### Synthesis, Characterization, and Reactivity of Cationic Palladium(II) and Platinum(II) Iodo Complexes Containing a Linear or a Tripodal Aminophosphine. The X-Ray Crystal Structures of [Pd{HN(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>}I]I and [Pd<sub>3</sub>{N(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>}<sub>3</sub>)<sub>2</sub>I<sub>4</sub>]I<sub>2</sub>

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Dedicated to Professor Joachim Strähle on the Occasion of his 65th Birthday

Abstract. The complexes [M(PNHP)I]I (PNHP = bis[2-(diphenylphosphino)ethylamine; M = Pd (1), Pt (2)) and  $[M(NP_3)I]I$  $(NP_3 = tris[2-(diphenylphosphino)ethyl]amine; M = Pd (3), Pt (4))$ were prepared by interaction of the appropriate aminophosphine in CH<sub>2</sub>Cl<sub>2</sub> with aqueous solutions containing [MCl<sub>4</sub>]<sup>2-</sup> salts and NaI in a ratio 1:4. Complexes 2 and 3 form the polynuclear compounds [Pt<sub>2</sub>(PNHP)<sub>3</sub>]I<sub>4</sub> (2a) and [Pd<sub>3</sub>(NP<sub>3</sub>)<sub>2</sub>I<sub>4</sub>]I<sub>2</sub> (3a) in the presence of coordinating solvents such as the mixture CD<sub>3</sub>OD/D<sub>2</sub>O/ DMSO-d<sub>6</sub> and CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH, respectively. Complex 1 consists of distorted square-planar cations [Pd(PNHP)I]<sup>+</sup> and iodide anions able to establish short N-H…I interactions of 2.850 Å. The aminophosphine adopts a boat conformation and is coordinated to palladium in a tridentate chelating fashion. The crystal structure for cations of 3a reveals the presence of two types of distorted square-planar Pd<sup>II</sup> atoms, PdNP<sub>2</sub>I and trans-PdP<sub>2</sub>I<sub>2</sub>, NP<sub>3</sub> acting as tridentate chelating and bridging ligand, respectively. On the basis of <sup>31</sup>P {<sup>1</sup>H} NMR data it has been shown that each distorted square-planar Pt(II) centre of 2a contains one PNHP acting as tridentate chelating ligand with the other aminophosphine bridging the two metals via the P atoms. Complexes 3 and 4 were shown by  $^{31}P \{^{1}H\}$  NMR to have the metal atom bound to the three P atoms of NP3 and one iodo ligand. Additions of AcCysSH and GSH to 4 result, by a ring-opening process, in the formation of  $[Pt(NP_2PO)(SR)]$  (RS = Acys (4a), GS (4b)) in which the ligand contains a dangling arm phosphine oxide group and the platinum atom achieves the four-coordination involving the N atom of the aminophosphine. Compounds  $[Pt_2(PNHP)_3]Cl_4$  (2a', 2a"). [PtAu(PNHP)<sub>2</sub>I]I<sub>2</sub> (2b), and [Pt(PNHP)(ONO<sub>2</sub>)](NO<sub>3</sub>) (2c) were detected in some extent in solution by reaction of complex 2 with Au(tdg)Cl (tdg = thiodiglycol), AuI and excess AgNO<sub>3</sub>, respectively. While 1 does not react with AuI, complex 3 affords the heterobimetallic complexes PdCu(NP<sub>3</sub>)I<sub>3</sub> (5), PdAg<sub>2</sub>(NP<sub>3</sub>)I<sub>4</sub> (6) and  $PdAu(NP_3)I_3$  (7) by interaction with the appropriate iodide M'I (M' = Cu, Ag, Au) via a chelate ring-opening.

Keywords: Palladium; Platinum; Iodo complexes; NMR spectroscopy; Polynuclear cationic species; Crystal structures

### Synthese, Charakterisierung und Reaktivität der Palladium(II)- und Platin(II)-Iod-Komplexe mit einem linearen bzw. einem tripodalen Aminophosphan-Liganden. Die Kristallstrukturen von [Pd{HN(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>}]] und [Pd<sub>3</sub>{N(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>}<sub>2</sub>I<sub>4</sub>]I<sub>2</sub>

Inhaltsübersicht. Die Komplexe [M(PNHP)I]I (PNHP = Bis[2-(diphenylphosphino)ethyl]amin; M = Pd(1), Pt(2)) und [M(NP<sub>3</sub>)I]I  $(NP_3 = Tris[2-(diphenylphosphino)ethyl]amin; M = Pd (3), Pt (4))$ wurden präpariert durch Umsetzung des betreffenden Aminophosphans in CH2Cl2 mit wäßrigen Lösungen der [MCl4]2--Salze und NaI im Verhältnis 1:4. Die Komplexe 2 und 3 bilden die mehrkernige Verbindungen [Pt<sub>2</sub>(PNHP)<sub>3</sub>]I<sub>4</sub> (2a) und [Pd<sub>3</sub>(NP<sub>3</sub>)<sub>2</sub>I<sub>4</sub>]I<sub>2</sub> (3a) in Gegenwart von Lösungsmittelgemischen wie CD<sub>3</sub>OD/D<sub>2</sub>O/ DMSO-d<sub>6</sub> bzw. CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH. Komplex 1 enthält die verzerrt quadratisch-planaren Kationen [Pd(PNHP)I]<sup>+</sup> und Iod-Anionen mit kurzen N-H…I-Kontakten von 2,850 Å. Aminophosphan hat Boot-Konformation und ist dreizähnig, chelatartig an Palladium koordiniert. Die Kristallstruktur der Kationen von 3a zeigt die Anwesenheit von zwei Arten von verzerrt guadratisch-planaren Pd<sup>II</sup>-Atomen in PdNP<sub>2</sub>I und trans-PdP<sub>2</sub>I<sub>2</sub>; NP<sub>3</sub> ist ein dreizähniger Chelat- bzw. –Brückenligand. Auf Basis der <sup>31</sup>P{<sup>1</sup>H}-NMR-Daten wird gezeigt, dass jedes der verzerrt quadratisch-planar koordinierten Pt<sup>II</sup>-Atome von **2a** ein PNHP als dreizähnigen Chelatliganden enthält und mit dem anderen Aminophosphan werden die zwei Metallatome verbrückt. In den Komplexen **3** und **4** ist nach den <sup>31</sup>P{<sup>1</sup>H}-NMR-Daten das Metallatom an die drei P-Atome des NP<sub>3</sub> und an einen Iod-Liganden gebunden.

Zusatz der Thiole AcCysSH und GSH zu **4** führt zu einer Ringöffnung und Bildung von [Pt(NP<sub>2</sub>PO)(SR)] (RS = Acys (**4a**), GS (**4b**)) in denen der Ligand eine angehängte Phosphanoxid-Gruppe enthält und das Platinatom vierfache Koordination erreicht unter Einbeziehung des N-Atoms des Aminophosphans. Die Verbindungen [Pt<sub>2</sub>(PNHP)<sub>3</sub>]Cl<sub>4</sub> (**2a**', **2a**''), [PtAu(PNHP)<sub>2</sub>I]I<sub>2</sub> (**2b**) und [Pt(PNHP)(ONO<sub>2</sub>)](NO<sub>3</sub>) (**2c**) wurden in Lösung bei der Reaktion von **2** mit Au(tdg)Cl (tdg = Thiodiglykol), AuI bzw. einem ξberschuß an AgNO<sub>3</sub> beobachtet. Während **1** nicht mit AuI reagirt, ergibt **3** die heterobimetallischen Komplexe PdCu(NP<sub>3</sub>)I<sub>3</sub> (**5**), PdAg<sub>2</sub>(NP<sub>3</sub>)I<sub>4</sub> (**6**) und PdAu(NP<sub>3</sub>)I<sub>3</sub> (**7**) beim Umsatz mit den Iodiden von Cu, Ag bzw. Au durch die Ringöffnungsreaktion.

### Introduction

The flexible coordination behaviour of hemilabile ligands containing "soft" and "hard" donor atoms such as phosphorus and nitrogen, respectively, have been exploited to maximize the stability of a series of metal complexes implicated in several catalytic and biologically relevant reactions [1-3]. The coordination chemistry of terdentate PNP aminophosphines toward palladium(II) has been explored and PP-dimeric, PNP-monomeric and PP-monomeric modes of coordination were found [2,4]. Due to the weaker donor ability of the nitrogen atom to latter transition metal atoms than phosphines, these complexes can isomerize between *cis* and *trans* configurations the ligand altering between the biand terdentate modes. By changing the steric and electronic requirements of the R substituent at the nitrogen atom, the ligand backbone and the other coligands, it is possible to control metal-nitrogen bond dissociation or association and consequently improve the catalytic or biological efficiency of conventional reactions [2,3,5a]. There was no influence of the coligand in the structures found for Pd<sup>II</sup> and Pt<sup>II</sup> complexes of the types M(PNP)X [PNP = deprotonated  $Z,Z-PPh_2CH_2CBu^t=N-N=CBu^tCH_2PPh_2$ , (M = Pd; X = Cl, Br, Me), (M = Pt; X = Cl, Br, I)] where PNP is acting as a tridentate chelating ligand [5b] or  $Pt(PNP)X_2$  (PNP =  $(Cy_2PCH_2)_2NMe$ , Cy = Cyclohexyl, X = Cl, I) with PNP adopting a bidentate PP-coordination mode [5c]. However, while the Pt<sup>II</sup> chloro complex of the ligand, (R)-N,N-bis(2-(diphenylphosphino)ethyl)-1-phenyl-ethylamine shows a cis configuration in *cis*-Pt( $\eta^2$ -P,P-PNP)Cl<sub>2</sub>, its reaction with KI in the presence of SnCl<sub>2</sub> leads to the formation of the ionic complex [Pt(PNP)I](SnCl<sub>3</sub>) with the nitrogen atom involved in the coordination to the platinum atom [5a].

There are only a few X-ray crystal structures reported in the literature corresponding to palladium(II) and platinum(II) complexes of the aminophosphine bis[2-(diphenylphosphino)ethyl]amine (PNHP) [4,6] and its NH substituted derivative, tris[2-(diphenylphosphino)ethyl]amine (NP<sub>3</sub>) [7–9]. On the other hand, the structural studies in solution for halo complexes are very limited [10]. To the best of our knowledge there are no crystallographic studies on polynuclear complexes of d<sup>8</sup> metal ions with these aminophosphines.

The aim of this work is to increase the knowledge on the coordination chemistry of PNHP and NP<sub>3</sub> to latter transition metals. For this reason we report the preparation and characterization of the mononuclear iodo compounds [M(PNHP)I]I and  $[M(NP_3)I]I$  (M = Pd, Pt) and their reactivity as a function of the metal, the tripodal or linear amin-

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(i) 2 in  $(CD_3OD/D_2O/DMSO-d_6)$ ; 2 + 3RSH (RSH = AcCysSH, GSH) (ii) 2 + 2Au(tdg)Cl (cation 2a' = cation 2a). (iii) 2 + 2AuI (iv) 2 + 6AgNO<sub>3</sub>

Scheme 1 The formation of the diplatinum ionic complex 2a from solutions of [Pt(PNHP)I]I in CD<sub>3</sub>OD/D<sub>2</sub>O/DMSO-d<sub>6</sub>. Reactions of [Pt(PNHP)I]I with thiols, gold(I) salts and silver(I) nitrate to form 2a, (2a', 2a'', 2b) and 2c, respectively.

ophosphine arrangement and the iodo ligand substitutions. We describe the formation of polynuclear cationic complexes, thiolate adducts containing an uncoordinated phosphine oxide group and heterobimetallic complexes involving gold group metal ions which induce a chelate ring-opening of the precursor.

### **Results and Discussion**

### Preparations and characterization

Schemes 1 and 2 show the complexes prepared in this work with the linear aminophosphine PNHP and the tripodal NP<sub>3</sub>. Both aminophosphines were synthesized following a variation of the methods described in the literature [11-13].

Complexes 1-4 were obtained from the organic phase by addition of dichloromethane solutions of the hydrochloride salt of PNHP or the free NP<sub>3</sub> to aqueous solutions of  $[MCl_4]^{2-}$  salts (M = Pd, Pt) in the presence of sodium iod-ide (M:I ratio 1:4).

The presence of coordinating solvents in solutions of **2**  $(CD_3OD/D_2O/DMSO-d_6)$  and **3**  $(CH_2Cl_2/CH_3OH)$  allowed the formation of the dinuclear and trinuclear ionic complexes  $[Pt_2(PNHP)_3]I_4$  (**2a**) and  $[Pd_3(NP_3)_2I_4]I_2$  (**3a**), respectively, complex **2a** coexisting with **2**. The reactions of solu-

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Scheme 2 The formation of the trinuclear ionic complex 3a from solutions of  $[Pd(NP_3)I]I(3)$  in  $CH_2Cl_2/CH_3OH$ . Reations of 3 with gold group metal iodides to form 5, 6 and 7 and reactivity of  $[Pt(NP_3)I]I(4)$  with thiols to form 4a and 4b.

tions of 2 with Au(tdg)Cl in CD<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH leads to the formation of dinuclear ionic species [Pt<sub>2</sub>(PNHP)<sub>3</sub>]Cl<sub>4</sub> (2a', 2a"). Complex 2a' was obtained as a solid by reaction of aqueous solutions of K<sub>2</sub>[PtCl<sub>4</sub>] with (PNHP).HCl in dichloromethane using the appropriate Pt:(PNHP).HCl ratio, 2:3. When this reaction was carried out using a 1:1 ratio the diplatinum compound [Pt<sub>2</sub>(PNHP)<sub>3</sub>]Cl<sub>4</sub> (2a') was majority revealing that complex [Pt(PNHP)Cl]Cl can not be achieved under the same experimental conditions as [Pt(PNHP)I]I (2). Furthermore, the analogous bromo complex was previously prepared by us [14] as the dinuclear system  $[Pt_2(PNHP)_3]Br_4$ . The formation of  $[PtAu(PNHP)_2I]I_2$  (2b) in a mixture with 2 and [Pt(PNHP)(ONO<sub>2</sub>)](NO<sub>3</sub>) (2c) in a mixture with [Pt<sub>2</sub>(PNHP)<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub> (2a\*) was detected by reaction of 2 with AuI (CDCl<sub>3</sub>/CD<sub>2</sub>Cl<sub>2</sub>) and excess AgNO<sub>3</sub>  $(CD_3OD/D_2O/DMSO-d_6)$ , respectively.

The reactions of **4** with the thiols AcCysSH and GSH in DMSO-d<sub>6</sub>/D<sub>2</sub>O afford the systems [Pt(NP<sub>2</sub>PO)(SR)] [RS = ACysS (**4a**), GS (**4b**)]. By addition of an small excess of CuI and AuI over the 1:1 stoichiometric ratio to dichloromethane solutions of **3**, complexes PdCu(NP<sub>3</sub>)I<sub>3</sub> (**5**) and PdAu(NP<sub>3</sub>)I<sub>3</sub> (**7**) were obtained, respectively. The formation of a heterobimetallic PdAg complex required the use of a 1:2 stoichiometric ratio in PdAg<sub>2</sub>(NP<sub>3</sub>)I<sub>4</sub> (**6**). Attempts to obtain heterobimetallic complexes of the types PdM'(PNHP)I<sub>3</sub> and PtM'(PNHP)I<sub>3</sub> (M' = Cu, Ag, Au) starting from **1** and **2** were unsuccessful as was previously observed for [Pd(PNHP)X]X (X = Cl, Br) [15].

Complexes 1, 3 - 6 gave satisfactory microanalyses for hydrates, while 2 and 7 were isolated as ether and dichloromethane solvates, respectively.

The molar conductivities for complexes 1 - 3 in CH<sub>3</sub>CN and for 4 in DMF are indicative of a 1:1 electrolyte behaviour. Complexes 5 and 6 behaves as neutral species in  $10^{-3}$  M DMF solutions while solutions of 7 in CH<sub>3</sub>CN are conductors [16].

The FAB mass spectra for complexes 1 - 4 showed peaks due to MLI fragments resulting by the loss of the iodo counteranion. The same tendency of fragmentation was found for the analogous chloro and bromo complexes [Pd(PNHP)X]X or [M(triphos)X]X (triphos = bis[2-(diphenylphosphino)ethyl]phenylphosphine) [15,17]. Complexes 5 and 7 showed peaks assigned to the fragments PdM'(NP<sub>3</sub>)I<sub>2</sub> (M' = Cu, Au) in accordance with the formation of heterobimetallic compounds.

The N-H vibration observed in the near infrared spectra  $(4000 - 500 \text{ cm}^{-1})$  of complexes 1 and 2 is shifted to higher energy compared to the free amine as a result of the complexation [18]. The far infrared spectra  $(500-100 \text{ cm}^{-1})$  for complexes 1-5 and 7 showed Pd-I stretchs assignable to terminal bonds [19].

### Structural Studies in Solution: ${}^{31}P {}^{1}H NMR$ Spectra of Complexes 1-4

The singlets at  $\delta$  37.9 for 1 and  $\delta$  3.5 and 36.0 (integration ratio 1:2) for **3** in their  ${}^{31}P$  { ${}^{1}H$ } NMR spectra (Table 1) are indicative of a distorted square-planar geometry at palladium with PNHP and NP<sub>3</sub> acting as PNP and PPP-tridentate chelating ligands, respectively. This contrasts with the behaviour of the chloro complex [Pd(NP<sub>3</sub>)Cl]Cl which seems to involve the N atom of NP<sub>3</sub> in the coordination to the metal [10b,20]. The <sup>31</sup>P {<sup>1</sup>H} NMR spectra for 2 (Figure 1a) and 4 (Table 1) in CDCl<sub>3</sub> and DMSO-d<sub>6</sub> consist of one and two signals, respectively at  $\delta$  33.2 and  $\delta$  -4.4 and 27.6 with <sup>1</sup>J(<sup>195</sup>Pt, <sup>31</sup>P) values in accordance with P trans to P [2625 Hz (2), 2597 Hz (4)] and P trans to I [3726 Hz (4)]. These data suggest for 2 and 4 a square-planar arrangement to the metal in solution similar to 1 and 3, respectively although on the basis of the broadening of the signals in 4, the participation in some extent of the N atom in the coordination to platinum should not be excluded.

The <sup>31</sup>P {<sup>1</sup>H} NMR spectrum for **2** in the coordinating solvents mixture (CD<sub>3</sub>OD/D<sub>2</sub>O/DMSO-d<sub>6</sub>) shows the presence of two species (Table 1). The signal at  $\delta$  37.5 with <sup>1</sup>J(<sup>195</sup>Pt,<sup>31</sup>P) of 2596 Hz is due to complex **2** (55 %) and the two signals at  $\delta$  -5.5 and 43.1 integrating by 2P and 4P with <sup>1</sup>J(<sup>195</sup>Pt,<sup>31</sup>P) couplings of 3130 Hz (P *trans* to N) and 2568 Hz (P *trans* to P), respectively evidence the formation of the diplatinum compound [Pt<sub>2</sub>(PNHP)<sub>3</sub>]I<sub>4</sub> (**2a**) (45 %). This complex contains two PNHP ligands involving the three donor atoms in the coordination to the platinum and the third aminophosphine bridges the two PtNP<sub>2</sub><sup>A</sup> centres through the P<sup>B</sup> atoms (Scheme 1).

<b>Table 1</b> ${}^{31}P$ { ${}^{1}H$ } NMR data for complexes 1–7 and react
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	δP <sup>a)</sup>	Solvent	<sup>1</sup> J( <sup>195</sup> Pt, <sup>31</sup> P)
1	37.9s	CDCl <sub>3</sub>	
1 + 2 eq. AuI	37.0s	CDCl <sub>3</sub>	
2	33.2s	CDCl <sub>3</sub>	2625
2	37.5s[2P] (2)	CD <sub>3</sub> OD/D <sub>2</sub> O/DMSO-d <sub>6</sub>	2596
	-5.5s[2P], 43.1s[4P] (2a)		3130, 2568
2a'	-6.6s[2P], 41.7s[4P]	CDCl <sub>3</sub>	3114,2594
<b>2</b> + 2 eq. Au(tdg)Cl	-1.1s[2P], 33.9bs[4P] <sup>b)</sup> (2a')	CD <sub>2</sub> Cl <sub>2</sub> /CH <sub>3</sub> OH	2343 <sup>b</sup> )
1 ( )	$0.9bs[2P], 19.9s[2P]^{b}, 28.6s[2P]^{b}$ (2a")	2 2 5	1610 <sup>b)</sup> , 2630 <sup>b)</sup>
2 + 2 eq. AuI	33.8s[2P] ( <b>2</b> )	CDCl <sub>3</sub> /CD <sub>2</sub> Cl <sub>2</sub>	2614
	-0.9s[1P], 42.1s[1P], 45.4s[2P] (2b)	5 2 2	
$2 + 6 \text{ eq. AgNO}_3$	$-5.9t[2P], 43.2d[4P]^{b,c}$ (2a*)	CD <sub>3</sub> OD/D <sub>2</sub> O/DMSO-d <sub>6</sub>	2564 <sup>b)</sup>
105	46.1 [2P] (2c)	5 2 0	2582
2 + 3 eq. AcCysSH <sup>d</sup>	35.5s[2P](2)	CD <sub>3</sub> OD/D <sub>2</sub> O/DMSO-d <sub>6</sub>	2591
1 5	-7.1bs[2P], 41.9d[4P] <sup>b),c)</sup> (2a)	5 2 0	2589 <sup>b</sup> )
$2 + 6 \text{ eq. AgNO}_3$			
+ 3 eq. AcCvsSH <sup>d</sup> )	48.1s[2P]	CD <sub>3</sub> OD/D <sub>2</sub> O/DMSO-d <sub>6</sub>	2531
	$-5.2t[2P], 44.5d[4P]^{c}$ (2a*)	51 21 110	3130, 2297
$2 + 3 \text{ eq. GSH}^{d}$	35.58 (2)	CD <sub>3</sub> OD/D <sub>2</sub> O/DMSO-d <sub>6</sub>	2586
1	37.5d <sup>e)</sup>	5 2 0	
	$-7.0s[2P], 40.9d[4P]^{c}$ (2a)		
3	3.5s[1P], 36.0s[2P]	$CD_2Cl_2$	
4	-4.4bs[1P], 27.6bs[2P]	DMSO-d <sub>6</sub>	3726, 2597
4 + 2 eq. AcCvsSH <sup>d)</sup>	$36.4s[2P]^{b}$ , $37.7s[1P]$ (4a)	DMSO-d <sub>6</sub> /D <sub>2</sub> O	2719 <sup>b)</sup>
$4 + 2  \text{eq. GSH}^{(d)}$	$36.9bs[2P]^{b}$ , $38.1bs[1P]$ (4b)	DMSO-d <sub>6</sub> /D <sub>2</sub> O	2831 <sup>b)</sup>
5	-26.5bs[1P], 34.4s[2P]	CDCl <sub>2</sub>	
	-26.8bs[1P], 2.2s[2P]	2	
6	-4.0bs[2P], 40.1s[1P]	CDCl <sub>2</sub>	
7	18.7s[1P], 33.6s[2P]	CDCl <sub>2</sub>	
	32.2s[1P], 33.8s[2P]		

<sup>a)</sup> [Relative intensities: nP]. <sup>b)</sup>  $\delta/^{1}J(^{195}Pt, ^{31}P)$ . <sup>c)</sup>  $^{2}J(^{31}P, ^{31}P) = 20$  Hz. <sup>d)</sup> pH = 3.0-4.5. <sup>c)</sup>  $^{2}J(^{31}P, ^{31}P) = 11$  Hz



Figure 1  ${}^{31}P$  { ${}^{1}H$ } NMR spectra for: (a) [Pt(PNHP)I]I (2) in CDCl<sub>3</sub>, (b) [Pt<sub>2</sub>(PNHP)<sub>3</sub>]Cl<sub>4</sub> (2a') in CDCl<sub>3</sub>, (c) [Pd(NP<sub>3</sub>)I]I (3) in CD<sub>2</sub>Cl<sub>2</sub>, (d) PdAu(NP<sub>3</sub>)I<sub>3</sub> (7) in CDCl<sub>3</sub>. For atom labelling see Schemes 1 and 2 and Figure 2.

### Reactions of complexes 1-4

*Reactions with metal salts.* While complex 1 retains its structure in solution by addition of AuI (Table 1) showing the absence of interaction, complex 2 reacts with Au(tdg)Cl and AuI to form diplatinum and heterobimetallic complexes, respectively. The addition of two equivalents of Au(tdg)Cl to 2 in CD<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH leads to a <sup>31</sup>P {<sup>1</sup>H} NMR spectrum

showing signals at  $\delta$  –1.1 and 33.9 integrating by 2P and 4P atoms, respectively due to  $[Pt_2(PNHP)_3]Cl_4$  (**2a**') and three resonances at  $\delta$  0.9, 19.9 and 28.6 integrating for 2P in each case attributable to an potential isomer **2a**" (Eq. (1)).

$$3[Pt(PNHP)I]I + 6Au(tdg)Cl \xrightarrow[CD_2Cl_2/CH_3OH]{} (1)$$

$$[Pt_2(PNHP)_3]Cl_4 + 6Au(tdg)I + PtCl_2$$

$$(2a', 2a'')$$

The <sup>1</sup>J(<sup>195</sup>Pt, <sup>31</sup>P) value of 1610 Hz for the signal at  $\delta$  19.9 suggests a five-coordination of platinum (**2a**'') in accordance with the proposed structure of Figure 2. The signal at downfield for **2a**'' was attributed to P<sup>A</sup> atoms in a square-planar arrangement [<sup>1</sup>J(<sup>195</sup>Pt, <sup>31</sup>P) = 2630 Hz, P *trans* to P] while the signals at  $\delta$  19.9 and 0.9 can be attributed to P<sup>A'</sup> and (P<sup>B</sup>, P<sup>B'</sup>), respectively the P<sup>A'</sup> and P<sup>B'</sup> atoms being involved in a trigonal-bipyramidal geometry.

Complex 2a' containing the same cation as 2a (Scheme 1) was isolated as a solid and its <sup>31</sup>P {<sup>1</sup>H} NMR spectrum in CDCl<sub>3</sub> is shown in Figure 1b. This spectrum unequivocally confirms the presence of two aminophosphines coordinating in a tridentate chelating fashion (P<sup>A</sup>) and the third acting as a PP-bridging ligand (P<sup>B</sup>), the coupling constants <sup>1</sup>J(<sup>195</sup>Pt,<sup>31</sup>P<sup>A</sup>) = 2594 Hz and <sup>1</sup>J(<sup>195</sup>Pt,<sup>31</sup>P<sup>B</sup>) = 3114 Hz being characteristic of P *trans* to P and P *trans* to N, respectively.

In spite of the higher inertness of platinum complexes compared to the analogous of palladium the reaction be-



**Figure 2** Structures proposed in solution for the cation  $[Pt_2(PNHP)_3]^{4+}$  of **2a**",  $[PtAu(PNHP)_2I]I_2$  (**2b**),  $PdCu(NP_3)I_3$  (two isomers of **5**),  $PdAg_2(NP_3)I_4$  (**6**) and  $PdAu(NP_3)I_3$  (two isomers of **7**).

tween [Pt(PNHP)I]I and AuI in CDCl<sub>3</sub>/CD<sub>2</sub>Cl<sub>2</sub> seems to occur in some extent (Table 1). Besides the signal due to the precursor **2** at  $\delta$  33.8 with <sup>1</sup>J(<sup>195</sup>Pt,<sup>31</sup>P) = 2614 Hz there appeared three singlets at  $\delta$  –0.9, 42.1 and 45.4 with integration ratios 1:1:2 suggesting the formation of the heterobimetallic complex [PtAu(PNHP)<sub>2</sub>I]I<sub>2</sub> (**2b**). The structure proposed for **2b** (Figure 2) is in agreement with an assignation of the signal at downfield to P<sup>A</sup> and the signals at  $\delta$  42.1 and –0.9 to P<sup>B'</sup> and P<sup>B</sup>, respectively.

The formation of the nitrate derivative  $[Pt(PNHP)-(ONO_2)](NO_3)$  (2c) coexisting with  $[Pt_2(PNHP)_3](NO_3)_4$ (2a\*) (Table 1) requires the interaction of 2 with excess AgNO<sub>3</sub> (Eq. (2), cs = coordinating solvents).

$$\begin{array}{ccc} 4[Pt(PNHP)I]I + 6AgNO_3 & \stackrel{cs}{\longrightarrow} & [Pt_2(PNHP)_3](NO_3)_4 \\ (2) & (2a^*) \end{array}$$
(2)

+ [Pt(PNHP)(ONO<sub>2</sub>)](NO<sub>3</sub>) +  $6AgI \downarrow + Pt(cs)_2I_2$ (2c)

Copper(I), silver(I) and gold(I) are able to induce a chelate ring-opening of 3 with formation of the heterobimetallic complexes  $PdCu(NP_3)I_3$  (5),  $PdAg_2(NP_3)I_4$  (6) and PdAu(NP<sub>3</sub>)I<sub>3</sub> (7). The <sup>31</sup>P {<sup>1</sup>H} NMR spectra of 5 and 7 are different to that of the precursor 3 (Figure 1c) and reveal the presence of two isomers. The signals at  $\delta$  34.4 (5) and 33.6 (7, Figure 1d) can be attributed to the axial  $P^{G}$ atoms of the distorted trigonal-bipyramidal centre for the neutral isomer (Figure 2) and the resonances at  $\delta$  -26.5 and 18.7 to the  $P^{H}$  atoms of the PM'I fragments (M' = Cu, Au). The second isomer seems to be neutral and ionic for 5 and 7, respectively in accordance with conductivity measurements. The resonances at  $\delta$  2.2 (5) and 33.8 (7) can be assigned to the P<sup>L</sup> and P<sup>E</sup> atoms of the neutral and cationic distorted square-planar palladium centres for 5 and 7, respectively, the signals at higher field  $\delta$  -26.8 (5) and 32.2 (7) corresponding to the linear PM'I moieties  $[P^{H}](M' =$ Cu),  $P^F (M' = Au)$ ].

The two signals found in the <sup>31</sup>P {<sup>1</sup>H} NMR spectrum of **6** in CDCl<sub>3</sub> at  $\delta$  -4.0 and 40.1 with integration ratio 2:1 are consistent with the structure proposed in Figure 2. The signal at higher field corresponds to P<sup>N</sup> atoms of the linear PAgI fragments while the resonance at  $\delta$  40.1 can be as-



Figure 3 Molecular Structure of 1



Figure 4 Molecular Structure for the cation of 3a

signed to the  $P^M$  atom involved in a five-membered chelate ring around palladium. The conductivity measurements also support this proposal of a neutral complex in solution.

**Reactions with thiols.** The interaction of 2 with thiols such as AcCysSH or GSH in a 1:3 stoichiometric ratio (Table 1) gives the dinuclear species 2a coexisting with unreacted complex 2. The signal at  $\delta$  37.5 for the reaction (2 + 3GSH) atributable to the thiolate adduct was not observed in the same process involving AcCysSH. Likewise from the reaction (2 + 3AcCysSH) in the presence of 6 eq. of AgNO<sub>3</sub> is difficult to evidence the Pt-thiol interaction. However, complex 4 interacts with these thiols in (DMSO $d_6/D_2O$  (Table 1), undergoing a chelate ring-opening with spontaneous oxidation of one P atom of NP<sub>3</sub>, to give compounds 4a (AcCysSH) and 4b (GSH) (Scheme 2). The resonances at  $\delta$  37.7 (4a) and 38.1 (4b) were assigned to the  $P^{F}=O$  groups and the signals at  $\delta$  36.4 (4a) and 36.9 (4b) with <sup>1</sup>J(<sup>195</sup>Pt, <sup>31</sup>P) values of 2719 and 2831 Hz, respectively were attributed to PE trans to PE involved in the two fused five-membered chelate rings.

fable 2 Summary of crysta	al parameters	, data collection	and refinement	for 1	$\cdot H_2O^{a}$	and <b>3a</b> <sup>a)</sup>
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	$1 \cdot H_2O$	3a
Empirical formula	$C_{28}H_{31}I_2NP_2OPd$	$C_{84}H_{84}I_6N_2P_6Pd_3$
Formula weight/gmol <sup>-1</sup>	819.68	2387.95
T/K	150(2)	150(2)
λ/Å	0.71073 (Mo)	0.71073 (Mo)
Crystal size/mm	$0.28 \times 0.25 \times 0.21$	$0.48 \times 0.20 \times 0.19$
Colour/habit	yellow/ block	orange/block
Crystal system	monoclinic	triclinic
Space group	$P2_{1/c}$	ΡĪ
a/Å	18.601(5)	11.3850(13)
b/Å	11.413(3)	12.8047(15)
c/Å	14.934(4)	15.4113(18)
$\alpha l^{\circ}$	90	94.7940(10)
βl°	111.06(2)	104.128(2)
γ/°	90	100.585(2)
V/Å <sup>3</sup>	2958.5(13)	2122.1(4)
Z	4	1
Calculated density/Mg m <sup>-3</sup>	1.840	1.869
Absorption coefficient/mm <sup>-1</sup>	2.844	2.968
F(000)	1584	1148
$\theta$ range for data collection/°	2.73 to 25.03	1.38 to 28.91
Reflections collected	5214	19097
Independent reflections	$5212 [R_{int} = 0.0332]$	9936 $[R_{int} = 0.0210]$
Max. and min. transmission	0.133/0.188	1/0.626
Data/restraints/parameters	5212/0/317	9936/0/457
Goodness of fit on $F^2$	1.022	1.005
Final <i>R</i> indices	$R_1 = 0.0482$	$R_1 = 0.0269$
	$\dot{wR}_2 = 0.1287$	$\dot{wR}_2 = 0.0663$
Criterion for observation	$I > 2\sigma$ (I)	$I > 2\sigma(I)$
Largest diff. peak and hole (e Å <sup>-3</sup> )	2.631/-1.299	1.223/-0.603

<sup>a)</sup> Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC 176099 and CCDC 176100. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk; e-mail for deposition: deposit@ccdc.cam.ac.uk).

# Solid state structures of $1 \cdot H_2O$ and 3a: X-ray crystallography

Perspective views of the molecular structures and numbering schemes of complexes  $1 \cdot H_2O$  and 3a are shown in Figures 3 and 4. A summary of crystal structure parameters, data collection and refinement is given in Table 2, and selected bond lengths and angles are listed in Table 3.

Palladium(II) exhibits a distorted square-planar geometry in both complexes  $1 \cdot H_2O$  and 3a. The aminophosphine PNHP in  $1 \cdot H_2O$  is a tridentate chelating ligand bound through the three donor atoms (PNP) and the fourth coordination site is occupied by an iodide. A second iodide is the counteranion. The structural arrangement for  $1 \cdot H_2O$ is the same as that found for [Ni(PNHP)Cl]Cl [4] and analogous to [Pt(triphos)X]X (X = Cl, Br, I) [21].

The Pd-N bond length [2.093(5) Å] is slightly higher than the same distances for [Pd(PNHP)X]X [X = Cl, 2.061(5) Å; X = Br, 2.070(5) Å] in consistence with the higher *trans* effect of iodo over chloro and bromo ligands [15,22]. On the other hand, the smaller *trans* influence of the nitrogen over the phosphorus produces a Pd-I bond distance [2.5912(8) Å] shorter than for the triphos complex [Pd(triphos)I]I [2.665(2) Å] [23]. The Pd-P distances [2.2961(2), 2.2948(2) Å] are close to values given in the literature for other Pd<sup>II</sup> complexes with two mutually *trans* – PPh<sub>2</sub> moieties [24].

Table 3	Selected	distances/Å	and	angles/°	for	complexes	1	•	$H_2O$
and <b>3a</b>									

	$1 \cdot H_2O$	3a
Pd(1)-P(1)	2.2961(2)	2.3069(7)
Pd(1)-P(2)	2.2948(2)	2.2802(7)
Pd(2)-P(3)		2.3415(7)
Pd(2)-P(3a)		2.3415(7)
Pd(1)-N(1)	2.093(5)	2.114(2)
Pd(1)-I(1)	2.5912(8)	2.5757(4)
Pd(2)-I(2)		2.5863(3)
Pd(2)-I(2a)		2.5863(3)
P(2)-Pd(1)-P(1)	164.98(7)	170.06(3)
P(3)-Pd(2)-P(3a)		180.00(2)
N(1)-Pd(1)-P(1)	84.58(2)	86.14(6)
N(1)-Pd(1)-P(2)	83.60(2)	84.75(6)
P(2)-Pd(1)-I(1)	95.38(5)	93.38(2)
P(1)-Pd(1)-I(1)	96.61(5)	96.011(2)
P(3)-Pd(2)-I(2)		93.069(2)
P(3)-Pd(2)-I(2a)		86.931(2)
P(3a)-Pd(2)-I(2a)		93.069(2)
P(3a)-Pd(2)-I(2)		86.931(2)
N(1)-Pd(1)-I(1)	178.48(2)	175.10(6)
I(2a)-Pd(2)-I(2)		180.000(2)

The coordination sphere for palladium is tetrahedrally distorted from planar arrangement, with the two phosphorus atoms on one side (0.099/0.101 Å) of the least-squares plane defined by [P(1), P(2), N(1), I(1)] and with

the nitrogen (0.120 Å) and the iodine (0.079 Å) atoms on the opposite side. The palladium atom is displaced 0.081 Å from the least-squares plane and to the same side as the nitrogen and iodine atoms.

The N-Pd-I angle is 178.48(2) Å which is close to the ideal 180°. In contrast, the P-Pd-P angle is found to be only 164.98(7) Å, probably as a result of ring strain in the tridentately bonding PNP ligand. The small P-Pd-N angles for the two adjacent five-membered chelate rings [83.60(2)°, 84.58(2)°] also display the strained coordination geometry of the rings, as generally observed in five-membered phosphine chelate rings [25]. In this case, the ethylene chains of the ligand adopt a boat conformation (Figure 3) which was also previously observed for [Pd(PNHP)Br]Br and which is absent in  $[Pd(PNHP)X]X (X = Cl, NO_3)$ . Furthermore, 1 · H<sub>2</sub>O shows N-H…I bonds of 2.850 Å involving the I counteranion. This type of short interactions were also found for the bromo derivative (N-H. Br, 2.371 Å) while were not observed in  $[Pd(PNHP)X]X (X = Cl, NO_3) [15]$ . The short contacts can be explained as a consequence of the greater trans effect of iodo and bromo over chloro or oxygen of  $NO_3^-$  which allows the approach of the counteranions to the N-H bonds. On the other hand, the presence of a water molecule in the opposite side of the iodo ligand also leads to short iodo counteranion-oxygen and carbon(6)-oxygen contacts (3.630 and 3.375 Å, respectively). The value of C(6)-H···O bond was found to be 2.414 Å.

The X-ray crystal structure of **3a** is made up of  $[Pd_3(NP_3)_2I_4]I_2$  units consisting of trinuclear dications  $[Pd_3(NP_3)_2I_4]^{2+}$  (Figure 4) and iodide anions. The cations contain two distorted square-planar PdNP<sub>2</sub>I centres with NP<sub>3</sub> acting as tridentate chelating ligand through the nitrogen and two phosphorus atoms and forming two fused five-membered chelate rings at palladium. The remaining phosphorus of each ligand are bound to a PdI<sub>2</sub> fragment in a *trans*-PdI<sub>2</sub>P<sub>2</sub> arrangement there being this palladium atom the centre of symmetry of each cation. As far as we know this is the first example of a crystal structure for a NP<sub>3</sub> compound with two types of square-planar metal centres. Likewise, there is not described in the literature any other crystal structure for a tripalladium(II) complex of NP<sub>3</sub>.

The Pd-N [2.114(2) Å], Pd-I [2.5757(4) Å] and Pd-P [2.2802(7) Å, 2.3069(7) Å] bond distances in the squareplanar PdNP<sub>2</sub>I centres are very close to those found for **1**  $\cdot$  H<sub>2</sub>O with identical arrangement at palladium. The Pd-I [2.5863(3) Å] and Pd-P [2.3415(7) Å] bond lengths in the *trans*-PdI<sub>2</sub>P<sub>2</sub> centre are slightly greater than the analogous distances in the PdNP<sub>2</sub>I centres.

The deviation of the palladium atom from the leastsquares plane defined by [P(1), P(2), N(1), I(1)] is of 0.009 Å. This deviation together with deviations of phosphorus atoms (0.078/0.082 Å) on the same side and of nitrogen and iodine (0.094/0.066 Å) on the opposite side are a consequence of the slight tetrahedral distortion from the planar geometry.

The N-Pd-I  $[175.10(6)^{\circ}]$  and P-Pd-P  $[170.06(3)^{\circ}]$  angles for the PdNP<sub>2</sub>I centres reveal a lower ring strain than in 1

•  $H_2O$ . The *trans*-PdI<sub>2</sub>P<sub>2</sub> centres show I-Pd-I angles of 180° and P-Pd-I angles slightly above [93.069(2)°] and less [86.931(2)°] than 90°.

### Conclusions

Iodide is a better hydrogen bonding acceptor site for N-H in [Pd(PNHP)X]X complexes than chloride or nitrate and behaves similarly to the bromide. The iodo complex [Pt(PNHP)I]I is mononuclear while the chloro and bromo complexes are dinuclear compounds of the type [Pt<sub>2</sub>(PNHP)<sub>3</sub>]X<sub>4</sub>. While Pt<sup>II</sup> and PNHP favoured the formation of dinuclear compounds, Pd<sup>II</sup> and NP<sub>3</sub> allowed the obtention of crystals of the unusual trinuclear ionic complex [Pd<sub>3</sub>(NP<sub>3</sub>)<sub>2</sub>I<sub>4</sub>]I<sub>2</sub>. Although [Pd(PNHP)I]I does not react with AuI the platinum derivative seems to react and form a heterobimetallic compound. Complex [Pd(NP<sub>3</sub>)I]I reacts with M'I (M' = Cu, Ag, Au) salts to obtain heterobimetallic compounds. The formation of Pt<sup>II</sup>-thiolate adducts was only observed quantitatively for interactions between thiols and the iodide derivative of NP<sub>3</sub>.

### **Experimental Part**

General Procedures. Diphenylphosphine, potassium tetrachloroplatinate(IV) and palladium(II) chloride were purchased from Strem Chemicals, potassium tert-butoxide, 2,2'-thiodiethanol and bis(2chloroehyl)amine hydrochloride from Aldrich, tris(2-chloroethyl)amine hydrochloride from Acros and sodium chloride and iodide from Panreac. THF was dried over Na and freshly distilled before use. Microanalyses were performed on a Fisons Instrument EA 1108 CHNS-O. Fast Atom Bombardment (FAB) mass spectra were obtained in a Micromass Autospec spectrometer using nitrobenzylic alcohol as the matrix. Conductivities were measured at 25 °C using 10<sup>-3</sup> M solutions in DMF or CH<sub>3</sub>CN on a WTW model LF-3 instrument. Infrared spectra were recorded at ambient temperature as KBr pellets (4000-500 cm<sup>-1</sup>) or Nujol mulls (500-100 cm<sup>-1</sup>) on a Mattson Cygnus 100 spectrophotometer. The bands are reported as s = strong, m = medium, w = weak, sh = shoulder, b = broad. <sup>31</sup>P {<sup>1</sup>H} NMR spectra were recorded on a Bruker DMX500 NMR spectrometer at 202.46 MHz. Chemical shifts ( $\delta$ ) are reported in ppm relative to external 85 % H<sub>3</sub>PO<sub>4</sub>. The signals are reported in Table 1 as s = singlet, d = doulet and bs =broad signal.

### Syntheses and titrations

Au(tdg)Cl. Solutions of Au<sup>I</sup> were prepared by treating Au with HCl and HNO<sub>3</sub> in an oil bath (120 °C) and reduction from Au<sup>III</sup> to Au<sup>I</sup> with 2,2'-thiodiethanol (thiodiglycol) as it was indicated in the literature [17,26,27].

Synthesis of PNHP. Bis[2-(diphenylphosphino)ethyl]amine (PNHP) was prepared as an air-stable hydrochloride (PNHP.HCl) [11,12]. Diphenylphosphine (14 ml, 15.0 g, 80.4 mmol) was added to a suspension of potassium tert-butoxide (23.4 g, 208.5 mmol) in dry THF (450 ml) under argon. The resulting deep red solution was stirred for 20 min and bis(2-chloroethyl)amine hydrochloride (7.1 g, 40.0 mmol) was added as a powder. The mixture was refluxed for 28 h at 80 °C and after that a 1 M solution of HCl (*ca.* 100 ml)

was added. After removing the solvents a white solid precipitated and was dried *in vacuo*. It was recrystallised from CH<sub>2</sub>Cl<sub>2</sub>/ether and washed with CH<sub>3</sub>CN. Yield: 60 %, mp 155 °C. Calc. for C<sub>28</sub>H<sub>30</sub>NP<sub>2</sub>Cl: C, 70.4; H, 6.3; N, 2.9. Found for C<sub>28</sub>H<sub>30</sub>NP<sub>2</sub>Cl (PNHP.HCl): C, 70.1; H, 6.4; N, 3.0 %.

 $^{31}\text{P}$  {<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta_{\text{P}}$  -22.7s. IR:  $\nu_{max}/$  cm $^{-1}$  (N-H) 3300. MS (FAB): m/z = 442 (M^+, 100 %).

**Synthesis of NP<sub>3</sub>.** Tris(2-diphenylphosphinoethyl)amine (NP<sub>3</sub>) was prepared as free amine [10b,13]. Diphenylphosphine (11 ml, 11.8 g, 62.9 mmol) was added to a suspension of potassium tert-butoxide (18.1 g, 160.9 mmol) in dry and freshly distilled THF (250 ml) under argon. The resulting deep red solution was stirred for 15 min and tris(2-chloroethyl)amine hydrochloride (5.0 g, 20.8 mmol) was added as a powder. The mixture was refluxed for 20 h at 80 °C, poured into 700 ml of water and cooled in an ice bath. The ligand precipitated and was filtered off, recrystallised from DMF/H<sub>2</sub>O and washed with ethanol. Yield: 78 %, mp 102 °C. Anal. Calc. for C<sub>42</sub>H<sub>42</sub>NP<sub>3</sub>: C, 77.1; H, 6.5; N, 2.1. Found: C, 77.1; H, 6.9; N, 2.1 %.

<sup>31</sup>P {<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  -22.7s.

Synthesis of [Pd(PNHP)I]I (1). Complex 1 was isolated as  $1 \cdot H_2O$ . A suspension of PdCl<sub>2</sub> (0.0743 g, 0.4188 mmol) and NaCl (0.0489 g, 0.8376 mmol) in H<sub>2</sub>O (15 ml) was heated on a water bath (80 °C) until a clear solution was obtained. This was allowed to cool to ambient temperature and NaI (0.2511 g, 1.6752 mmol) was added as a powder. Inmediately a solution of PNHP.HCl (0.2000 g, 0.4188 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (16 ml) was added dropwise and the mixture reaction was stirred for 15 h at room temperature. After that the organic phase was extracted with CH<sub>2</sub>Cl<sub>2</sub>, dried over anhidrous Na<sub>2</sub>SO<sub>4</sub>, filtered and solvent removed *in vacuo* to leave dark red solid. By recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/n-hexane, yellow crystals suitable for X-ray diffraction were obtained. Yield: 71 %, mp 239 °C. Found: C, 40.9; H, 3.8; N, 1.7. Calc. For C<sub>28</sub>H<sub>31</sub>NOP<sub>2</sub>PdI<sub>2</sub>: C, 40.9; H, 3.8; N, 1.7 %.

IR  $\nu_{max}/cm^{-1}$  (Pd-I) 1908. MS (FAB):  $m/z=673~(M^+-I,~100~\%);~547~(M^+-2I,~10~\%). \ ^{31}P \ \{^1H\}$  NMR (CDCl\_3): See Table 1.  $\Lambda(CH_3CN)=116.8~ohm^{-1}cm^2mol^{-1}.$ 

**Synthesis of [Pt(PNHP)I]I (2).** This compound was prepared as the ether solvate  $2 \cdot 1.5(CH_3CH_2)_2O$ . To a solution of  $K_2PtCl_4$  (0.1449 g, 0.3491 mmol) in H<sub>2</sub>O (16 ml) NaI (0.2318 g, 1.3964 mmol) was added as a powder. Inmediately a solution of PNHP.HCl (0.2500 g, 0.5236 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (18 ml) was added dropwise and the reaction mixture was stirred for 14 h at room temperature. After that the organic phase was extracted with CH<sub>2</sub>Cl<sub>2</sub>, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. Solvent was partially removed *in vacuo* and n-hexane was added to precipitate the light yellow solid which was filtered off and dried *in vacuo*. Yield: 72 %, mp 172 °C. Found: C, 40.9; H, 4.1; N, 1.5. Calc. For C<sub>34</sub>H<sub>44</sub>NO<sub>1.5</sub>P<sub>2</sub>PtI<sub>2</sub>: C, 40.8; H, 4.4; N, 1.4 %.

IR  $v_{max}$  /cm^{-1} (Pt-I) 151s. MS (FAB): m/z = 762 (M^+ - I, 27 %); 636 (M^+ - 2I, 4 %).  $^{31}P$  {<sup>1</sup>H} NMR (CDCl\_3): See Table 1.  $\Lambda(CH_3CN)$  = 121.8 ohm^{-1}cm^2mol^{-1}.

#### Synthesis of 2a (See Table 1).

Synthesis of  $[Pt_2(PNHP)_3]Cl_4$  (2a'). This complex was isolated as the solvate 2a'·2CH<sub>2</sub>Cl<sub>2</sub>. To a solution of K<sub>2</sub>PtCl<sub>4</sub> (0.1449 g, 0.3491 mmol) in H<sub>2</sub>O (16 ml) a solution of PNHP (0.2500 g, 0.5236 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (18 ml) was added dropwise and the reaction mixture was stirred for 22 h. After that the organic phase was extracted with CH<sub>2</sub>Cl<sub>2</sub>, dried over anhidrous Na<sub>2</sub>SO<sub>4</sub> and filtered. Solvent was partially removed *in vacuo* and n-hexane was added to precipitate the solid which was filtered off and dried *in vacuo*. Yield: 40 %, mp 175 °C. Found: C, 50.1; H, 4.8; N, 2.0. Calc. For  $C_{86}H_{91}N_3P_6Pt_2Cl_8$ : C, 49.5; H, 4.5; N, 2.0 %.

MS (FAB): m/z = 1077 (M<sup>+</sup> - 4Cl - PNHP -Pt, 8 %); 636 (M<sup>+</sup> - 4Cl - 2PNHP -Pt, 23 %). <sup>31</sup>P {<sup>1</sup>H} NMR (CDCl<sub>3</sub>): See Table 1.  $\Lambda$ (CH<sub>3</sub>CN) = 131.7 ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>.

Synthesis of [Pd(NP<sub>3</sub>)I]I (3). This complex was obtained as dihydrate 3·2H<sub>2</sub>O. A suspension of PdCl<sub>2</sub> (0.1358 g, 0.7657 mmol) and NaCl (0.0895 g, 1.5314 mmol) in CH<sub>3</sub>OH (25 ml) was heated on a water bath (80 °C) until a clear solution was obtained. This was allowed to cool to ambient temperature and NaI (0.4591 g, 3.0628 mmol) was added as a powder. Inmediately a solution of NP<sub>3</sub> (0.5000 g, 0.7657 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) was added drop-wise and the reaction mixture was stirred for 5 h at room temperature. Solvents were partially removed *in vacuo* untill an orange brown solid started to precipitate. Then ether was added to complete the precipitation of the complex which was filtered off and washed with H<sub>2</sub>O. Solid was recrystallised in CH<sub>2</sub>Cl<sub>2</sub>/ether and dried *in vacuo*. Yield: 85 %, mp > 250 °C. Found: C, 48.1; H, 4.6; N, 1.4. Calc. For C<sub>42</sub>H<sub>46</sub>NO<sub>2</sub>P<sub>3</sub>PdI<sub>2</sub>: C, 48.0; H, 4.4; N, 1.3 %.

IR  $v_{max}$  /cm<sup>-1</sup> (Pd-I) 185m. MS (FAB): m/z = 886 (M<sup>+</sup> - I, 100 %); 759 (M<sup>+</sup> - 2I, 6%).<sup>31</sup>P {<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): See Table 1.  $\Lambda$ (CH<sub>3</sub>CN) = 134.2 ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>.

Synthesis of  $[Pd_3(NP_3)_2I_4]I_2$  (3a). Methanol (*ca.* 8 ml) was added to a solution of  $[Pd(NP_3)I]I \cdot 2H_2O$  (0.010 g, 0.0095 mmol) in  $CH_2CI_2$ (10 ml) and the final solution was filtered. Orange crystals suitable for X-ray diffraction were obtained after the solution had stood at ambient temperature for some days.

**Synthesis of [Pt(NP<sub>3</sub>)I]I (4).** The compound was obtained as dihydrate 4·2H<sub>2</sub>O. To a solution of K<sub>2</sub>PtCl<sub>4</sub> (0.1907 g, 0.4594 mmol) in H<sub>2</sub>O (20 ml) NaI (0.2754 g, 1.3964 mmol) was added as a powder. Inmediately a solution of NP<sub>3</sub> (0.3000 g, 0.4594 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (12 ml) was added dropwise and the reaction mixture was stirred for 5 h at room temperature. After that CH<sub>2</sub>Cl<sub>2</sub> was extracted *in vacuo* to leave a yellow solid which was filtered off, washed with methanol and dried *in vacuo*. Yield: 73 %, mp 217 °C. Found: C, 44.5; H, 4.3; N, 1.0. Calc. For C<sub>42</sub>H<sub>46</sub>NO<sub>2</sub>P<sub>3</sub>PdI<sub>2</sub>: C, 44.3; H, 4.1; N, 1.2 %.

IR  $\nu_{max}$  /cm^{-1} (Pt-I) 151s. MS (FAB): m/z = 974 (M<sup>+</sup> - I, 16 %); 848 (M<sup>+</sup> - 2I, 3 %).<sup>31</sup>P {<sup>1</sup>H} NMR (DMSO-d\_6): See Table 1.  $\Lambda(DMF) = 64.6 \ ohm^{-1}cm^{2}mol^{-1}.$ 

Synthesis of PdCu(NP<sub>3</sub>)I<sub>3</sub> (5). This complex was prepared as  $5 \cdot 1.5 H_2O$ . To a solution of [Pd(NP<sub>3</sub>)I]I·2H<sub>2</sub>O (0.1600 g, 0.1524 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (30 ml) CuI (0.0336 g, 0.1764 mmol) was added as a solid and the reaction mixture was stirred under nitrogen in an ice bath for 24 h. After that an orange solid precipitated. Ether was added to complete the precipitation and the solid formed was filtered off and dried *in vacuo*. Yield: 86 %, mp > 250 °C. Found: C, 41.5; H, 3.9; N, 1.2. Calc. For C<sub>42</sub>H<sub>45</sub>NO<sub>1.5</sub>P<sub>3</sub>PdCuI<sub>3</sub>: C, 41.2; H, 3.6; N, 1.1 %.

IR  $\nu_{max}$  /cm^{-1} (Pd-I) 176s; (Cu-I) 159sh. MS (FAB): m/z = 1074 (M^+ - I, 3 %); 885 (M^+ - 2I - Cu, 64 %); 759 (M^+ - 3I - Cu, 2 %).^{31}P {^1H} NMR (CDCl\_3): See Table 1.  $\Lambda(CH_3CN/DMF) = 40.6/26.5 \ ohm^{-1}cm^2mol^{-1}.$ 

Synthesis of PdAg<sub>2</sub>(NP<sub>3</sub>)I<sub>4</sub> (6). The complex was prepared as dihydrate  $6.2H_2O$ . AgI (0.0695 g, 0.2958 mmol) was added as a solid to a solution of [Pd(NP<sub>3</sub>)I]I·2H<sub>2</sub>O (0.1500 g, 0.1429 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (35 ml) and the mixture was stirred for 24 h in the absence of light. The solution was filtered, concentrated to a small volume and ether was added to precipitate a yellow solid which was filtered off and dried *in vacuo*. Yield: 69 %, mp > 180–182 °C. Found: C, 32.9; H, 3.3; N, 0.9. Calc. For C<sub>42</sub>H<sub>46</sub>NO<sub>2</sub>P<sub>3</sub>PdAg<sub>2</sub>I<sub>4</sub>: C, 33.2; H, 3.1; N, 0.9 %.

MS (FAB):  $m/z = 885 (M^+ - 3I - 2Ag, 6\%)$ . <sup>31</sup>P {<sup>1</sup>H} NMR (CDCl<sub>3</sub>): See Table 1.  $\Lambda$ (DMF) = 21.5 ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>.

Synthesis of PdAu(NP<sub>3</sub>)I<sub>3</sub> (7). The compound was prepared as the solvate 7·4CH<sub>2</sub>Cl<sub>2</sub>. To a solution of [Pd(NP<sub>3</sub>)I]I·2H<sub>2</sub>O (0.1200 g, 0.1054 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (35 ml) AuI (0.0383 g, 0.1183 mmol) was added as a solid and the reaction mixture was stirred under nitrogen in an ice bath for 2 h during which a solution was obtained. It was filtered and partially concentrated *in vacuo* and ether was added to precipitate a brown solid, which was filtered off and dried *in vacuo*. Yield: 52 %, mp 162 °C (dec.). Found: C, 32.9; H, 3.3; N, 0.9. Calc. For C<sub>46</sub>H<sub>50</sub>NP<sub>3</sub>PdAuCl<sub>8</sub>I<sub>3</sub>: C, 32.9; H, 3.0; N, 0.8 %.

IR  $v_{max}$  /cm<sup>-1</sup> (Pd-I) 189w. MS (FAB): m/z = 1208 (M<sup>+</sup> - I, 10%); 885 (M<sup>+</sup> - 2I - Au, 4%).<sup>31</sup>P {<sup>1</sup>H} NMR (CDCl<sub>3</sub>): See Table 1.  $\Lambda$ (CH<sub>3</sub>CN) = 116.8 ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>.

## Titrations of 1 and 2 with gold group metal salts and of 2 and 4 with thiols

Solutions of AgNO<sub>3</sub> in CD<sub>3</sub>OD, Au(tdg)Cl in CH<sub>3</sub>OH or AuI as solid were added to a solution of complex **2** in CD<sub>2</sub>Cl<sub>2</sub> or solutions of **1** and **2** in CDCl<sub>3</sub> and CDCl<sub>3</sub>/CD<sub>2</sub>Cl<sub>2</sub>, respectively achieving different stoichiometric ratios. After 12 h the <sup>31</sup>P {<sup>1</sup>H} NMR spectrum was recorded.

The same procedure was followed for titrations of 2 (CD<sub>3</sub>OD/DMSO-d<sub>6</sub>) and 4 (DMSO-d<sub>6</sub>) with ACysSH and GSH in D<sub>2</sub>O.

The details of the experimental conditions for titrations resulting in the formation of **2a**", **2b**, **2c**, **4a** and **4b** are described in Table 1.

### X-ray crystallography

Table 2 summarises the crystal data, data collection, structural solution and refinement parameters for complexes  $1 \cdot H_2O$  and 3a. A yellow block of  $1 \cdot H_2O$  and an orange block of 3a were mounted on glass fibers and used for data collection. Crystal data were collected at 150(2) K using a Stoe Stadi4 four-circle diffractometer equipped with an Oxford Cryosystem variable temperature device for  $1 \cdot H_2O$  and a Bruker SMART CCD area detector diffractometer for 3a. Graphite monochromated Mo-K<sub> $\alpha$ </sub> radiation was used throughout for data collection. A psi-scans [28] and a SADABS [29] absorption correction was made for  $1 \cdot H_2O$  and 3a, respectively.

Structures of  $1 \cdot H_2O$  and 3a were solved by Patterson (DIRDIF) [30]. The structures were refined by full-matrix least-squares techniques on F<sup>2</sup> using the program SHELXL-97 [31]. Hydrogen atoms were placed geometrically and positional parameters were refined using a riding model. Hydrogen atoms of water molecules were not placed for  $1 \cdot H_2O$ . Atomic scattering factors were obtained with the use of International Tables for X-ray crystallography [32]. Molecular graphics were obtained from SHELXTL.

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