Polyhedron

Reactivity of platinum(II) triphenylphosphino complexes with nitrogen donor divergent ligands

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Abstract: Dinuclear platinum(II) complexes [{$PtCl_2(PPh_3)$}$_2$(μ-N—N)], where N—N is a divergent bidentate nitrogen ligand, were prepared by reacting *cis*-[$PtCl_2(PPh_3)(NCMe)$] with N—N in a Pt/N—N molar ratio 2. The *(trans,trans*)-isomers were obtained as kinetic products and recovered in good yields and high purity {**1**, N—N = pyrazine (pyrz); **2**, N—N = 4,4'-bipyridyl (bipy); **3**, N—N = piperazine (pipz); **4**, N—N = p-xylylendiamine ($xylN_2$)}. *cis*-[$PtCl_2(PPh_3)(NCMe)$] was also reacted with the tridentate divergent ligand 2,4,6-tris-(pyrid-4'-yl)1,3,5-triazine (py3TRIA) in molar ratio 3 with formation of the trinuclear (*trans,trans,trans*)-[{$PtCl_2(PPh_3)$}$_3$(μ-py3TRIA)], **5**. On the other hand, the treatment of *cis*-[$PtCl_2(PPh_3)(NCMe)$] with the monodentate pyridine (py) produced a mixture of both *trans*-[$PtCl_2(PPh_3)(py)$] (**6a**) and *cis*-[$PtCl_2(PPh_3)(py)$] (**6b**). The reactions of *cis*-[$PtCl_2(PPh_3)(NCMe)$] with N—N = pyrz, bipy, pipz, carried out with a Pt/ N—N molar ratio 1, were monitored by ^{31}P-NMR spectroscopy. Equilibria were observed in solution, involving dinuclear (*trans-trans*)-[{$PtCl_2(PPh_3)$}$_2$(μ-N—N)], mononuclear [$PtCl_2(PPh_3)$(N—N)] and free N—N. The addition of an excess of the divergent ligand allowed the complete conversion to the corresponding mononuclear complexes. With the heteroaromatic ligands both geometric isomers were observed (**7a**, **7b** and **8a**, **8b**, for pyrz and bipy derivatives, respectively) while with pipz the *trans*-isomer only was detected, **9**. In the system involving bipy, the scarcely soluble dinuclear (*cis,cis*)-[{$PtCl_2(PPh_3)$}$_2$(μ-bipy)], **2b**, was also obtained. Products **2**, **2b**, **3**·2($CHCl_3$) and **6a**·0.5($C_2H_4Cl_2$) were structurally characterized by single crystal X-Ray diffraction methods.

Keywords: platinum(II); triphenylphosphine; dinuclear complexes; divergent ligands; *cis-trans* isomerism.

1. Introduction

Divergent ligands are molecules containing at least two functional groups able to coordinate metal ions in a non-chelating fashion to afford oligo- or polynuclear architectures. In the field of platinum complexes, N-donor divergent bidentate ligands constitute important building blocks in the synthesis of polynuclear 2D and 3D supramolecular derivatives,[1] with potential applications in the fields of luminescent materials[2] and medicinal chemistry.[3] While ionic supramolecular coordination compounds of platinum (mainly tri- and tetranuclear) originate from well-studied self-assembly procedures,[4,5] much less is known about neutral dinuclear complexes.[6] Thus, with the aim to prepare dinuclear species and in the context of our studies concerning the synthesis of platinum(II) complexes containing the PPh_3 ligand,[7] the reactivity of *cis*-$[PtCl_2(PPh_3)(NCMe)]$[7e] towards N—N divergent bidentate nitrogen donor ligands (pyrz, bipy, pipz and $xylN_2$) has been investigated. In addition, the reactivity towards the tridentate 2,4,6-tris-(pyrid-4'-yl)1,3,5-triazine) (py3TRIA)[8] was studied. The use of a precursor with a single available coordination site on platinum, due to the facile nitrile substitution, prevents the formation of derivatives with a nuclearity higher than the denticity of the divergent ligand. Moreover, the presence of the phosphorous donor ligand in the platinum coordination sphere influences the stereochemistry of the processes; in addition it allows the tracking of the reactions via ^{31}P-NMR spectroscopy providing useful pieces of information also in the presence of equilibria involving several species. The outcome of the reactions in dependence on the molar ratio between reagents is here reported and discussed, as well as the stereochemistry of the products.

2. Experimental

2.1. Materials and general methods

All manipulations were performed under a dinitrogen atmosphere, if not otherwise stated. Solvents and liquid reagents were dried according to reported procedures [9]. ^{1}H-, ^{13}C-, ^{31}P and ^{195}Pt NMR spectra were recorded with a Bruker ‘‘Avance DRX400’’ spectrometer, in $CDCl_3$ solution if not otherwise stated. Chemical shifts were measured in ppm (δ) from TMS by residual solvent peaks for ^{1}H and ^{13}C, from aqueous (D_2O) H_3PO_4 (85%) for ^{31}P and from aqueous (D_2O) hexachloroplatinic acid for ^{195}Pt. A sealed capillary containing C_6D_6 was introduced in the NMR tube to lock the spectrometer to the deuterium signal when non-deuterated solvents were used. FTIR spectra in solid phase were recorded with a Perkin–Elmer ‘‘Spectrum One’’ spectrometer, equipped with an ATR accessory. Elemental analyses (C, H, N) were performed at Dipartimento di Scienze e Tecnologie Chimiche, Università di Udine. *Cis*-$[PtCl_2(PPh_3)(NCMe)]$,[7e] *trans*-$[Pt_2(\mu$-

$Cl)_2Cl_2(PPh_3)_2]$ [7e] and 2,4,6-tris-(pyrid-4'-yl)-1,3,5-triazine[8] were prepared according to a reported procedure. In the text the following abbreviations were used: 4,4'-bipyridyl (bipy); pyrazine (pyrz); piperazine (pipz); p-xylylendiamine ($xylN_2$); pyridine (py); 2,4,6-tris-(pyrid-4'-yl)-1,3,5-triazine (py3TRIA); 1,2-dichloroethane (1,2-DCE).

2.2. General procedure for the synthesis of dinuclear species (trans,trans)-[{$PtCl_2(PPh_3)$}$_2$(μ-N—N)]

A suspension of *cis*-[$PtCl_2(PPh_3)(NCMe)$] (≈ 1.0 mmol) in 1,2-DCE (5.0-10.0 mL) was treated with a solution of the divergent ligand *N—N* in the minimal amount of the same solvent (Pt/*N—N* molar ratio = 2.0). The resulting yellow solution was refluxed under stirring until the complete conversion was obtained (^{31}P-NMR). A yellow, fine solid separated out of the solution on cooling to room temperature (25 °C) or after heptane addition (10.0-15.0 mL). The solid was filtered, washed with two portions of heptane and dried under vacuum (10^{-2} mmHg). For each dinuclear complex the isolated product % yield, the elemental analysis and the spectroscopic (IR and NMR) characterization are reported below.

2.2.1 (Trans,trans)-[{$PtCl_2(PPh_3)$}$_2$(μ-pyrz)], ***1***.

73 % yield. *Anal.* Calcd. for $C_{40}H_{34}Cl_4N_2P_2Pt_2$: C 42.3, H 3.0, N 2.5 %. Found: C 42.0, H 2.8, N 2.4 %. IR (ATR, cm^{-1}): 3107, 1484, 1435, 1422, 1167, 1098, 879, 744, 690; ^{1}H-NMR: 9.33 (m, 4H, NCH), 7.79 (m, 12H, H_{arom} phosphine), 7.48 (m, 18H, H_{arom} phosphine); ^{13}C-NMR: 147.1, 134.9 (J_{C-P} = 10.0 Hz), 131.2, 128.2, 128.3 ($^1J_{C-P}$ = 63.0 Hz), 128.2 (J_{C-P} = 11.0 Hz); ^{31}P-NMR: 2.80 ($^1J_{P-Pt}$ = 3725 Hz); ^{195}Pt-NMR: -3561 ($^1J_{Pt-P}$ = 3725 Hz).

2.2.2.(Trans,trans)-[{$PtCl_2(PPh_3)$}$_2$(μ-bipy)], ***2***.

60 % yield. *Anal.* Calcd. for $C_{46}H_{38}Cl_4N_2P_2Pt_2$: C 45.6, H 3.2, N 2.3 %. Found: C 45.3, H 3.0, N 2.3 %. IR (ATR, cm^{-1}): 3052; 1610; 1481; 1220; 1095; 812; 743; 690.; ^{1}H-NMR: 9.22 (m, 4H, NC<u>H</u>), 7.83 (m, 12H, H_{arom} phosphine), 7.68 (m, 4H, NCHC<u>H</u>), 7.47 (m, 18H, H_{arom} phosphine); ^{13}C-NMR: 152.2, 146.3, 134.9 (J_{C-P} = 10.3 Hz), 131.0, 128.5 ($^1J_{C-P}$ = 65.3 Hz), 128.0 (J_{C-P} = 11.3 Hz), 122.8; ^{31}P-NMR: 2.64 ($^1J_{P-Pt}$ = 3611 Hz); ^{195}Pt-NMR: -3538 ($^1J_{Pt-P}$ = 3611 Hz);. A sample of solid was dissolved in $CHCl_3$ and crystallized by slow diffusion of pentane vapors. A single crystal was selected for X-ray diffraction analysis, which confirmed the (*trans,trans)* stereochemistry.

2.2.3.(Trans,trans)-[{$PtCl_2(PPh_3)$}$_2$(μ-pipz)], ***3***.

91 % yield. *Anal.* Calcd. for $C_{40}H_{40}Cl_4N_2P_2Pt_2$: C 42.0, H 3.5, N 2.5 %. Found: C 41.8, H 3.3, N 2.6%. IR (ATR, cm^{-1}): 3227; 3190; 3055; 1482; 1098; 880; 745; 690; ^{1}H-NMR: 7.69 (m, 12H, H_{arom}), 7.43 (m, 18H, H_{arom}), 3.96 (bs, $^2J_{H-Pt}$ = 68.5 Hz, 2H, NH), 3.58 (m, 4H, C<u>H</u>H), 3.36 (m, 4H, CH<u>H</u>). ^{13}C-NMR: 134.8 (J_{C-P} = 10.0 Hz), 131.0, 128.3 ($^1J_{C-P}$ = 63.0 Hz), 128.0 (J_{C-P} = 11.0 Hz), 48.7; ^{31}P-NMR: 3.56 ($^1J_{P-Pt}$ = 3603 Hz); ^{195}Pt-NMR: -3606 ($^1J_{Pt-P}$ = 3603 Hz);. A sample of solid was dissolved in $CHCl_3$ and crystallized by slow diffusion of pentane vapors. A single crystal was selected for X-ray diffraction analysis, which confirmed *trans,trans* geometry.

*2.2.4. (Trans,trans)-[{$PtCl_2(PPh_3)$}$_2$(μ-xylN$_2$)], **4**.*

37 % yield. *Anal.* Calcd. for $C_{44}H_{42}Cl_4N_2P_2Pt_2$: C 44.3, H 3.6, N 2.4 %. Found: C 44.1, H 3.4, N 2.4%. IR (ATR, cm^{-1}): 3207; 3056; 1568; 1098; 990; 743; 691; ^{1}H-NMR: 7.73 (m, 10H, H_{arom}), 7.45 (m, 24H, H_{arom}), 4.25 (m, 4H), 3.60 (m, 4H); ^{13}C-NMR: 138.2, 134.8 (J_{C-P} = 10.0 Hz), 131.0 (J_{C-P} = 2.0 Hz), 129.2, 128.5 ($^1J_{C-P}$ = 63.0 Hz), 128.0 (J_{C-P} = 11.0 Hz), 48.1; ^{31}P-NMR: 3.87 ($^1J_{P-Pt}$ = 3646 Hz); ^{195}Pt-NMR: -3606 ($^1J_{Pt-P}$ = 3646 Hz);

2.3.Preparation of mononuclear derivatives

*2.3.1. Synthesis of trans- + cis-[$PtCl_2(PPh_3)(Py)$] (**6a** + **6b**)*

A suspension of *cis*-[$PtCl_2(PPh_3)$(NCMe)] (0.254 g, 0.445 mmol) in 15.0 mL of 1,2-DCE was treated, under stirring, with pyridine (Py/Pt molar ratio = 1.1). The reaction was monitored by ^{31}P-NMR spectroscopy. The mixture was refluxed until the precursor signal disappeared, substituted by two new signals (2h), then it was cooled. A fine yellow precipitate was filtered, washed with cold heptane and dried under vacuum (10^{-2} mmHg). 64 % yield. *Anal.* Calcd. for $C_{23}H_{20}Cl_2NPPt \cdot 1/2\ C_2H_4Cl_2$: C 43.9, H 3.4, N 2.1 %. Found: C 43.7, H 3.8, N 2.0 %. IR (ATR, cm^{-1}): 3064; 1481; 1096; 996; 752; 690; ^{1}H-NMR (solvent, the two *trans* and *cis* isomers, **6a** and **6b**, in approximately 1:1 molar ratio, were observed): 9.03 (m, 2H, $^3J_{H-Pt}$ = 32 Hz, NC<u>H,</u> *trans* isomer), 8.45 (m, 2H, $^3J_{H-Pt}$ = 40 Hz, NC<u>H</u> *cis* isomer), 7.83 (m, 8H), 7.69 (m, 6H), 7.45 (m, 14H), 7.33 (m, 6H), 6.93 (m, 2H); ^{13}C-NMR (*trans* and *cis* isomers): 153.4, 151.4, 138.5, 137.4, 134.7 (J_{C-P} = 10.0 Hz), 134.6 (J_{C-P} = 10.0 Hz), 131.2, 130.9, 128.5 ($^1J_{C-P}$ = 55.0 Hz, 2C), 128.3 (J_{C-P} = 11.0 Hz), 128.1 (J_{C-P} = 11.0 Hz), 125.9, 125.1; ^{31}P-NMR (*trans* and *cis* isomers): 7.24 ($^1J_{P-Pt}$ = 3904 Hz, *cis* isomer); 2.59 ($^1J_{P-Pt}$ = 3581 Hz, *trans* isomer); ^{195}Pt-NMR (*trans* and *cis* isomers): -3379 ($^1J_{Pt-P}$ = 3904 Hz, *cis* isomer); -3540 ($^1J_{Pt-P}$ = 3581 Hz, *trans* isomer); A sample of solid was dissolved in $CHCl_3$ and crystallized by slow diffusion of pentane vapors. Some single crystals were selected for X-ray diffraction analysis, which revealed the *trans* stereochemistry of the complex. ^{31}P-NMR (crystals in $CDCl_3$, freshly prepared solution): 2.59 ($^1J_{P-Pt}$ = 3581 Hz).

*2.3.2. Synthesis of trans- + cis-[$PtCl_2(PPh_3)(pyrz)$] (**7a** + **7b**)*

Method a. A suspension of 0.139 g (0.244 mmol) of *cis*-[$PtCl_2(PPh_3)(NCMe)$] in 15.0 mL of 1,2-DCE was treated with a large excess of pyrazine (pyrz/Pt molar ratio = 10) and refluxed (3h). A yellow solution was initially obtained and, upon cooling, a colorless powder formed, which was filtered, washed with heptane, dried and characterized (**7b**, isomer *cis*, 0.0129 g, 14 % yield). The filtrate was treated under vacuum (10^{-2} mmHg) up to dryness. The solid residue was washed with several portions of diethyl ether to remove the pyrazine excess. The light yellow powder was dried under vacuum (*trans* + *cis* isomers, **7a** + **7b**; 0.0178 g, 21 % yield). *Anal.* Calcd. for $C_{22}H_{19}Cl_2N_2PPt$: C 43.4, H 3.2, N 4.6 %. Found: C 43.6, H 3.0, N 4.6 %. IR (ATR, cm^{-1}): 3053; 1482; 1417; 1098; 996; 804; 746; 692; ^{1}H-NMR (isomer *cis*): 8.40 (dd, 2H, $^3J_{H-H}$ = 4.4 Hz, $^5J_{H-H}$ = 1.3 Hz, $^3J_{H-Pt}$ = 41 Hz, PtNC<u>H</u>), 8.18 (dd, 2H, $^3J_{H-H}$ = 4.4 Hz, $^5J_{H-H}$ = 1.3 Hz, PtNCHC<u>H</u>), 7.69 (m, 6H, H_{arom} phosphine), 7.48 (m, 3H, H_{arom} phosphine), 7.37 (m, 6H, H_{arom} phosphine); ^{1}H-NMR (isomer *trans*, selected signals from ^{1}H-NMR of the mixture): 9.09 (m, 2H, $^3J_{H-Pt}$ = 21 Hz, PtNC<u>H</u>), 8.79 (m, 2H, PtNCHC<u>H</u>), 7.81 (m, 6H, H_{arom} phosphine), 7.50 (m, 9H, H_{arom} phosphine). ^{31}P-NMR (isomer *cis*): 7.13 ($^1J_{P-Pt}$ = 3808 Hz); ^{31}P-NMR (isomer *trans*, selected signal from ^{31}P-NMR of the mixture): 2.68 ($^1J_{P-Pt}$ = 3661 Hz).

A solution of **7b** in $CDCl_3$ was monitored through 1H-NMR spectroscopy. Formation of **7a**, **1** and free pyrazine was observed. The equilibrium composition was reached after about 48 h. The relative concentrations of the species involved in the equilibrium were obtained by the integrals of the signals at 9.09 and 8.79 ppm for **7a**, 8.40 and 8.18 ppm for **7b**, 9.33 ppm for **1**, 8.62 ppm for free pyrz.

Method b. A suspension of 0.201 g (0.177 mmol) of **1** in 1,2-DCE (9.0 mL) was treated with 0.0400 g of pyrazine (0.500 mmol, pyrz/ Pt molar ratio = 1.42) under stirring at room temperature and turned quickly to a yellow-green solution. A sample of the solution was analyzed after 30 minutes (^{31}P-NMR) and showed two signals: 2.78 ppm (65 %, $^1J_{P-Pt}$ = 3685 Hz), 6.36 ppm (35 %, $^1J_{P-Pt}$ = 3790 Hz). After 30 minutes the mixture was concentrated under vacuum until a pale yellow solid formed. After two days the solid was filtered, washed with heptane (2 × 2.0 mL) and dried under vacuum (63% yield). ^{1}H- and ^{31}P-NMR, carried out in $CDCl_3$ solution showed the presence of *isomer cis* (66 %) and *isomer trans* (34 %, cfr. characterization described for method a).

*2.3.3. Treatment of **2** with bipy with formation of trans- + cis-[$PtCl_2(PPh_3)(bipy)$] (**8a** + **8b**)*

To a solution of (*trans,trans*)-[{$PtCl_2(PPh_3)$}$_2$(μ-bipy)], **2**, in CD_2Cl_2 bipy was added in two portions corresponding to bipy/**2** molar ratios 1 and 2, respectively. After each addition the system was monitored by ^{1}H-and ^{31}P-NMR spectroscopies (Table 3SI).

*2.3.4. Isomerization of **2** to (cis,cis)-[{$PtCl_2(PPh_3)$}$_2$(μ-bipy)], **2b**.*

A sample of (*trans,trans)*-[{$PtCl_2(PPh_3)$}$_2$(μ-bipy)] was dissolved in chloroform in the presence of a slight amount of bipyridyl. After two weeks, colorless crystals separated out of the solution. ^{1}H-NMR ($CDCl_3$): 8.55 (m, 4H, NC<u>H</u>); 7.72 (m, 12H, H_{arom} phosphine); 7.49 (m, 6H, H_{arom} phosphine); 7.38 (m, 12H, H_{arom} phosphine); 7.00 (m, 4H, NCHC<u>H</u>). A single crystal was selected for X-ray diffraction analysis, which confirmed the (*cis,cis)* stereochemistry.

*2.3.5. Treatment of **3** with pipz with formation of trans-[$PtCl_2(PPh_3)$(pipz)], **9**.*

To a solution of (*trans,trans*)-[{$PtCl_2(PPh_3)$}$_2$(μ-pipz)], **3**, in CD_2Cl_2 piperazine was added in two portions corresponding to pipz/**3** molar ratios 0.5 and 2, respectively. After each addition the system was monitored by ^{1}H- and ^{31}P-NMR (Table 4SI).

2.4. X-ray structure determinations

The X-ray diffraction experiments were carried out at room temperature by means of a Bruker Smart Breeze CCD diffractometer operating with graphite-monochromated Mo-Kα radiation. The samples were sealed in glass capillaries and their lattice parameters were evaluated as a preliminary step to the crystallographic study (Table 1). On the basis of these results the intensity data collections were done up to the limits mentioned in the table. The low limit adopted in the collection of intensities of **2**·is mainly due to the disorder which sharply cuts down the diffraction intensities at high ϑ values. The intensities were corrected for Lorentz and polarization effects and for absorption by means of a multi-scan method.[10] The structure solutions were obtained by the automatic direct methods contained in SHELX97 program.[11] After the completion of the main molecule model, the difference Fourier maps of **2**, **3** and **6a** showed clusters of broad maxima placed within cavities still present in the crystal structure. These were regarded as the crystallization solvent molecules affected by different degrees of disorder. In the crystal structure of **3** a cluster of maxima was attributed to a disordered chloroform molecule, while in the structure of **6a** the cluster was recognized as a 1,2-dichloroethane placed on an inversion centre. The residual maxima in the difference Fourier maps of the structures of **2** and **3**, are probably due to a heavily disordered solvent molecule, most likely *n*-heptane, but cannot be fitted with any reasonable conformer of this species. So the intensity data for those two structures were treated with the SQUEEZE[12]

procedure in order to remove the contribution of the disordered solvent still missing from the model.

After the introduction of hydrogen atoms in calculated positions all the heavy atoms of the main molecules were refined with anisotropic displacement parameters up to the reliability factors listed in Table 1. The presence of disorder limits the accuracy of some of these refinements but still lets discuss with a sufficient degree of reliability the connectivity and conformation of the main molecules.

In addition to the aforementioned software, other control calculations and preparation of publication material were performed with the programs contained in the suite WINGX.[13]

Table 1. Crystal data and structure refinements for compounds **2**-**3**[a]

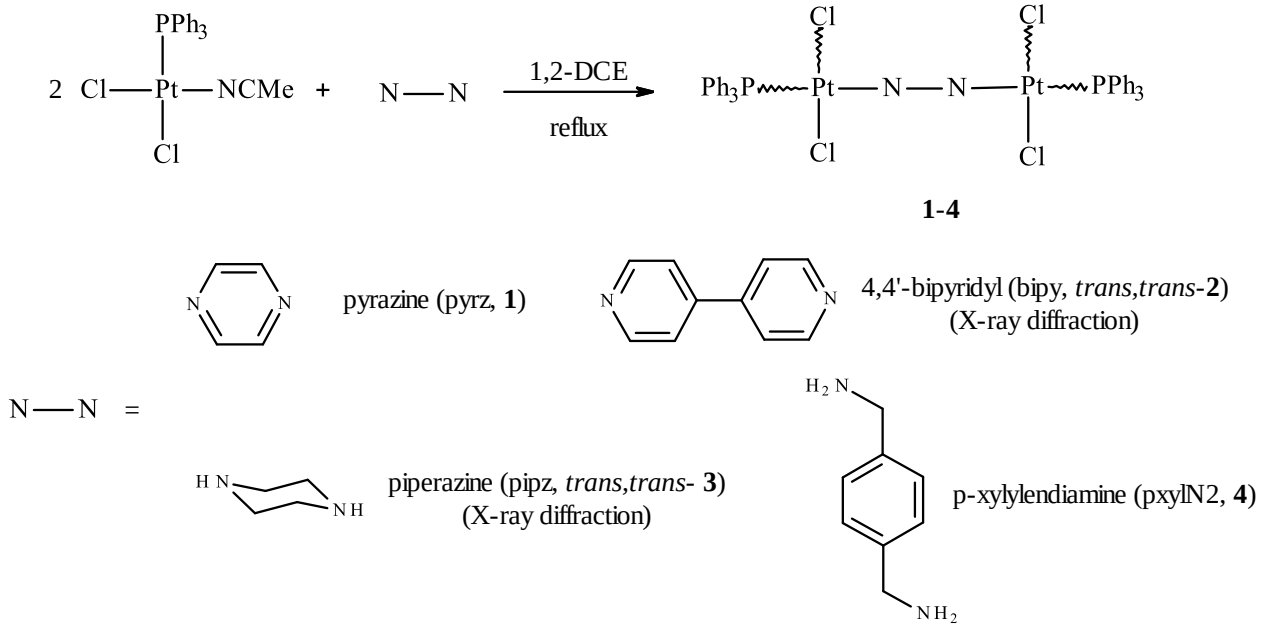
Compound	**2**	**2b**	**3** · 2($CHCl_3$)
Empirical formula	$C_{46}H_{38}Cl_4N_2P_2Pt_2$	$C_{46}H_{38}Cl_4N_2P_2Pt_2$	$C_{42}H_{42}Cl_{10}N_2P_2Pt_2$
Formula weight	1212.70	1212.70	1381.39
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$Pbca$ (No. 61)	$C2/c$ (No. 15)
a / Å	10.0774(19)	10.8826(4)	25.1921(5)
b / Å	9.5758(18)	15.5332(5)	16.3487(3)
c / Å	28.126(5)	24.8585(9)	14.0157(3)
α / °	-	-	-
β / °	99.639(8)	-	103.0420(10)
γ / °	-	-	-
U / Å^3	2675.8(9)	4202.1(3)	5623.6(2)
Z	2	4	4
Dcalc / Mg · m^{-3}	1.505	1.917	1.632
μ / mm^{-1}	5.510	7.018	5.539
ϑ_{max} /°	23.81	25.79	30.45
No. measured	17030	13715	28828
No. unique [R_{int}]	4081 [0.0404]	3928 [0.0597]	8269 [0.0354]
No. parameters	255	253	281
R_1, wR_2 [$I>2\sigma(I)$] [a]	0.0294, 0.0650	0.0408, 0.0808	0.0478, 0.1362
R_1, wR_2 [all data] [a]	0.0440, 0.0688	0.0870, 0.0941	0.0863, 0.1593
Goodness of fit [b] on F^2	0.879	0.976	0.794

[a] Crystal data and structure refinements for complex **6a** are reported in Table 5SI. [b] $R(F_o) = \Sigma\,||F_o|-|F_c||\,/\,\Sigma|F_o|$; $Rw(F_o^2) = [\Sigma[w(F_o^2-F_c^2)^2]\,/\,\Sigma[\,w(F_o^2)^2]]^{½}$; $w = 1\,/\,[\sigma^2\,(F_o^2) + (AQ)^2 + BQ]$ where $Q = [MAX(F_o^2,0) + 2F_c^2]\,/\,3$; GOF = $[\Sigma\,[w(F_o^2-F_c^2)^2]/(N-P)]^{½}$, where N, P are the numbers of observations and parameters, respectively

3. Results and discussion

3.1. Syntheses.

The syntheses of the dinuclear complexes **1**-**4**, [{$PtCl_2(PPh_3)$}$_2$(μ-N—N)], were carried out by reacting *cis*-[$PtCl_2(PPh_3)$(NCMe)][7e] with the nitrogen bidentate divergent N—N ligands in molar ratio 2:1 (Scheme 1).



Scheme 1. Synthesis of the dinuclear complexes **1**-**4**

The reactions were carried out in refluxing 1,2-DCE for two reasons: a) under these conditions fast isomerisation of the precursor to the *trans* form is observed; b) at lower temperature attack to the nitrile is possible in the case of the secondary and primary amine.[7b,d] The processes were monitored by ^{31}P-NMR spectroscopy and in all cases the signal attributable to the platinum precursor (4.83 ppm, $^{1}J_{P\text{-}Pt}$ = 3570 Hz) disappeared in about 3 hours, while a new signal with satellites was observed (Table 2).

Table 2. Observed ^{31}P-NMR signals in dinuclear complexes **1**-**4**.

product	N—N	δ/ppm ($^{1}J_{P\text{-}Pt}$/Hz)
1	pyrz	2.79 (3728)
2	bipy	2.64 (3611)
3	pipz	3.56 (3603)
4	pxylN2	3.87 (3646)

A yellow, crystalline solid product separated out of each reaction mixture or precipitated upon addition of heptane. Spectroscopic analyses were carried out on the isolated complexes. The ^{31}P-, ^{13}C- and ^{195}Pt-NMR ($CDCl_3$) spectra were in agreement with the presence of a single product. In the ^{1}H-NMR spectra the N—N hydrogen atoms closest to the coordination centers showed downfield shifted signals with respect to the free ligand (Table 1 SI). Moreover, in each case, the integration of the observed ^{1}H-NMR signals matched with a 1:2 molar ratio between the coordinated N—N and PPh_3, in accordance with the dinuclear nature of the complexes. Elemental analyses too were in good agreement with the proposed formulas.

Similar dinuclear complexes containing pyrazine-derived ligands had been described in a previous study [6a] concerning the reactivity of chloro-bridged dinuclear derivatives $[Pt_2(\mu\text{-}Cl)_2Cl_2L_2]$, (L=$PEt_3$, PMe_2Ph, $PMePh_2$, ethylene). In the article, the authors underline the importance of the molar ratio between the reagents in directing the synthesis to dinuclear or mononuclear derivatives. The dinuclear products showed *trans,trans* geometry, while the formation of other geometric isomers was not observed. As for our cases, the prompt isomerisation of the precursor, *cis*-$[PtCl_2(NCMe)(PPh_3)]$,[7d,e] to the *trans*-complex (T = 80 °C) is consistent with the formation of the *trans,trans* dinuclear isomer as kinetic product, in view of the well-known *trans* effect exerted by triphenylphosphine. Nevertheless, geometrical isomerization of the product in solution (Figure 1) could not be excluded *a priori*. As a matter of fact, the presence of a single signal with satellites in ^{31}P-NMR spectra of complexes **1**-**4** allowed to rule out the *trans,cis* geometry, but both *trans,trans* and *cis,cis* isomers were compatible with the observed pattern.

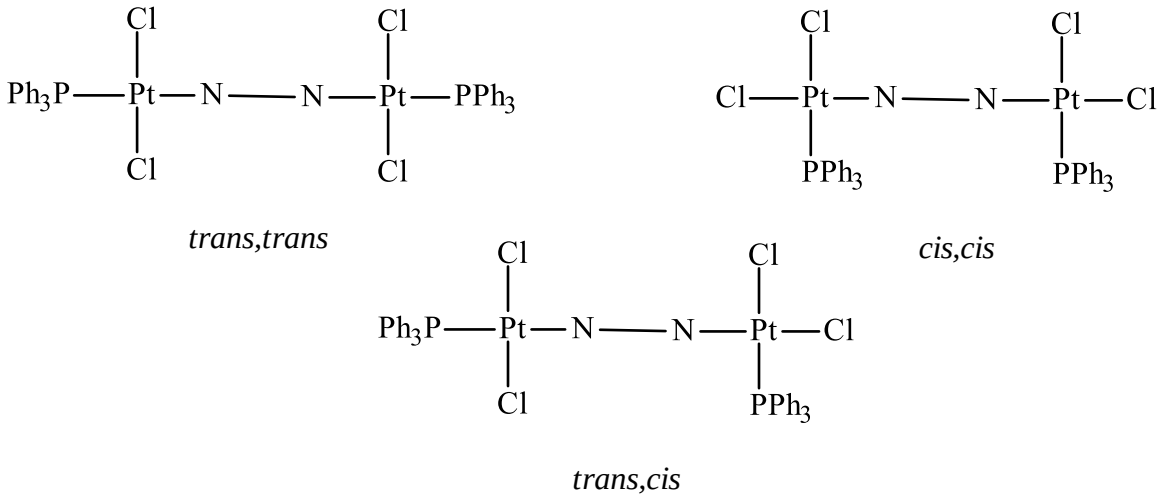


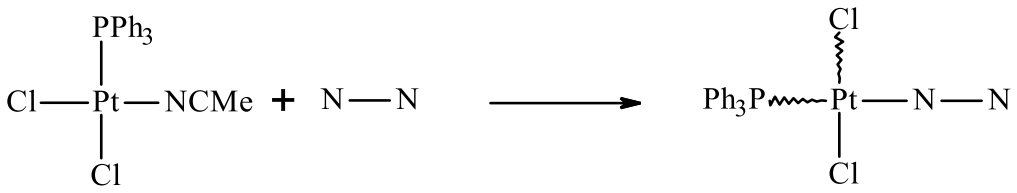
Figure 1: Possible geometric isomers for $[\{PtCl_2(PPh_3)\}_2(\mu\text{-N—N})]$ complexes

Single crystal X-ray diffraction studies established the square planar coordination around platinum centers and the *trans,trans* geometry for complexes **2** and **3** (See *3.2*).

Since the observed ^{31}P-NMR chemical shifts and $^{1}J_{P\text{-}Pt}$ coupling constants (Table 2) are similar for all dinuclear compounds **1**-**4**, we can assign them a common *trans,trans* geometry. The pure complexes do not isomerize in $CHCl_3$ solution, as checked by ^{31}P-NMR.

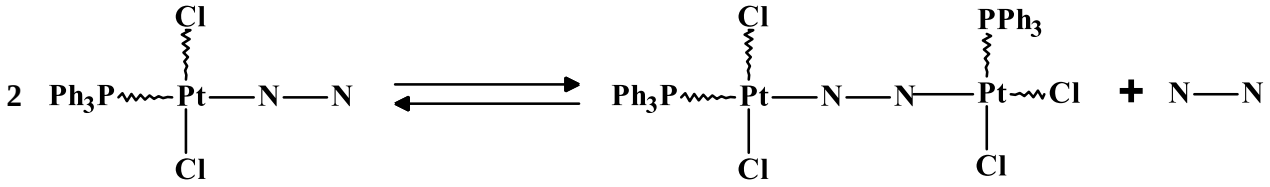
The synthetic procedure can be extended to higher nuclearity complexes following the denticity of the divergent ligand. As an example, the tridentate ligand py3TRIA [8] was reacted with *trans*-$[Pt(\mu\text{-}Cl)_2Cl_2(PPh_3)_2]$ in 1,2-DCE affording a product identified as *(trans,trans,trans)*-$[\{PtCl_2(PPh_3)\}_3(\mu\text{-py3TRIA})]$, **5** (see experimental details and discussion in SI).

Within this study the reaction of *cis*-[$PtCl_2(PPh_3)(NCMe)$] [7e] with N—N in 1/1 molar ratio (Scheme 2) was tested. It is expected the formation of mononuclear complexes, retaining one dangling donor atom on the bidentate divergent ligand (Scheme2).



Scheme 2. Synthesis of mononuclear complexes

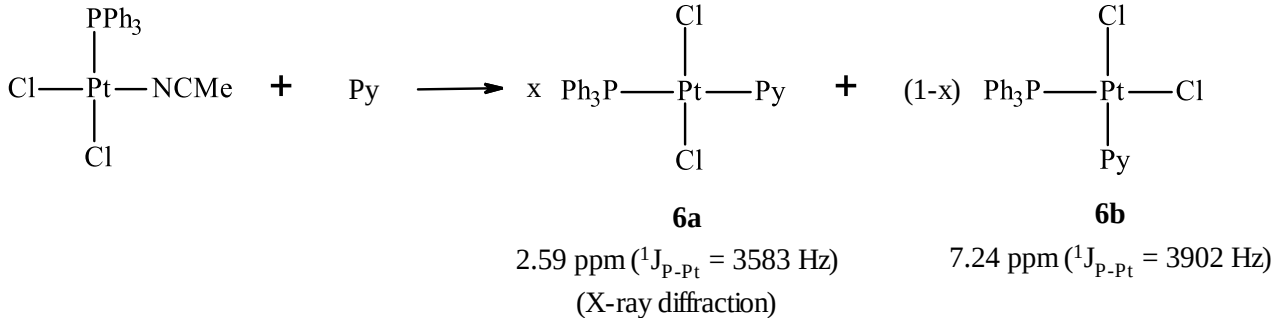
However, the literature reports that mononuclear species of the type *trans*-[$PtCl_2L(N—N)$] (L = phosphine or $CH_2=CH_2$ and N—N a bidentate divergent hetero-aromatic base) are in equilibrium with the corresponding *trans,trans* dimers [{$PtCl_2(PPh_3)$}$_2$(μ-N—N)] (Scheme 3).[6a]



Scheme 3. Equilibrium between mononuclear and dinuclear species.

When the reaction between *cis*-[$PtCl_2(PPh_3)(NCMe)$] and pyrazine was carried out with molar ratio 1:1, preliminary results showed the presence of a complex system containing the dinuclear *trans,trans* derivative **1**, free pyrazine and two mononuclear products, as revealed by the ^{1}H-NMR spectrum of the reaction mixture. The most reasonable hypothesis was that both geometrical isomers of the mononuclear product were formed. Nevertheless, in previous experiences concerning the preparation of [$PtCl_2(PPh_3)(NHRR')$] with a series of monodentate aliphatic amines [7a-d,14], the exclusive formation of *trans*-[$PtCl_2(PPh_3)(NHRR')$] complexes was observed and no isomerisation of the product was detected, probably because of the higher stability of these geometric isomers.[7a-d,14] It could be expected that also the reaction sketched in Scheme 2 afforded the *trans* isomer of the mononuclear product. Anyway, since heteroaromatic bases in place of amines could in principle affect the relative stability of the two geometrical isomers,[15] we first studied the reaction between *cis*-[$PtCl_2(PPh_3)(NCMe)$][7e] and pyridine, as the monodentate base allowed to reduce the number of species present at equilibrium. The reaction, monitored by ^{31}P-NMR spectroscopy, proceeded to completion in a couple of hours with formation of two products. Two signals of about the same intensity [2.59 ppm ($^1J_{P\text{-}Pt}$ = 3583 Hz) and 7.24 ppm ($^1J_{P\text{-}Pt}$ = 3902

Hz)] were observed. Moreover, the solid product obtained after the work up of the reaction mixture showed an elemental analysis in agreement with the formula $[PtCl_2(PPh_3)(py)]$. Solutions of the product revealed in the ^{31}P-NMR spectrum the two signals previously observed in the spectrum of the reaction mixture. These data showed that we were dealing with the two geometrical isomers *cis*- and *trans*-$[PtCl_2(PPh_3)(py)]$ (Scheme 4).



6a

2.59 ppm ($^1J_{P\text{-}Pt}$ = 3583 Hz)

(X-ray diffraction)

6b

7.24 ppm ($^1J_{P\text{-}Pt}$ = 3902 Hz)

Scheme 4. Synthesis of $[PtCl_2(py)(PPh_3)]$

A sample was dissolved in $CHCl_3$ and pentane was added by slow diffusion with formation of single crystals suitable for X-ray diffraction studies which showed that the isomer *trans*-$[PtCl_2(PPh_3)(py)]$ had been separated by crystallization (Figure 1.SI).

The NMR spectra of a freshly prepared solution of the crystals allowed the assignment of the resonances due to the *trans* isomer and as a consequence also to the *cis* isomer. At variance with the previously reported cases involving the aforementioned amines,[7a-d] both the geometric isomers formed with pyridine (Scheme 4).

This outcome supported our hypothesis concerning the formation of both geometrical isomers of the mononuclear product $[PtCl_2(PPh_3)(pyrz)]$ by reacting *cis*-$[PtCl_2(PPh_3)(NCMe)]$ with pyrazine in molar ratio 1:1. The reaction, carried out with an excess of pyrazine, yielded a suspension of a colourless solid that was recovered by filtration and characterized by NMR spectroscopy. Its ^{31}P-NMR ($CDCl_3$) spectrum showed a single signal at 7.13 ppm ($^1J_{P\text{-}Pt}$ = 3810 Hz), while the integration of ^{1}H-NMR signals confirmed the mononuclear nature of the product, that was supported also by elemental analysis data. On the basis of ^{31}P-NMR analogy with **6b**, the complex was identified as *cis*-$[PtCl_2(PPh_3)(pyrz)]$ (**7b**). From the filtrate of the reaction mixture a second crop of solid was obtained, containing **7b** and a second product showing the same composition, corresponding to the geometric isomer *trans*-$[PtCl_2(PPh_3)(pyrz)]$ (**7a**) according to its NMR spectral features. Selected ^{1}H- and ^{31}P-NMR signals of **7a**, **7b** are reported in Table 3, together with those of **1**, **6a**, **6b** and free pyrazine.

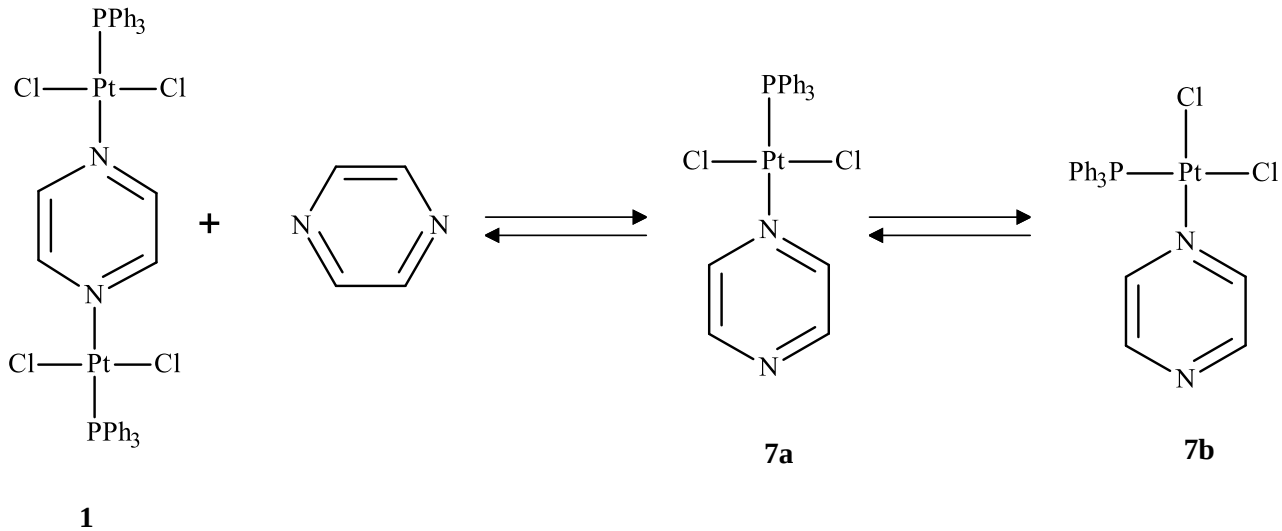
Table 3. Selected ^{1}H- (Pt-NC<u>H</u>) and ^{31}P-NMR signals of free pyrz, **1**, **6** and **7** in $CDCl_3$

Species	^{1}H/ppm ($^{3}J_{H\text{-}Pt}$/Hz)	^{31}P/ppm ($^{1}J_{P\text{-}Pt}$/Hz)
pyrazine	8.59	/
1	9.33 (nd)	2.79 (3728)
6a	9.03 (32)	2.59 (3583)
6b	8.45 (40)	7.24 (3902)
7a	9,09 (21)	2.69 (3662)
7b	8,40 (41)	7.13 (3810)

nd= not detectable

For both isomers it was possible to measure $^{3}J_{H\text{-}Pt}$ for hydrogen atoms closest to coordinated nitrogen, with *cis* isomer showing a higher coupling constant. It has to be underlined that *trans* mononuclear **7a** and dinuclear **1** complexes show very similar ^{31}P-NMR chemical shifts and $^{1}J_{P\text{-}Pt}$ coupling constants, so that it is necessary to carry out an accurate integration of ^{1}H-NMR signal to clearly distinguish between the two species. A mixture of the two isomers **7a** and **7b** was also obtained by reacting *trans*-$[Pt_2(\mu\text{-}Cl)_2Cl_2(PPh_3)_2]$ with a slight excess of pyrazine (pyrz/Pt molar ratio = 1.3).

In a further experiment, the formation of the mononuclear derivatives was studied starting from the dinuclear complex **1** that was dissolved in $CDCl_3$ into an NMR test tube and treated with portions of pyrazine (Table 2 SI). After the first addition corresponding to a pyrz/**1** molar ratio = 1), both **1** and **7a** were observed (^{1}H- and ^{31}P-NMR). After the further addition (pyrz/**1** molar ratio = 2), signals due to **1** disappeared and the mononuclear *trans*-complex **7a** was initially detected as the main component. However, partial isomerisation to the *cis*-complex **7b** was soon observed in solution (Scheme 5). Although both isomers were present in solution, the lower solubility of **7b** allowed its separation in pure form.



1 **7a** **7b**

Scheme 5. Equilibria for the system **1**/pyrz.

A sample of pure **7b** was dissolved in $CDCl_3$ and ^{1}H- and ^{31}P-NMR spectra were recorded. They clearly show both partial isomerization to **7a** and partial dimerization to **1**. The equilibrium composition at room temperature was reached in about 48 h. The ^{1}H-NMR spectrum integrals allowed the assessment of the equilibrium constant concerning the reaction sketched in Scheme 3 (N-N = pyrz). The constant, calculated as $K = \{[\mathbf{1}] \times [pyrz]\}/\{[\mathbf{7a}] + [\mathbf{7b}]\}^2$, corresponded to about 5.4×10^{-3}. This value is similar to that reported in the literature for an analogous system where only the *trans* isomer of the mononuclear species was detected.[6a]

The reaction of the *trans,trans* dinuclear **2** complex with bipy to obtain the mononuclear derivative $[PtCl_2(PPh_3)(bipy)]$, was similarly monitored by ^{1}H- and ^{31}P-NMR in CD_2Cl_2 as solvent. Selected spectroscopic data are reported in Table 3SI, together with the characteristic resonances for dinuclear **2** in the same solvent. Since ^{1}H-NMR signals of different species were partially superposed, it was not possible to integrate them correctly, nevertheless the main features of the system could be described.

For a bipy/**2** molar ratio of 1, ^{31}P-NMR spectrum did not vary appreciably, while two new signals with the same intensity appeared in the ^{1}H-NMR spectrum (9.14 and 8.79 ppm), besides a multiplet due to free bipy (8.75 ppm) and the signal of dinuclear **2** (9.20 ppm). Signals at 9.14 and 8.79 ppm were ascribed, in analogy with the system **1**/pyrz, to *trans*-$[PtCl_2(PPh_3)(bipy)]$ (**8a**). It has to be noted that ^{31}P-NMR signals of **2** and **8a** were not distinguishable in CD_2Cl_2. For a bipy/**2** molar ratio of 2, the signals due to **2** disappeared in ^{1}H-NMR spectrum, where, besides the multiplets due to free bipy and **8a**, a new one at 8.59 ppm was attributed to the mononuclear species *cis*-$[PtCl_2(PPh_3)(bipy)]$ (**8b**). The molar ratio between **8a** and **8b** was estimated about 1. In a few days a colorless solid separated out and single crystals were chosen for structural X-ray determination (Figure 5). Quite unexpectedly, the solid turned out to be the dinuclear complex with *cis,cis* geometry (*cis,cis*)-$[\{PtCl_2(PPh_3)\}_2(\mu\text{-bipy})]$, **2b**).

Despite the very scarce solubility of the complex **2b** in CD_2Cl_2 it was possible to carry out a ^{1}H-NMR experiment, showing the following, not previously observed signals (Figure 2): δ 8.55 (m, 4H, Hα); 7.72 (m, 12H, PPh_3); 7.49 (m, 6H, PPh_3); 7.38 (m, 12H, PPh_3); 7.00 (m, 4H, Hβ).

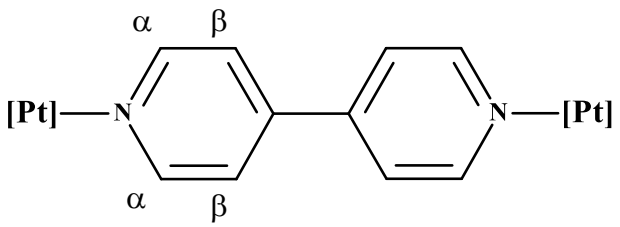
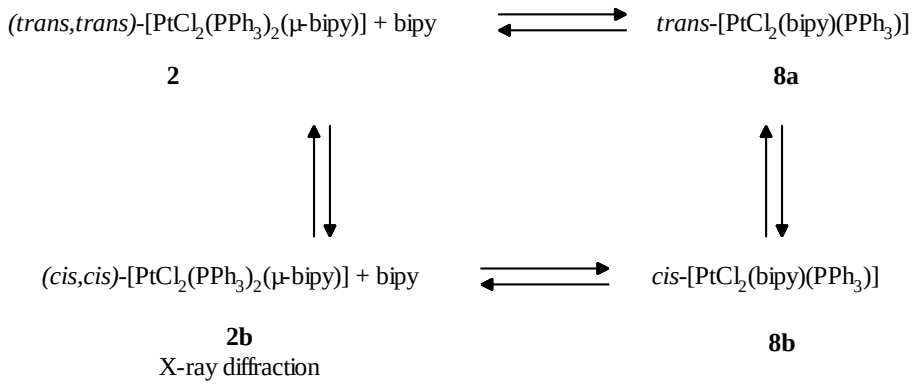


Figure 2. Magnetically non-equivalent bipy hydrogen nuclei in **2b**.

All these data can be rationalized by the simultaneous presence of equilibria concerning the nuclearity of the species, their geometrical isomerism and, finally, their solubility (Scheme 6). It is to be underlined that *trans* to *cis* isomerization of both mononuclear and dinuclear species appears detectable only in the presence of free ligand. This behavior is in agreement with the known catalytic effect of free ligands in the isomerization processes concerning platinum(II) complexes.



Scheme 6. Equilibria involving the system "**2**/bipy"

For the system "**3** + piperazine", where a secondary aliphatic diamine was involved, the formation of a single product was revealed by ^{31}P- and ^{1}H-NMR spectroscopy in the presence of an excess of the ligand, reasonably the mononuclear complex *trans*-[$PtCl_2(PPh_3)$(pipz)] (**9**), by comparison with the NMR parameters of the products discussed before (Table 4 SI).

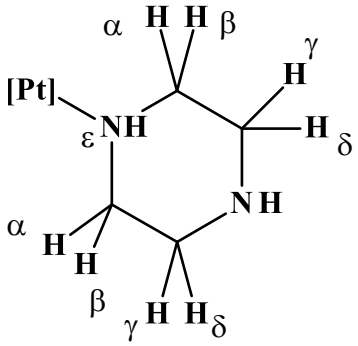


Figure 3. Magnetically non-equivalent piperazine hydrogen nuclei in **9**.

^{1}H-NMR spectrum of mononuclear complex **9** is characterized by five signals for non-equivalent hydrogen atoms (Figure 3), while a signal with satellites is present in the ^{31}P-NMR spectrum, with values of chemical shift and coupling constants very close to those observed for the *trans* dinuclear precursor. Moreover, at variance with systems containing heteroaromatic ligands (py, pyrz and bipy), no isomerization of the piperazine complexes was observed.

When the preparation of **9** was attempted by using a stoichiometric amount of piperazine, an equilibrium involving **3**, **9** and the free ligand was again observed (Scheme 3). The integration of ^{1}H-NMR signals allowed an assessment of the constant of the equilibrium K = {[**3**] × [piper]}/[**9**]^2, corresponding to about 0.15.

3.2 Structural determinations

Selected bond lengths and angles for complexes **2**, **2b** and **3** (Figures **4**-**6**) are summarized in Table 4. The Pt coordination is square planar with very little distorsions presumably due to the encumbrance of the different ligands. The Cambridge Crystallographic Database [**Errore. Il segnalibro non è definito.**] contains the structural data of several compounds including the unit {$PtCl_2$aminophosphine}, more commonly with the chloride ligands in *trans* configuration (43 examples) and less commonly in the *cis* one (8 examples). The bond lengths we found in our compounds (Table 4) are all within the range of expected values: 2.30(2) Å for Pt–Cl *trans* to Cl, 2.36(1) Å for Pt–Cl *trans* to the phosphine, 2.03(2) Å for Pt–N *trans* to Cl, 2.13(4)Å for Pt–N *trans* to the phosphine and 2.23(1) Å for Pt–P.

Table 4. Bond lenghts [Å] and angles [°] around Pt atom

	2	**2b**	**3**
Pt–N	2.102(5)	2.035(6)	2.138(5)
Pt–P	2.2272(14)	2.249(2)	2.2388(15)
Pt–Cl(1)	2.2731(16)	2.299(2)	2.289(2)
Pt–Cl(2)	2.2791(16)	2.348(2)	2.2872(18)
N–Pt–P	178.47(13)	93.25(18)	179.79(15)
N–Pt–Cl(1)	87.85(13)	175.22(18)	89.07(17)
N–Pt–Cl(2)	88.82(13)	86.55(18)	83.61(17)
P–Pt–Cl(1)	93.67(6)	91.44(8)	90.78(7)
P–Pt–Cl(2)	89.66(6)	178.58(8)	96.55(7)
Cl(1)–Pt–Cl(2)	176.67(6)	88.74(8)	172.19(7)

The molecular structures of **2** and **2b** are reported in figures 4 and 5.

The metal coordination planes in **2** are parallel and almost coplanar (deviation 0.23 Å). The plane of the bipyridyl ligand makes with them a dihedral angle of 53.4°.

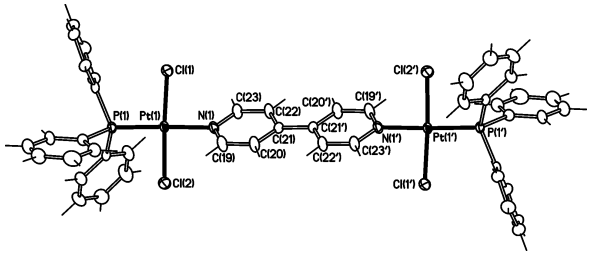


Figure 4 View of the molecular structure of **2** as found in the crystals of **2** . Thermal ellipsoids are at 20% probability. ′ = 3 – *x*, – *y*, 2 – *z*.

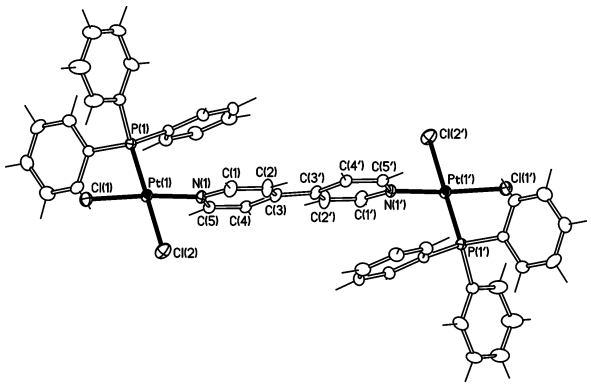


Figure 5. View of the molecular structure of **2b**. Thermal ellipsoids are at 20% probability. ′ = 2 – *x*, – *y*, 1 – *z*.

In **2b** (Figure 5) platinum coordination planes are parallel and almost coplanar (deviation 0.20 Å) and make a dihedral angle of 70.7° with the plane of the bipyridyl ligand. It is worth to note that each phosphine ligand have a phenyl group slanted towards the nearest pyridyl ring. The two rings are almost parallel (dihedral angle 13.9°) with a relatively short distance between the centroids (3.56 Å), suggesting an intramolecular π-stacking interaction.

The platinum coordination planes in **3** (Figure 6) are again parallel and almost coplanar. The hydrogen atom connected with the nitrogen N(1) also lies on the metal coordination plane with a N(1)–Pt(1)–Cl(2) angle of 83.3°, suggesting at some extent a H···Cl(2) interaction.

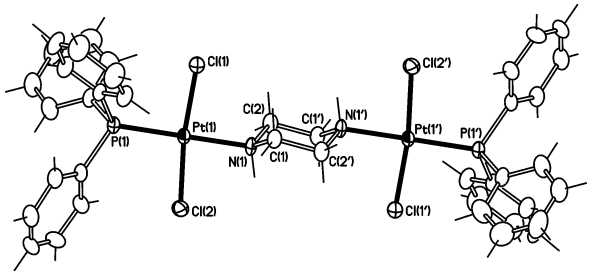


Figure 6. View of the molecular structure of **3** as found in the crystals of **3** · 2 ($CHCl_3$) . Thermal ellipsoids are at 20% probability. ′ = 1 – *x*, 1 – *y*, 2 – *z*.

4. Conclusions

The preparation of dinuclear complexes [{$PtCl_2(PPh_3)$}$_2$(μ-N—N)], where N—N = nitrogen bidentate divergent ligand, can be carried out with good yields starting from *cis*-[$PtCl_2(PPh_3)$(NCMe)], with an accurate control of the molar ratio between reagents (Pt/N—N molar ratio = 2). Products, characterized by *trans,trans* geometry, appear stable in solution for many days.

If a different molar ratio between reagents is used (Pt/N—N molar ratio = 1) equilibria are established involving the already described dinuclear derivatives, the corresponding mononuclear complexes [$PtCl_2(PPh_3)$(N—N)] and the free ligand. Equilibrium constants were estimated as instability constants of the mononuclear species containing pyrazine ($K = 5.4 \cdot 10^{-3}$) and piperazine (K = 0.15). The comparison between the obtained values show the higher stability of the mononuclear species containing the heteroaromatic base. The existence of such equilibria suggests some prudence in planning syntheses involving the mononuclear complexes of the type here described. For instance, they could in principle be considered suitable precursors of heterobimetallic dinuclear compounds, as they retain one dangling donor atom on the bidentate divergent ligand, able to penetrate the coordination sphere of another metal, Nevertheless, in view of their facile dimerization, a mixture of products could be obtained. Under the conditions useful to obtain mononuclear derivatives, the geometrical isomerization of the species in solution was observed with the heteroaromatic bases pyrazine and 4,4'-bipyridyl. Moreover, besides isomerization and dimerization equilibria, solubility can play a role. For instance, in the case of the bipy based system, the very low solubility of the dinuclear *(cis,cis)*-[$\{PtCl_2(PPh_3)\}_2$(μ-bipy)], **2b**, allowed its isolation and structural characterization.

With the secondary diamine piperazine, only products (both dinuclear and mononuclear) with *trans* geometry were observed, even when an excess of the ligand was added. This result is in agreement with previous data,[7a-d,14] where platinum(II) complexes containing amines of the type *(trans)*-[$PtCl_2(PPh_3)$(RR'NH)] did not show any isomerization to the *cis* isomers in solution, probably for the significantly higher stability of the isomer having the π-acid phosphine *trans* to the rather basic amine.

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Appendix A. Supplementary data

Experimental details concerning the preparation of **5** as well as some spectroscopic data are reported as Supplementary Information.

CCDC 1484284-1484287 contain the supplementary crystallographic data for the derivatives **2**$^{\cdot}$, **2b**, **3**$\cdot$2($CHCl_3$) and **6a**$\cdot$0.5($C_2H_4Cl_2$). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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