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### Structural characterization of the head-to-head isomers of the $[Pd_2(Ph_2Ppy)_2Cl_2]$ and $[PtPd(Ph_2Ppy)_2I_2]$ complexes $(Ph_2Ppy = 2-(diphenylphosphino)pyridine)$

László Párkányi <sup>a</sup>, Gábor Szalontai <sup>b</sup>, Gábor Besenyei <sup>a,\*</sup>

<sup>a</sup> Chemical Research Center, Hungarian Academy of Sciences, 1525 Budapest, P.O. Box 17, Hungary <sup>b</sup> University of Veszprém, NMR Laboratory, 8201 Veszprém, P.O. Box 158, Hungary

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Dedicated to Professor Brian James on the occasion of his 70th birthday.

### Abstract

The molecular structures of the thermodynamically unstable head-to-head isomers, HH-[Pd<sub>2</sub>(Ph<sub>2</sub>Ppy)<sub>2</sub>Cl<sub>2</sub>] and HH-[PtPd(Ph<sub>2</sub>Ppy)<sub>2</sub>I<sub>2</sub>], have been determined by single crystal X-ray diffraction. The two complexes have proved to be isostructural. The severe distortions of the bond angles from the ideal square planar geometry around the metal centers ligating the *trans* phosphorus donor atoms are indicative of a more pronounced internal strain in the *HH* isomers as compared to the *HT* counterparts. The enhanced internal strain is thought to be the major driving force responsible for the spontaneous conversion of the head-to-head isomers to their head-totail congeners. <sup>13</sup>C NMR spectra in solution phase as well as solid-state <sup>31</sup>P MAS NMR spectra have proved to be informative regarding the orientation of the asymmetric Ph<sub>2</sub>Ppy ligands.

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### 1. Introduction

Binuclear, metal-metal bonded palladium and platinum complexes ligating bridging diphosphine ligands have received special attention since their first syntheses [1]. The ease with which most of these compounds add small molecules across the metal-metal bond initiated intense research activities in many laboratories, which explored the diverse chemical and structural features of the substrate complexes and the products as well. Outstanding interest has been devoted to the potential use of dimeric palladium complexes in gas separation processes, particularly to the reversible binding of carbon monoxide from coal-gas streams and to the removal of  $H_2S$  from gas mixtures by

E-mail address: besenyei@chemres.hu (G. Besenyei).

using  $[Pd_2(P-P)_2Cl_2]$  complexes as active components (P– P denotes bis(diphenylphosphino)methane, dppm, or 1,1bis(diphenylphosphino)ethane, dppmMe) [2]. The major achievements of the early years have been summarized in comprehensive review articles [3]. Recently, the interaction of  $[Pd_2(dppm)_2Cl_2]$  with arenesulfonyl azides, benzoyl azides and aryl azides has offered a convenient access to dinuclear nitrene and azide adducts [4].

Our interest in dimeric complexes has been rekindled by the expectation that they may serve as easily variable model compounds for studying internal molecular motions in solution phase or can be used as touchstones in the extension of MAS NMR spectroscopy to the structural characterization of coordination compounds in the solid state. In respect to the former subject, we have demonstrated that the *syn* and *anti* isomers of [Pd<sub>2</sub>(dppmMe)<sub>2</sub>Cl<sub>2</sub>] are different not only by their reactivities [5] but the activation barrier of the specific intramolecular motion called "swinging" is

<sup>\*</sup> Corresponding author. Tel.: +36 1 438 4141x122/325 7547; fax: +36 1 325 7554.

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remarkably lower for the sterically more congested syn dimer [6]. Our first efforts to gain structural information on a series of seemingly simple palladium dimers  $[Pd_2(dppm)_2X_2]$  (X = Cl, Br, I) have shown that <sup>31</sup>P MAS NMR spectra can truly reflect the non-uniform structural environments of the phosphorus nuclei, in line with the X-ray diffraction studies on the same complexes [7]. Although the solid-state spectra of these four-spin systems were informative regarding certain scalar couplings (e.g. two-bond trans P-Pd-P coupling constants) which are usually not available under isotropic conditions, the dependence of the <sup>31</sup>P MAS NMR spectra on the rotation rate could not be treated in terms of the average Hamiltonian [8]. Afterwards, we turned our attention to simpler models in which less phosphorus nuclei are involved and which allow an intentional change of the relative positions of the coordinated phosphine ligands.

We have found promising model compounds satisfying the above requirements among the known complexes of the asymmetric 2-(diphenylphosphino)pyridine,  $Ph_2Ppy$ , such as  $[Pd_2(Ph_2Ppy)_2Cl_2]$  [9].

Here we report on the isolation of the hitherto elusive head-to-head isomer HH-[Pd<sub>2</sub>(Ph<sub>2</sub>Ppy)<sub>2</sub>Cl<sub>2</sub>] and present solid-state structural data for the HH-[Pd<sub>2</sub>(Ph<sub>2</sub>Ppy)<sub>2</sub>Cl<sub>2</sub>] (**1-HH**) and HH-[PtPd(Ph<sub>2</sub>Ppy)<sub>2</sub>I<sub>2</sub>] (**2**) complexes by using single-crystal X-ray diffraction. Solution phase NMR data as well as <sup>31</sup>P MAS NMR spectra allowing unambiguous identification of the HH and HT isomers will also be presented.

### 2. Experimental

### 2.1. NMR spectroscopy

Both the liquid-phase and the solid-state NMR experiments were performed on a Varian UNITY 300 NMR spectrometer equipped with a 5 mm broadband variable temperature liquid and a room temperature double-bearing Doty XC5 probe. The solution-phase spectra were recorded in CD<sub>2</sub>Cl<sub>2</sub> at room temperature. Approximately 20-30 mg samples were used for the solution studies. The <sup>13</sup>C and <sup>31</sup>P resonance frequencies,  $\omega_0/2\pi$  were -121.4 and -75.42 MHz, respectively. The MAS spectra were recorded with high-power (~100-120 W) proton decoupling. Sample spinning speeds were typically varied between 3000 and  $11000 \pm 10$  Hz. Stable rotation below 1500 Hz was not possible on this probe. 60–100 mg sample quantities were used in 5 mm o.d. zirkonia or Si<sub>3</sub>N<sub>4</sub> rotors. The number of scans varied between 32 and 128. Both MAS (with recycling delays of 12-15 s) and CP/MAS spectra (with contact times of 0.7–1.2 ms and recycling delays of 6 s) were recorded and gave practically identical results. The chemical shifts are referred to external TMS  $(\delta CD_2Cl_2 = 54 \text{ ppm was used for the conversion})$  and 85% H<sub>3</sub>PO<sub>4</sub>. The <sup>31</sup>P 90° pulse width was about 3.6  $\mu$ s. For referencing and set-up purposes, polycrystalline PPh<sub>3</sub> was applied ( $\delta_{iso} = -6 \text{ ppm}$  relative to the 85% H<sub>3</sub>PO<sub>4</sub>) by the substitution method. The 11 T <sup>31</sup>P MAS spectrum  $(\omega_0/2\pi \text{ was } -202.5 \text{ MHz})$  was recorded on a Bruker Avance DRX500 using 4 mm zirkonia rotors. The Haeberlen convention [10]  $(|\sigma_{33} - \sigma_{iso}| > |\sigma_{11} - \sigma_{iso}| > |\sigma_{22} - \sigma_{iso}|, \eta = \sigma_{22} - \sigma_{11}/\sigma_{33} - \sigma_{iso})$  was used to calculate the principal components of the shielding tensor. The calculations were done by the Varian's STRARS program package.

### 2.2. Crystallography

1-HH and 2 crystallize in the tetragonal space group  $I4_1/a$ . Data collections were performed on an Enraf-Nonius CAD4 diffractometer at room temperature, using graphitemonochromated Mo K $\alpha$  ( $\lambda = 0.7107$  Å) (**1-HH**) and Cu K $\alpha$ radiation ( $\lambda = 1.5418$  Å) (2). Empirical absorption correction (psi-scans) was applied for the intensity data of 2 (the max. and min. transmissions were 0.3079 and 0.1077). Data resolution for 2 is rather low  $(\sin \theta / \lambda = 0.5262)$  due to the high absorption. The structures were determined by direct methods [11] and refined by anisotropic full matrix leastsquares [12] against  $F^2$  for the non-hydrogen atoms. The hydrogen atoms were generated from assumed geometry. Hydrogen atoms were included in structure factor calculations and were treated as riding atoms. The hydrogen isotropic temperature factors were derived from the carbon atoms they were bonded to. Molecular graphics were prepared by the program PLATON [13].

### 2.3. Syntheses

 $[Pd(Ph_2Ppy)_2Cl_2]$  [9a],  $[Pd_2(dba)_3 \cdot CHCl_3]$  [14] and *HH*-[PtPd(Ph\_2Ppy)\_2I\_2] [15] were prepared according to the literature procedures. Ph\_2Ppy was purchased from Aldrich and used as received. Dichloromethane and diethyl ether were freshly distilled from calcium hydride and Na/benzophenone, respectively.

### 2.4. Preparation and isolation of HH-[Pd<sub>2</sub>(Ph<sub>2</sub>Ppy)<sub>2</sub>Cl<sub>2</sub>] (1-HH)

To a solution of 257 mg (0.365 mmol) of  $[Pd(Ph_2-Ppy)_2Cl_2]$  in 50 ml of dry dichloromethane was added dropwise 190 mg (0.184 mmol) of  $[Pd_2(dba)_3 \cdot CHCl_3]$  in 50 ml of dichloromethane at ambient temperature. The progress of the conproportionation reaction was monitored by using TLC (Merck, Kieselgel 60 F 254, eluens: CH\_2Cl\_2/EtOAc 2:1). After stirring for 90 min, the reaction mixture was filtered to remove any insoluble impurities and the solution was evaporated to ca. 10 ml under vacuum. To the resulting dark red solution, 40 ml of diethyl ether was slowly added, which caused the precipitation of a bright red microcrystalline solid. Yield 287 mg (97%). The <sup>31</sup>P NMR spectrum of a sample indicated that the product is a ca. 2:1 mixture of the *HH* and *HT* isomers (the proportion of the *HH* isomer varied between 64% and 66%).

A mixture of the *HH* and *HT* isomers obtained as described above (532 mg) was dissolved in  $CH_2Cl_2$  and

filtered through a Celite layer. The volume was reduced to 40 ml under vacuum and 80 ml of methanol was added. The chlorinated solvent was partly removed under vacuum causing a sharp drop of the temperature of the solution, which was accompanied by a partial precipitation of the dimer (224 mg). The isolated fraction proved to be the *HH* isomer of 96% purity, as shown by the integration of the <sup>31</sup>P NMR spectrum. <sup>31</sup>P NMR (CH<sub>2</sub>Cl<sub>2</sub>): -12.6 ppm (s).

## 2.5. Preparation and isolation of HT-[Pd<sub>2</sub>(Ph<sub>2</sub>Ppy)<sub>2</sub>Cl<sub>2</sub>] (1-HT)

105 mg (0.10 mmol) of  $[Pd_2(dba)_3 \cdot CHCl_3]$  as a solid was added in small portions to a solution of 142 mg (0.20 mmol) of  $[Pd(Ph_2Ppy)_2Cl_2]$  dissolved in 10 ml of dry dichloromethane. The reaction mixture was stirred under N<sub>2</sub> at 25 °C for 75 min. After filtration and partial removal of the solvent, dropwise addition of 25 ml of dry diethyl ether resulted in a red solid which was dried under vacuum. Yield 150 mg (93%). <sup>31</sup>P NMR spectroscopy indicated that the product is pure *HT* isomer. <sup>31</sup>P NMR (CH<sub>2</sub>Cl<sub>2</sub>): 5.9 ppm (s).

### 3. Results and discussion

# 3.1. Synthesis and isolation of HH-[Pd<sub>2</sub>(Ph<sub>2</sub>Ppy)<sub>2</sub>Cl<sub>2</sub>] (1-HH)

Although the conproportionation reaction of  $[Pd_2(dba)_3 \cdot CHCl_3]$  with  $[Pd(Ph_2Ppy)_2Cl_2]$  (Eq. (1)) yielding dimeric palladium(I) complexes with bridging Ph\_2Ppy ligands has been known for more than twenty years, the contradictory observations regarding the number and the stability of the products deserve some attention.

$$\frac{1}{2}[Pd_2(dba)_3] + [Pd(Ph_2Ppy)_2Cl_2] \rightarrow [Pd_2(Ph_2Ppy)_2Cl_2] + 1.5dba$$
(1)

The first synthesis of the  $[Pd_2(Ph_2Ppy)_2Cl_2]$  dimer was described by Balch and coworkers [9a]. It was envisaged that the two possible arrangements of the bridging ligands might result in the formation of head-to-head, *HH*, and head-to-tail, *HT*, isomers (Scheme 1). It was observed that reaction (1) yields a single product that was assumed to hold the bridging groups in a *HT* orientation. This conclusion was based on structural studies carried out on the related heterodinuclear *HT*-[PtPd(Ph\_2Ppy)\_2Cl\_2] complex whose <sup>31</sup>P NMR spectra allowed to establish unequivocally that the phosphorus nuclei are bound to different metal centers.

The identification of Balch's product as a HT isomer was later confirmed by Fujita and coworkers in their comparative study on the ligating properties of Me<sub>2</sub>Ppy and Ph<sub>2</sub>Ppy ligands (Me<sub>2</sub>Ppy stands for 2-(dimethylphosphino)pyridine) [16]. Monitoring the conproportionation reaction (1) by NMR spectroscopy, they detected the intermediacy of new complexes which were assumed to be the unstable head-to-head isomers HH-[Pd<sub>2</sub>(Ph<sub>2</sub>Ppy)<sub>2</sub>X<sub>2</sub>]

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(X = Cl, Br or I). The relatively fast isomerization, especially when X = Cl, hampered, however, the isolation of the less stable products.

In agreement with the observation of Fujita and coworkers, reaction (1) delivered two products in our hands as shown by the two singlet resonances in the solution phase <sup>31</sup>P NMR spectra. We have found, however, a simple route for the isolation of the hitherto elusive HH- $[Pd_2(Ph_2Ppy)_2Cl_2]$  dimer. The progress of the conproportionation reaction was followed by using thin-layer chromatography allowing to stop the reaction when the Pd(0) complex could not be detected any more. Full conversion of the starting dimer was achieved after 60-90 min at 25 °C at which stage the product proved to be an approximately 2:1 mixture of the HH and HT isomers. The close monitoring of the reaction has allowed to shorten the reaction time suggested earlier (20 h, [16]), which certainly had a beneficial effect in preserving the relatively high proportion of the unstable isomer. From this mixture, the HH-[Pd<sub>2</sub>(Ph<sub>2</sub>Ppy)<sub>2</sub>Cl<sub>2</sub>] complex could be isolated in 96% purity if the precipitated raw product was redissolved in dichloromethane, diluted with methanol and the chlorinated solvent was partly removed immediately under vacuum (for details of the work-up procedure see Section 2). The compound isolated in this way proved to be sufficiently pure for liquid phase and solid-state investigations and to grow single crystals for crystallographic studies.

We note that the concentration of the reaction mixture has been found to exert a remarkable effect on the chemoselectivity of reaction (1). While the proportion of the *HH* isomer was in the range of 64–66% when the total Pd-concentration was kept at ca. 8 mM, we could observe only the *HT* complex at [Pd] = 40 mM. It was not our aim to explore the kinetic or mechanistic aspects of reaction (1) and this observation was not further investigated.

Identification, although not quite straightforward, of the two isomers was possible by simulations of the AXX' spin systems ( $A = {}^{13}C$ ,  $X = X' = {}^{31}P$ ) observed in the solution phase  ${}^{13}C$  NMR spectra for all carbon atoms *J*coupled to phosphorus atoms (see Figs. 1 and 2). The splitting of the signal A is influenced by the scalar coupling between the two magnetically non-equivalent P atoms. The distinction is based on the general observation that the two-bond scalar coupling values between *trans* related



Fig. 1. <sup>13</sup>C{<sup>1</sup>H} NMR of the *HT* isomer (expansion of the signal of the pyridyl carbon atom carrying the Ph<sub>2</sub>P moiety), bottom: experimental, top: simulation of the A part of an AXX' system. Parameters obtained from simulations:  $J_{AX} = {}^{1}J({}^{31}P_{-}{}^{13}C) = 75.3 \text{ Hz}$ ,  $J_{AX'} = {}^{3}J({}^{31}P_{-}{}^{13}C) = -5.8 \text{ Hz}$ ,  $J_{XX'} = {}^{3}J({}^{31}P_{-}{}^{31}P) = 18.0 \text{ Hz}$ . The two almost identical central transitions (indicated by an arrow) are burried by the noise at about 172.1 ppm.

P nuclei are significantly larger than the similar couplings between *cis* related P atoms [17]. Consequently, simulations of the A part of the AXX' spin systems can deliver the  $J_{PP}$  coupling constants we are looking for.

In our case (only resonances of the pyridine  $\alpha$  carbon atoms are shown in the figures), the distance between the second and fourth lines gives the sum of the one- and three-bond <sup>31</sup>P–<sup>13</sup>C couplings. The one-bond coupling values obtained from the simulation are larger than expected (70–80 Hz), indicating strong s electron involvement in that particular P–C bond, and are, perhaps, characteristic for this arrangement. The relevant coupling values between the *ipso*-carbon of the phenyl rings and the same P nucleus are somewhat smaller (Fig. 1).

We note, however, that only the lower limit (e.g. >180 Hz) of the coupling is available from the simulations in the case of large  ${}^{2}J(P-M-P)$  coupling (i.e. *HH* isomer, Fig. 2), due to the diminishing intensities of the outer transitions (Table 1).

More convincing evidence could be obtained from straightforward <sup>31</sup>P MAS spectra of the complexes. The



Fig. 2. <sup>13</sup>C{<sup>1</sup>H} NMR of the **1-***HH* isomer (expansion of the signal of the pyridine C2 carbon atom (for numbering see Fig. 5), top: experimental spectrum, bottom: simulation of the A part of an AXX' system). Parameters:  $J_{AX} = {}^{1}J({}^{31}P_{-}{}^{13}C) = 70$  Hz,  $J_{AX'} = {}^{3}J({}^{31}P_{-}{}^{13}C) = -11$  Hz,  $J_{XX'} = {}^{2}J({}^{31}P_{-}{}^{31}P) = 430$  Hz. (The splitting does not change any more upon increasing  $J'_{XX}$  if its value surpasses 200 Hz, the weak outer transitions are expected to disappear in the noise.)

dipolar and scalar coupled isolated <sup>31</sup>P spin pair of the *HH* isomers is expected to show rotational rate-dependent MAS spectra [18,19]. In the case of *HT* isomers, due to the much smaller scalar PP couplings, this phenomenon must be absent. As revealed by the X-ray data, the relevant internuclear  $d(P \cdots P)$  distances are: **1-HH**: 4.447 Å, **1-HT**: 4.417 Å, **2**: 4.408 Å and *HT*-[Pd<sub>2</sub>(Ph<sub>2</sub>Ppy)<sub>2</sub>I<sub>2</sub>]: 4.375 Å. Somewhat surprisingly, the  $P \cdots P$  separation is a little smaller in the *HT* isomer, due to the twist along the Pd–Pd axis).

Indeed, the spectra confirm these assumptions, in that at low rotation speeds (<3500 Hz) the spectrum of the *HH* isomer (Fig. 3) displays an unusual quartet splitting typical for the so-called *J*-recoupling phenomenon [19,20].

We feel important to emphasize that under MAS conditions, *J*-recoupling may arise even between chemically identical P atoms unless their chemical shielding tensors are coincident (i.e. they are related by a center of inversion). Separation of the first and third or the second and fourth lines give the  ${}^{2}J(P-M-P)$  coupling value we need.

Table 1 <sup>13</sup>C NMR chemical shift<sup>a</sup> (ppm) and splitting<sup>b</sup> values (in parentheses, Hz) observed for the *HH* and *HT* isomers at room temperature in  $CD_2Cl_2$ 

Pyridine carbor	18				Phenyl carbons					
C(N,P)	C(N)	C(para to N)	C(meta to N)	C(para to P)	ipso	ortho	meta	para		
170.9 (55.5) <sup>b</sup>	155.9 (10.5)	138.1 (4.6)	128.5 (8.2)	125.4 (s)	n.o.	135.2 (15.4)	131.4 (s)	129.3 (10.8)		
172.2 (70.6) <sup>b</sup>	155.5 (12.1)	139.7 (5.2)	131.7 (10.8)	125.4 (s)	132.3 (52.8)	135.6 (11.8)	132.4 (2.3)	130.4 (11.2)		
F (1)	<sup>2</sup> yridine carbor C(N,P) 70.9 (55.5) <sup>b</sup> 72.2 (70.6) <sup>b</sup>	C(N,P)         C(N)           170.9 (55.5) <sup>b</sup> 155.9 (10.5)           172.2 (70.6) <sup>b</sup> 155.5 (12.1)	C(N,P)         C(N)         C(para to N)           170.9 (55.5) <sup>b</sup> 155.9 (10.5)         138.1 (4.6)           172.2 (70.6) <sup>b</sup> 155.5 (12.1)         139.7 (5.2)	C(N,P)         C(N)         C(para to N)         C(meta to N)           170.9 (55.5) <sup>b</sup> 155.9 (10.5)         138.1 (4.6)         128.5 (8.2)           172.2 (70.6) <sup>b</sup> 155.5 (12.1)         139.7 (5.2)         131.7 (10.8)	C(N,P)         C(N)         C(para to N)         C(meta to N)         C(para to P)           170.9 (55.5) <sup>b</sup> 155.9 (10.5)         138.1 (4.6)         128.5 (8.2)         125.4 (s)           172.2 (70.6) <sup>b</sup> 155.5 (12.1)         139.7 (5.2)         131.7 (10.8)         125.4 (s)	Pyridine carbons         Phenyl carbon           C(N,P)         C(N)         C(para to N)         C(meta to N)         C(para to P)         ipso           170.9 (55.5) <sup>b</sup> 155.9 (10.5)         138.1 (4.6)         128.5 (8.2)         125.4 (s)         n.o.           172.2 (70.6) <sup>b</sup> 155.5 (12.1)         139.7 (5.2)         131.7 (10.8)         125.4 (s)         132.3 (52.8)	Pyridine carbons         Phenyl carbons           C(N,P)         C(N)         C(para to N)         C(meta to N)         C(para to P)         Phenyl carbons           170.9 (55.5) <sup>b</sup> 155.9 (10.5)         138.1 (4.6)         128.5 (8.2)         125.4 (s)         n.o.         135.2 (15.4)           172.2 (70.6) <sup>b</sup> 155.5 (12.1)         139.7 (5.2)         131.7 (10.8)         125.4 (s)         132.3 (52.8)         135.6 (11.8)	Pyridine carbons         Phenyl carbons           C(N,P)         C(N)         C(para to N)         C(meta to N)         C(para to P)         ipso         ortho         meta           170.9 (55.5) <sup>b</sup> 155.9 (10.5)         138.1 (4.6)         128.5 (8.2)         125.4 (s)         n.o.         135.2 (15.4)         131.4 (s)           172.2 (70.6) <sup>b</sup> 155.5 (12.1)         139.7 (5.2)         131.7 (10.8)         125.4 (s)         132.3 (52.8)         135.6 (11.8)         132.4 (2.3)		

<sup>a</sup> Relative to external TMS.

<sup>b</sup> Difference between the second and fourth lines; if one-bond PC coupling is involved its value is not identical with this coupling, in other cases the observed splitting can be considered a good estimate of the relevant  ${}^{n}J_{PC}$  coupling since contributions from  ${}^{4}J_{PC}$  couplings are generally small. s = singulet, n.o. = not observed due to overlap.



Fig. 3. <sup>31</sup>P MAS spectra of the **1-***HH* complex; rotation rate dependence of the homonuclear spin pair. Separation of the first and third lines of the low speed (1940 Hz) spectrum is about 430 Hz.

At higher rotation speeds this collapses to a singlet indicating a single chemical environment for the two P atoms in the crystalline phase. This is in agreement with the  $C_2$  symmetry of the molecule as shown by the crystallographic study (see below). The isotropic chemical shift, the shielding anisotropy and the asymmetry parameter of this phosphorus site are -8.6, 59.2 ppm and 0.95, respectively.

On the contrary, the spectrum of 1-HT does not show this phenomenon (see Fig. 4). The P atoms are separated by three bonds in this isomer, the expected value of this coupling is less than the observed linewidths of the MAS spectrum (150–250 Hz). At the same time, the magnitude of the dipolar coupling among the P nuclei, a *sine qua non* condition for the J-recoupling phenomenon, must be similar to that of the 1-HH isomer due to the similar internuclear distances among them (vide supra). The unchanged AB-like splitting of the isotropic signal observed in the whole rotation range studied indicates that either the  $C_2$ symmetry existing in liquid phase is lost in the solid phase or there are two different molecules in the asymmetry unit. The estimated isotropic chemical shifts are 11.6 and



Fig. 4. <sup>31</sup>P MAS spectra of the **1**-*HT* isomer. Apart from the disappearing of the spinning side-bands the spectra do not show rotation rate dependence. The signals indicated by asterisk are most probably due to a different polymorph, the solution spectrum did not show any evidence of impurity.

10.4 ppm. The minor difference observed in the relevant Pd–P bond length of the *HT* isomer (vide infra) supports the first alternative. Similar patterns have often been observed in dimeric palladium(I) complexes [7] and also in several types of A-frame adducts [21].

### 3.2. Crystallographic description of complexes HH-[Pd<sub>2</sub>(Ph<sub>2</sub>Ppy)<sub>2</sub>Cl<sub>2</sub>] (1-HH) and HH-[PtPd(Ph<sub>2</sub>Ppy)<sub>2</sub>I<sub>2</sub>] (2)

Although there are numerous structures reported with 2-(diphenylphosphino)pyridine, to our knowledge, none of the complexes with four coordinated transition metal centers with a *HH* orientation of the bridging ligands has been characterized by crystallographic methods.<sup>1</sup> The head-tohead orientation of the  $Ph_2Ppy$  pyridylphosphine has been observed, however, and such complexes have been charac-

<sup>&</sup>lt;sup>1</sup> A search of the Cambridge Crytallographic Database (updated August 2005) retrieved 50 dimetallic complexes incorporating  $Ph_2Ppy$  ligands in a *HH* orientation. None of these structures contained two four-coordinated metal centers.

terized in solution by using NMR spectroscopy [15,16a]. In order to reveal the structural differences and similarities of the *HH* and *HT* isomers, *HT*-[Pd<sub>2</sub>(Ph<sub>2</sub>Ppy)<sub>2</sub>Cl<sub>2</sub>] [16b] and *HT*-[Pd<sub>2</sub>(Ph<sub>2</sub>Ppy)<sub>2</sub>I<sub>2</sub>] [22] were selected as reference compounds for the structural discussion. The crystallographic data are collected in Table 2, selected bond lengths and bond angles are presented in Tables 3 and 4.

The asymmetric unit is half a molecule (Z' = 0.5). The molecular symmetry is  $C_2$ , the halogen and metal atoms sit on a twofold axis.

Table 2	Ta	ble	2
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Table 3

Crystal data and structure refinement

Empirical formula	$C_{34}H_{28}Cl_2N_2P_2Pd_2$	$C_{34}H_{28}I_2N_2P_2PdPt$
Formula weight	810.26	1081.85
Unit cell dimensions		
<i>a</i> (Å)	15.483(2)	15.694(5)
c (Å)	26.750(3)	28.172(5)
Volume (Å <sup>3</sup> )	6412.6(14)	6939(3)
Ζ	8	8
Density (calculated) (Mg/m <sup>3</sup> )	1.678	2.071
Absorption coefficient $(\mu m m^{-1})$	1.415	26.351
<i>F</i> (000)	3216	4048
Crystal colour	red	black
Crystal description	block	block
Crystal size (mm)	$0.50 \times 0.30 \times 0.30$	$0.18\times0.10\times0.05$
$\theta$ -Range for data collection (°)	$2.40 \leqslant \theta \leqslant 31.94$	$2.53 \leqslant \theta \leqslant 21.96^{\circ}$
Index ranges h;k;l	-23, 23;-23,	-11, 11;-16,
	23;-39, 39	16;-29, 29
Reflections collected	12147	4761
Independent reflections/ $R_{int}$	5474/0.0233	2109/0.0453
Reflections $I > 2\sigma(I)$	2817	1472
Data/restraints/parameters	5474/0/192	2109/0/193
Goodness-of-fit on $F_2$	0.816	0.984
Extinction coefficient		0.00016(2)
Final R indices	0.0312/0.0694	0.0389/0.1015
$[I > 2\sigma(I)], R_1/wR_2$		
R indices (all data), $R_1/wR_2$	0.0883/0.0797	0.0613/0.1086
Largest difference peak and hole (e $Å^{-3}$ )	0.557/-0.640	1.305/-1.080

Compound 1-*HH* is a typical side-by-side complex (Fig. 5, structure a) in which the two four-coordinated palladium centers are connected by a relatively short

Table 4 Selected bond lengths (Å) and bond angles (°) of HH-[PtPd(Ph<sub>2</sub>Ppy)<sub>2</sub>I<sub>2</sub>], **2** and HT-[Pd<sub>2</sub>(Ph<sub>2</sub>Ppy)<sub>2</sub>I<sub>2</sub>]

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	$\textit{HH-}[PtPd(Ph_2Ppy)_2I_2]$	HT-[Pd <sub>2</sub> (Ph <sub>2</sub> Ppy) <sub>2</sub> I <sub>2</sub> ] [22]
Bond lengths		
Pt1–Pd1	2.571(1)	
Pd1–Pd2		2.597(1)
Pt1–P1	2.254(2)	
Pd–P		2.217(1); 2.206(1)
Pd–N	2.024(8)	2.103(4); 2.121(4)
Pt1–I1	2.642(1)	
Pd1–I2	2.703(1)	2.696(1); 2.695(1)
N1-C2	1.36(1)	1.344(7); 1.355(6)
P1C2	1.80(1)	1.823(5); 1.827(5)
Bond angles		
P1–Pt1–P1 <sup>a</sup>	155.7(1)	
N1–Pd1–N1 <sup>a</sup>	174.6(4)	
P1-Pd1-N2		169.4(1)
P2-Pd2-N1		171.2(1)



	HH-[Pd2(Ph2Ppy)2Cl2]	HT-[Pd <sub>2</sub> (Ph <sub>2</sub> Ppy) <sub>2</sub> Cl <sub>2</sub> ] [16b]
Bond lengths		
Pd1–Pd2	2.561(1)	2.594(1)
Pd1–P1	2.278(1)	2.207(2)
Pd2–P2		2.203(2)
Pd2–N1	2.036(2)	2.106(5)
Pd1-N2		2.122(5)
Pd1–Cl1	2.400(1)	2.428(2)
Pd2-Cl2	2.411(1)	2.411(2)
N1-C2	1.348(3)	1.331(8); 1.355(9)
P1-C2	1.829(3)	1.842(7); 1.828(7)
Bond angles		
P1–Pd1–P1 <sup>a</sup>	154.9(1)	
N1–Pd2–N1 <sup>a</sup>	177.8(1)	
P1-Pd1-N2		170.2(2)
P2-Pd2-N1		173 3(1)

Fig. 5. Molecular diagrams of complexes 1-*HH* (a) and 2 (b), showing atomic displacement ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

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C8p

C9p

C3p

C2p

ſ7p

C12p

C10p

Selected	bond	lengths	(A)	and	bond	angles	(°)	of	HH-	and	HT-
[Pd <sub>2</sub> (Ph <sub>2</sub>	Ppy) <sub>2</sub> C	l <sub>2</sub> ]									

(2.561(1) Å) metal-metal bond. For comparison, the corresponding distance in 1-HT is 2.594(1) Å. The short Pd-Pd separation is in line with the rigid nature of the Ph<sub>2</sub>Ppv ligand that typically allows to span shorter metal-metal distances as compared to the more flexible dppm. From the structural point of view, the most interesting part of the complex is the coordination sphere of the palladium centers that ligate either two phosphorus or two nitrogen donor atoms as opposed to the uniform one phosphorus/ one nitrogen coordination in HT isomers. A survey of the structural data readily reveals the most significant differences in the environments of the two Pd centers. It seems noteworthy that the angles formed by neighboring ligands on the "nitrogen side" deviate from the ideal right angle only negligibly, the difference between the larger and smaller angle being only 2.2°. Severe distortion from the idealized square-planar geometry can be observed, however, on the "phosphorus side" where the same angles differ by 25.2°.

Undoubtedly, the notable distortions of the bond angles reflect a substantial amount of internal strain and may be the major driving force of the spontaneous  $HH \rightarrow HT$  isomerization.

As for the ligands in *trans* positions, the N1–Pd2–N1<sup>a</sup> angle (177.8°) approaches the linearity as opposed to the 154.9° of the P–Pd–P linkage. On the contrary, the two P–Pd–N axes in the *HT* isomer deviate from the linear arrangement only by 6.0° and 9.8°. The metal and the halogen atoms sit on a twofold axis, therefore the X–M–M–X (X = halogen, M = metal) chain is strictly collinear for both **1-HH** and **2**.

A remarkable difference of the *HT* and *HH* isomers is reflected by the Pd–P and Pd–N bond lengths. While the mean  $d_{Pd-P}$  is 2.205(2) Å in *HT*-[Pd<sub>2</sub>(Ph<sub>2</sub>Ppy)<sub>2</sub>Cl<sub>2</sub>], it is longer in the *HH* counterpart by 0.07 Å. The lengthening of the Pd–P bond can be rationalized in terms of the strong *trans* influence of the phosphine moieties and is also conform to the expectation that the bond strength of a strong  $\pi$ -acceptor ligand is decreased if another ligand of the same kind occupies the *trans* position. Not surprisingly, the opposite trend is observed for the pyridyl parts. While the head-to-tail arrangement results in a mean Pd–N bond length of 2.114 Å in the *HT*-[Pd<sub>2</sub>(Ph<sub>2</sub>Ppy)<sub>2</sub>Cl<sub>2</sub>] dimer, the Pd–N distance drops to 2.036(2) Å in the *HH* isomer, in agreement with the relatively weak *trans* influence of the nitrogen donor atoms.

Other bond lengths and bond angles of the two isomers do not show characteristic differences. We note, however, that the dihedral angle of the coordination planes is appreciably larger (46.81°) in the *HH* isomer than in the *HT* congener (37.43°). It has been demonstrated for a large set of dimeric palladium and platinum complexes incorporating bridging diphosphine ligands that increasing metal-metal distances are accompanied by decreasing dihedral angles [23]. The structural features of this isomer pair are conform to this general trend and support the earlier conclusion that a twist about the metal-metal bond reduces the interaction of the filled d orbitals that may be especially pronounced in Pt and Pd complexes with short metal-metal separation.

The most striking difference in the conformations of the HH and HT isomers is the orientation of the axial phenyl moieties. The axial phenyls point in opposite directions in the HH isomers with respect to the best plane containing the metal, phosphorus, and nitrogen atoms. In the HT isomers, these phenyl rings are on the same side of this plane (Fig. 6).

The conformation of the *HH* isomer leads to a more compact, close packed arrangement in the crystal lattice that contains no solvent accessible voids, 68.3% of the unit cell is filled with atoms (Fig. 7). There are large solvent accessible areas in the lattice of the *HT* isomers. The percent filled space for **1-HT** and *HT*-[Pd<sub>2</sub>(Ph<sub>2</sub>Ppy)<sub>2</sub>I<sub>2</sub>] is 63.1% and 61.4%. The potential solvent areas for these two compounds are 820.1 Å<sup>3</sup> (11.7%) and 1010.9 Å<sup>3</sup> (13.5%). These voids are in fact filled with disordered solvent molecules.

Compound 2, HH-[PtPd(Ph<sub>2</sub>Ppy)<sub>2</sub>I<sub>2</sub>], has been prepared by Balch and coworkers [15] and has been characterized by multinuclear NMR methods. The thermodynamic instability of the dimer was demonstrated unequivocally by its slow conversion to HT isomer, which could be catalyzed by free Ph<sub>2</sub>Ppy. Here we report on the molecular structure of **2**, based on a single crystal X-ray diffraction study.

**1-HH** and **2** are isostructural. The cell similarity index [24]  $\Pi$  is 0.03195 and the  $I_v$  index [25] (that involves all atoms of the structures) is 81.2%. There is only a relaxed isostructurality between **1-HT** and HT-[Pd<sub>2</sub>(Ph<sub>2</sub>Ppy)<sub>2</sub>I<sub>2</sub>] (space group C2/c,  $\Pi = 0.0147$ ,  $I_v = 52.2\%$ ).

In agreement with the close relationship of the two complexes, the structural features of **2** are very similar to those of complex **1-***HH*. The Pt–Pd bond length is 2.571(1) Å and adds to the number of structures with short metal–metal bonds. Although the Pt–P bonds (2.254(2) Å) are shorter than the corresponding distances in complex **1-***HH*, they are remarkably longer of the Pd–P bonds in the reference compound *HT*-[Pd<sub>2</sub>(Ph<sub>2</sub>Ppy)<sub>2</sub>I<sub>2</sub>] ( $d_{PdP, av.} = 2.210$  Å). This feature can be interpreted again in terms of the strong *trans* influence of the P nuclei. Accordingly, the Pd–N distances are notably shorter that those in the *HT* isomer [Pd<sub>2</sub>(Ph<sub>2</sub>Ppy)<sub>2</sub>I<sub>2</sub>] (2.024(8) vs.  $d_{PdN, av} = 2.112$  Å). It seems interesting to point out that the metal-iodine bond lengths



Fig. 6. The 1-HH and 1-HT isomers as viewed down the metal-metal axis.



Fig. 7. Packing diagrams for 1-HT (a) with the solvent accessible voids and 1-HH (b). Hydrogen atoms are omitted for clarity.

in the heterodinuclear complex are different by 0.06 Å. This contrasts with the observation that the Pd-halide bonds are practically equal in complexes **1-***HH* ( $d_{PdCl} = 2.400(1)$  and 2.411(1) Å), **1-***HT* ( $d_{PdCl} = 2.428(2)$  and 2.411(2) Å), and *HT*-[Pd<sub>2</sub>(Ph<sub>2</sub>Ppy)<sub>2</sub>I<sub>2</sub>] ( $d_{PdI} = 2.696(1)$  and 2.695(1) Å). Although the metal–metal bond has a strong *trans* influence this should equally affect both the Pd–I and the Pt–I bonds. We attribute the shorter Pt–I bond length to the smaller ionic radius of platinum as compared to that of palladium.

As expected, the deviations from the idealized square planar geometry around the metal centers are very similar in complexes 1-*HH* and 2. While the N1–Pd1–N1<sup>a</sup> angle in 2 is almost linear  $(174.6(4)^{\circ})$ , the P1–Pt1–P1<sup>a</sup> angle is severely bent  $(155.7(1)^{\circ})$ . Similarly, other angles around

the P-bound platinum center are more distorted than those formed by the neighboring substituents of palladium as indicated by the difference of the largest and smallest angles  $(24.2^{\circ} vs. 5.4^{\circ})$ . Like in the case of the *HH* and *HT*  $[Pd_2(Ph_2Ppy)_2Cl_2]$  isomer pair, the dihedral angle of the coordination planes incorporating the platinum and the palladium centers is larger (48.40°) than the same feature of the reference compound *HT*- $[Pd_2(Ph_2Ppy)_2I_2]$  (41.3°). All these structural features suggest that it is the *HH*- $[PtPd(Ph_2Ppy)_2I_2]$  complex that accumulates more internal strain and, consequently, is predestinate to isomerize to the more stable *HT* counterpart.

We find interesting to point out that the structural differences of the *HH* and *HT* isomers are reminding those of the *syn*- and *anti*-[Pd<sub>2</sub>(dppmMe)<sub>2</sub>Cl<sub>2</sub>] complexes. Of the latter

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pair of compounds, the *syn*-[Pd<sub>2</sub>(dppmMe)<sub>2</sub>Cl<sub>2</sub>] dimer proved to be sterically more congested, and consequently, the thermodynamically less stable product [23]. Similarly to the structural differences between the *HH* and *HT* complexes, larger dihedral angle, shorter Pd–Pd bond length and more extensive internal strain were characteristic to the *syn* isomer compared to the *anti* congener. Importantly, however, the enhanced internal strain of the *syn* dimer was accompanied by an increased reactivity. While the *anti* isomer was reluctant toward all typical reagents but the elemental selenium, the *syn* congener formed A-frame adducts with a series of small molecules [5]. Based on the above considerations, the *HH*-[Pd<sub>2</sub>(Ph<sub>2</sub>Ppy)<sub>2</sub>Cl<sub>2</sub>] dimer is expected to be more reactive than its *HT* counterpart if the isomerization can be suppressed efficiently.

### 4. Conclusions

The kinetic product of the conproportionation reaction  $[Pd(Ph_2Ppy)_2Cl_2]$  and  $[Pd_2(dba)_3]$ , HH- $[Pd_2(Ph_2$ of Ppy)<sub>2</sub>Cl<sub>2</sub>], has been isolated and the molecular structure was determined by using X-ray diffraction. This complex and the related HH-[PtPd(Ph<sub>2</sub>Ppy)<sub>2</sub>I<sub>2</sub>] dimer are the first structurally characterized members of the large number of HH-[M<sup>1</sup>M<sup>2</sup>(Ph<sub>2</sub>Ppy)<sub>2</sub>X<sub>2</sub>] complexes (M<sup>1</sup>, M<sup>2</sup> = Pd, Pt; X = anion). Although a survey of the structural data has revealed a host of distortions and unfavorable internal non-bonding interactions in both the HT and HH isomers, the bond angles around the P-bound metal centers have proved to be outstandingly distorted in the HH complexes. This structural feature is in line with the thermodynamically unstable nature of the head-to-head isomers and is seen as the major driving force of the spontaneous  $HH \rightarrow HT$  conversion. The structural differences of the HT and HH isomers remind those observed for the syn and anti isomers of [Pd<sub>2</sub>(dppmMe)<sub>2</sub>Cl<sub>2</sub>] but it remains to be cleared if the potentially enhanced reactivity of the HH dimers can be observed experimentally. The MAS <sup>31</sup>P NMR technique has proved to be a viable experimental method for recognizing the various arrangements of the Ph<sub>2</sub>Ppy ligand in dinuclear complexes.

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### Appendix A. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC, Nos. 288659 and 288660 for compounds 1-*HH* and 2. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2005.12.021.

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