4/3)[a^2\beta_{l,1}+b^2\beta_{2,2}+c^2\beta_{2,3}+ab(\cos\gamma)\beta_{l,2}+ac(\cos\beta)\beta_{l,3}+bc(\cos\alpha\beta)\beta_{2,3})$ 

 data collection and maintained at  $\sim 10$  K. Total counting times were approximately 26 h.

In order to distinguish the M-H vibrational modes from all the other vibrations involving hydrogen atoms of the ligands, a 'sample difference' technique [21] was used. The method is based on the fact that the incoherent neutron scattering cross sections of hydrogen and deuterium are very different, i.e. 79.91(4) and 2.04(3) barn, respectively [22]. Thus, vibrational modes involving deuterium atoms are difficult to detect by IINS in the presence of many hydrogens, and the difference between two experimental IINS spectra, i.e. those of the compounds containing the 'Pt-D-Pt' and 'Pt-H-Pt' moieties, respectively, should leave only the peaks involving the motion of the hydrides, provided that any possible coupling of the hydride modes to other molecular modes is negligible on the scale of the resolution of the IINS experiment. It is, therefore, unnecessary to prepare samples with fully deuterated ligands. However, this technique requires a spectrometer with very high counting rates in order to obtain reasonable statistical precision on the difference data set. The filter difference spectrometer (FDS) at LANSCE [23], is such an instrument as it utilizes a very large detected solid angle and its resolution can be relaxed to increase the counting rate.

In the FDS a pulsed 'white' beam of neutrons is scattered by the sample and energy analyzed by a cooled Be filter, placed between the sample and the detectors. The neutrons scattered by the sample will only reach the detectors if their energies fall within the bandpass (5.2 meV,  $\lambda \approx 4$  Å) of the filter analyzer system which thereby gives the final energy of the neutrons. The 'time-of-flight' of the neutrons reaching the detectors determines the incident energies of the neutrons

### 6. Supplementary material

Tables giving calculated positional parameters for the hydrogen atoms, anisotropic displacement parameters  $(B_{ij})$ , an extended list of bond distances (Å), angles (°) and torsion angles (°), figures giving the full numbering schemes, and tables of final observed and calculated structure factors for [6a][BPh\_] and [6b](CF\_3SO\_3)-CH\_2Cl\_2 are available from author A.A. upon request.

#### Acknowledgements

M.K.W. carried out the work during the tenure of a fellowship of the Swiss National Science Foundation. The authors are greatly indebted to Dr H. Rüegger for a detailed NMR study of  $[(PMe_3)_2(C_3F_3)P(t_H-H)Pt(C_3F_3)(PMe_3)_2]-(CF_3SO_3)$ . This work has benefited from the use of the Manuel Lujan Jr. Neutron Scattering Center, a national facility funded as such by the Department of Energy, Office of Basic Energy Sciences. A.A. acknowledges support from C.N.R.

#### References

- [1] (a) L.M. Venanzi, Coord. Chem. Rev., 43 (1982) 251; (b) A. Abinati, S. Chaloupka, F. Demartin, T.F. Koetzle, H. Rüegger, L.M. Venanzi and M.K. Wolfer, J. Am. Chem. Soc., 115 (1992) 169, and Refs. therein.
- [2] (a) B. Jezovska-Trebiatowska and B. Nissen-Sobocinska, J. Organomet. Chem., 322 (1987) 331; (b) R.G. Teller and R. Bau, Struct. Bonding, 44 (1980) 1; (c) R. Bau, R.G. Teller, S.W. Kirtley and T.F. Koetzle, Acc. Chem. Res., 12 (1979) 176.
- [3] R. Bau, W.E. Carroll, D.W. Hart, R.G. Teller and T.F. Koetzle, in R. Bau (ed.), *Transition Metal Hydrides*, Advances in Chemistry Series, Vol. 167, 1978, p. 93.
- [4] A. Dedieu (ed.), Transition Metal Hydrides, VCH, New York, 1992.
- [5] J.L. Petersen, L.F. Dahl and J.M. Williams, in R. Bau (ed.), Transition Metal Hydrides, Advances in Chemistry Series, Vol. 167, 1978, p. 11.
- [6] (a) F. Bachechi, Acta Crystallogr., Sect. C, 49 (1993) 460; (b) F. Bachechi, P. Mura and L. Zambonelli, Acta Crystallogr., Sect. C, 49 (1993) 2072; (c) F. Bachechi and L. Zambonelli, J. Organomet. Chem., 250 (1983) 589.
- [7] S. Chaloupka and L.M. Venanzi, unpublished observations.
- [8] D.W. Hart, R. Bau and T.F. Koetzle, Organometallics, 4 (1985) 1590.
- [9] A. Albinati, R. Naegeli, A. Togni and L.M. Venanzi, J. Organomet. Chem., 330 (1987) 85.
- [10] A. Albinati, T.F. Koetzle, J.S. Ricci and L.M. Venanzi, to be published.

- [11] R.A. Love, H.B. Chin, T.F. Koetzle, S.W. Kirtley, B.R. Whittlesley and R. Bau, J. Am. Chem. Soc., 93 (1976) 4491.
- [12] C.B. Cooper, D.F. Shriver and S. Onaka, Adv. Chem. Series, 167 (1978) 16.
- [13] (a) J. Rozière and A. Potier, Bull. Chem. Soc. Fr., (1982) I-339; (b)
  I.J. Braid, J. Howard and J. Tomkinson, J. Chem. Soc., Faraday Trans.
  2, 79 (1983) 253.
- [14] M.W. Howard, U.A. Jayasooriya, S.F.A. Kettle, D.B. Powell and N. Sheppard, J. Chem. Soc., Chem. Commun., (1979) 18.
- [15] J.G. Evans, P.L. Goggin, R.J. Goodfellow and J.G. Smith, J. Chem. Soc. A, (1968) 464.
- [16] (a) B.E. Mann and A. Musco, J. Chem. Soc., Dalton Trans., (1980) 776; (b) M.K. Wolfer, Dissertation No. 8151, ETH Zürich, Switzerland, 1986.
- [17] S. Chaloupka and L.M. Venanzi, unpublished observations.
- [18] MolEN, molecular structure solution procedure, Enraf-Nonius, Delft, Netherlands, 1990.
- [19] International Tables for X-ray Crystallography, Vol. IV, Kynoch, Birmingham, UK, 1974.
- [20] C.W. Hamilton, Acta Crystallogr., 17 (1965) 502
- [21] J. Eckert, Physica B, 136 (1986) 150.
- [22] V.F. Sears, Thermal Neutron Scattering Lengths and Cross-Sections for Condensed Matter Research, Atomic Energy of Canada Ltd., Chalk River Nuclear Laboratories, Chalk River, Ont., Canada, 1984.
- [23] A.D. Taylor, E.J. Wood, J.A. Goldstone and J. Eckert, Nucl. Instr. Methods, 221 (1984) 308.