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Platinum(II) and palladium(II) complexes containing a mixed donor $^{\circ}P_2N^{\circ}$ multidentate ligand

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Abstract

The 'P₂N' mixed donor ligand 2-(diphenylphosphino)-*N*-[2-(diphenylphosphino)benzylidene]benzeneamine (PNCHP) reacts with [MCl₂(1,5-cyclooctadiene)] and [M(CH₃)Cl(1,5-cyclooctadiene)] to give the complexes [M(PNCHP- $\kappa^3 P, N, P$)Cl]Cl (M = Pt or Pd) and [Pd(PNCHP- $\kappa^3 P, N, P$)(CH₃)]Cl, respectively. The ionic chloride can be exchanged with BF₄⁻ by reaction with AgBF₄. Abstraction of the covalent chloride with AgBF₄ in the presence of acetonitrile yields [Pt(PNCHP- $\kappa^3 P, N, P$)(CH₃CN)]²⁺. The acetonitrile ligand of this dication can be substituted with a variety of ligands to afford complexes of the type, [Pt(PNCHP- $\kappa^3 P, N, P$)(CH₃CN)]²⁺. The acetonitrile bigand is dication can be substituted with a variety of ligands to afford complexes of the type, [Pt(PNCHP- $\kappa^3 P, N, P$)L]²⁺ (L = the monodentate ligands: triphenylphosphine, 2-picoline, 3-picoline or the chelate ligands: 1,10-phenanthroline, 2,2'-bipyridine, bis(diphenylphosphino)ethane, 2,2':6',2''-terpyridine). The latter ligands all bind in a bidentate fashion to give five-coordinate complexes. The compounds have been characterised by spectroscopic and analytical means. The single crystal structures of the four-coordinate complexes, [Pt(PNCHP- $\kappa^3 P, N, P$)Cl]Cl and [Pt(PNCHP- $\kappa^3 P, N, P$)(PPh₃)](BF₄)₂, and the five-coordinate complexes, [Pt(PNCHP- $\kappa^3 P, N, P$)Cl]BF₄)₂ (L = 1,10-phenanthroline and 2,2':6',2''-terpyridine), have been determined. © 2004 Elsevier Ltd. All rights reserved.

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1. Introduction

Interest in the chemistry of the platinum group metals with mixed-donor, multidentate ligands [1] tends to be driven by interest in these systems as potential catalysts [1a,2]. To date, studies which involve ligands containing mixed phosphorus and nitrogen donor atoms have generally focussed on bidentate ligands [1,2c,3]. In contrast, mixed donor terdentate ligands, such as the 'P₂N' ligand, 2-(diphenylphosphino)-N-[2-(diphenylphosphino)benzylidene]benzeneamine (PNCHP), have received considerably less attention. PNCHP contains two inequivalent 'soft' phosphorus donor atoms and a 'borderline' nitrogen donor atom [4] (see Scheme 1). Therefore, with respect to the Hard and Soft Acid and Base (HSAB) principle, the ligand should be well suited to binding to platinum(II) and palladium(II). The favourable 'soft'-'soft' interactions of the phosphorus donor atoms of the PNCHP ligand with the low valent metal atom of concern are expected to anchor the ligand to the platinum(II) or palladium(II) metal centre. On one hand, the 'borderline'-'soft' nitrogen-metal atom interaction will have the potential for facile dissociation, and consequently the metal-PNCHP complex could exhibit interesting reactivity patterns [5]. For example, ring-opening, which is considered to be an important step in the mechanism of successful CO insertions 'into' metal-methyl bonds involving other terdentate ligands, allows an incoming CO ligand to bind to a coordination site in the square plane *cis* to the methyl group [6]. On the other hand, PNCHP has shown preference for terdentate coordination, occupying three sites of a square plane and has shown no previous signs of ringopening [7]. Therefore, in this study we have concen-

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trated on the replacement of the chloride group with 'strong' bidentate ligands, such as 1,10-phenanthroline (phen), 2,2'-bipyridine (bipy) and bis(diphenylphosphino)ethane (diphos) as well as the terdentate, 2,2':6',2''-terpyridine (terpy) and report that these additional ligands are forced to bind to the fifth coordination site of the metal to give five-coordinate d⁸ metal complexes.

2. Results and discussion

2.1. Synthesis of $[Pt(PNCHP-\kappa^3P, N, P)(MeCN)](BF_4)_2$ (3) and related compounds

The syntheses of $[M(PNCHP-\kappa^3P, N, P)Cl]Cl$ (M = Pd 1a or Pt 1b) and $[Pd(PNCHP-\kappa^3P, N, P)-(CH_3)]Cl$ (7) are depicted in Scheme 2. PNCHP coordinates to platinum(II) and palladium(II) in a terdentate fashion by displacing 1,5-cyclooctadiene (COD) and one chloride from $[M(COD)Cl_2]$ to yield complexes of the type $[M(PNCHP-\kappa^3P, N, P)Cl]Cl$ (M = Pd 1a and M = Pt 1b). Attempts to isolate $[M(PNCHP-\kappa^2P, P)Cl_2]$ were unsuccessful. However, several intermediates, which were suggestive of mono- and bidentate PNCHP species, were observed when monitoring the synthesis of $[M(PNCHP-\kappa^3P, N, P)Cl]Cl$ by ³¹P NMR. PNCHP



displaces COD and the chloro group from $[Pd(COD)(-CH_3)Cl]$ yielding the compound $[Pd(PNCHP-\kappa^3P, N, P)(CH_3)]Cl$ (7).

The ionic chloride of both 1a and 1b can be exchanged for a BF₄ ion to give [M(PNCHP- $\kappa^3 P, N, P$)Cl]BF₄ (M = Pd 2a and M = Pt 2b). In the presence of acetonitrile (MeCN) a second chloride of 1b can be abstracted with AgBF₄ to give [Pt(PNCHP- $\kappa^3 P$, N, P)(MeCN)]- $(BF_4)_2$ 3. The chloride of 7 is easily exchanged for $BF_4^$ by a metathetical reaction of 7 with AgBF₄, affording the compound [Pd(PNCHP- $\kappa^3 P, N, P$)(CH₃)]BF₄ 8. When compound 8 was subjected to CO (7 atm) at room temperature there was no evidence for the formation of a CO adduct or for an insertion reaction. This is in contrast to palladium complexes with terdentate nitrogen ligands [6a], where insertion likely occurs via a mechanism involving dissociation of one of the distal nitrogen atoms to from a four-coordinate intermediate. In 8 the PNCHP ligand cannot dissociate a distal phosphorus atom [6a].

The reaction of **3** with monodentate ligands, L (L = 2picoline, 3-picoline or triphenylphosphine) results in the substitution of the coordinated acetonitrile to give fourcoordinate, dicationic complexes of the type [Pt(PNCHP- $\kappa^3 P$, N, P)(L- κ^1)]²⁺ (**4**) (Scheme 3). Analogous substitution reactions with the bidentate ligands (L-L), 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen) or bis(diphenylphosphino)ethane (diphos)] gave complexes of the type [Pt(PNCHP- $\kappa^3 P$, N, P)(L-L- κ^2)]²⁺ (**5**), where the metal is now considered to be fivecoordinate. Reaction of **3** with the potentially terdentate ligand 2,2':6',2''-terpyridine (terpy) also gives rise to a five-coordinate complex, [Pt(PNCHP- $\kappa^3 P$, N, P)(terpy- $\kappa^2 N$, N)]²⁺ (**6**).

2.2. Single crystal X-ray diffraction studies

The X-ray determined crystal structures of **1b**, **4a**, **5a**, and **6** are shown as ORTEP plots of the cations in Figs. 1–4, respectively, and selected bond lengths and angles are given in Table 2.

2.2.1. Crystal structure of $[Pt(PNCHP-\kappa^3P, N, P)Cl]-Cl \cdot 2CH_2Cl_2$ (**1b**)

The structure of the cation [Pt(PNCHP- $\kappa^{3}P, N, P$)Cl]⁺ of **1b** (Fig. 1) contains a four-coordinate platinum atom with the two phosphorus atoms [P(1)]and P(2)] and the imine nitrogen atom (N' or N") of PNCHP and one chloride [Cl(1)] atom making up the four donor atoms. A second chloride (ionic) and two molecules of dichloromethane are also present but omitted from Fig. 1 for clarity. The coordination geometry around the platinum atom is slightly distorted square planar which can be attributed to the steric requirements of the coordinated PNCHP ligand. The mean C(1)=N imine bond length at 1.272 Å is similar to the value found for the free ligand (1.266 Å) [4] as well





as for the related compounds, 4a, 5a and 6 [1.290(6)–1.297(15) Å] reported in this study.

2.2.2. Crystal structure of $[Pt(PNCHP-\kappa^3P, N, P)-(PPh_3)](BF_4)_2$ (4a)

The structure of the dication, $[Pt(PNCHP-\kappa^{3}P, N, P)(PPh_{3})]^{2+}$ **4a** (Fig. 2), shows the two phosphorus atoms [P(1) and P(2)] and nitrogen atom (N) of PNCHP and the phosphorus atom of a triphenylphosphine [P(3)] coordinated to a central platinum atom (Pt).



Fig. 1. ORTEP diagram of the cation of complex **1b** (major disorder part) showing the numbering system used. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity.

As for **1b**, the coordination geometry of the platinum is slightly distorted square planar. Calculation of a plane involving the platinum atom and the four donor atoms, N, P(1), P(2) and P(3), shows a significant deviation from coplanarity of 0.146 Å, much greater than in the structure discussed above (0.095 for molecule A and 0.024 Å for molecule B). The Pt–P bond lengths to PNCHP [Pt–P(1), 2.3151(12) Å and Pt–P(2), 2.3247(12) Å] are similar



Fig. 2. ORTEP diagram of the cation of complex **4a** showing the numbering system used. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity.



Fig. 3. ORTEP diagram of the cation of complex 5a showing the numbering system used. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity.



Fig. 4. ORTEP diagram of the cation of complex 6 showing the numbering system used. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms have been omitted for clarity.

[2.332(2)–2.347(2) Å] to other square planar d⁸ complexes of platinum for compounds with two phosphines *trans* to each other [8] Pt–P and Pt–N bond lengths are similar to those found in the complexes *cis*-[Pt(PNH₂)]²⁺ and *trans*-[Pt(PNH₂)]²⁺ (PNH₂ = *o*-aminophenyldiphenylphosphine) [9]. However, the bond lengths Pt–P(1) and Pt–P(2) are significantly longer (by 0.0215 and 0.0390 Å, respectively) than those found for [Pt(PNCHP- $\kappa^3 P, N, P$)Cl]⁺ (**1b**), which is consistent with the greater steric requirement of the mutually *cis* coordinated triphenylphosphine ligand – effectively there are three bulky triphenylphosphino moieties in close proximity.

2.2.3. Crystal structure of $[Pt(PNCHP-\kappa^{3}P, N, P)-(phen-\kappa^{2}N, N)](BF_{4})_{2} \cdot CH_{2}Cl_{2}$ (5a)

For the dication, $[Pt(PNCHP-\kappa^3P, N, P)(phen (\kappa^2 N, N)$ ²⁺ of **5a** (Fig. 3), the platinum atom is five-coordinate with a slightly distorted square-pyramidal geometry. The PNCHP ligand occupies three sites of the basal plane, coordinating through the two phosphorus atoms [P(1) and P(2)] and the nitrogen atom (N). The remaining coordination site of the basal plane is filled by one of the nitrogen atoms [N(1)] of the 1,10-phenanthroline (phen) ligand. The second nitrogen atom [N(2)]of the 1,10-phenanthroline is located at the apex of the square pyramid. There is no significant difference between the Pt–N(imine) [2.038(2) Å] and Pt–N(1)(phen) [2.043(2) Å] bond lengths, which are trans to one another in the basal plane. The axial phen-N(2)-Pt distance of 2.526(2) Å is considerably greater than the equatorial N(1)-Pt distance of 2.043(2) Å, the latter being typical for platinum(II)-1,10-phenanthroline species [10]. Due to the rigid structure of 1,10-phenanthroline, the second nitrogen atom is forced to be in the vicinity of the metal, making it difficult to decide whether or not the axial nitrogen atom-to-metal distance N(2)-Pt corresponds to a weak bond. However, in 5a the phen is considered to be bidentate for the following reasons: (i) The platinum atom is displaced from the basal plane by 0.1052(8) Å towards the N(2) atom. (ii) The ratio of the axial/equatorial phen-N-Pt bond lengths at 1.24 is close to values for accepted five coordinate species [11]. For example, ratios of 1.17 are found for the five coordinate species $[Ni(CN)_5]^{2-}$ and 1.14 for the five coordinate $[PtI_2(CO)(dmphen)]$ (dmphen = 2,9dimethyl-1,10-phenanthroline), where the phenanthroline ligand is bound in an axial-to-equatorial bidentate mode. By contrast, in $[PtCl(phen)(PEt_3)_2]^+$, where the phen ligand is considered monodentate, the ratio is 1.33 [12]. (iii) The N(1)–Pt–N(2) angle of $74.54(8)^{\circ}$ lies close to the average phen N-M-N angle of 79.5° when the ligand is clearly bidentate [11]. For comparison, the equivalent angles in [Pt(CN)(phen)₂]⁺ and [PtCl- $(phen)(PEt_3)_2]^+$, where the phen ligand is monodentate, are 69.7(2)° and 68.2°, respectively [13,14]. (iv) The difference between the Pt-N(1)-C(105) and Pt-N(1)-C(101) angles of only -2.7°, is indicative of a phenanthroline ligand bound to both the basal plane and the apical site of the metal atom [15]. (v) Lastly, the axial phen–N–Pt distance [2.526(2) Å] in **5a** is considerably shorter than the analogous distances in [Pt(CN)- $(phen)_2$ ⁺ and $[PtCl(phen)(PEt_3)_2]^+$ [2.761(5) and 2.843(20) Å, respectively], which are considered to be too long for a bonding interaction.

2.2.4. Crystal structure of $[Pt(PNCHP-\kappa^3P, N, P)(ter-py-\kappa^2N, N)](BF_4)_2$ (6)

The geometry around the metal in $[Pt(PNCHP-\kappa^3 P, N, P)(terpy-\kappa^2 N, N)]^{2+}$ 6 (Fig. 4) is similar to that

Table 1 Crystal data and structure refinement for the complexes **1b**, **4a**, **5a**, and **6**

Compound	1b	4a	5a	6
Empirical formula	$C_{39}H_{33}Cl_6NP_2Pt$	$C_{57}H_{48}B_2Cl_4F_8NP_3Pt$	$C_{50}H_{39}B_2Cl_2F_8N_3P_2Pt$	$C_{52}H_{40}B_2F_8N_4P_2Pt$
M	985.39	1350.38	1183.39	1151.53
T (K)	203(2)	203(2)	203(2)	200(2)
Crystal system	triclinic	monoclinic	triclinic	monoclinic
Space group	$P\overline{1}$	P2(1)/c	$P\overline{1}$	P2(1)/m
a (Å)	10.7207(1)	13.1722(1)	10.3338(1)	11.289(2)
b (Å)	13.8244(2)	21.81280(10)	12.9595(2)	16.021(3)
c (Å)	14.5320(2)	19.7670(2)	18.5480(2)	13.684(3)
α (°)	114.840(2)	90	87.012(1)	90
β (°)	91.402(1)	91.942(1)	88.389(1)	107.97(3)
γ (°)	96.559(1)	90	76.211(1)	90
U (Å ³)	1935.45(4)	5676.24(8)	2408.78(5)	2354.3(8)
Ζ	2	4	2	2
Absorption	4.152	2.810	3.160	3.122
coefficient (mm ⁻¹)				
Reflections measured	18848	31955	20996	19782
Independent reflections	8348 ($R_{\rm int} = 0.0244$)	12425 ($R_{\rm int} = 0.0285$)	9682 ($R_{int} = 0.0130$)	4368 ($R_{\rm int} = 0.0992$)
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0268,$	$R_1 = 0.0449,$	$R_1 = 0.0207,$	$R_1 = 0.0458,$
	$wR_2 = 0.0654$	$wR_2 2 = 0.0996$	$wR_2 = 0.0547$	$wR_2 = 0.1047$
R indices (all data)	$R_1 = 0.0301,$	$R_1 = 0.0603,$	$R_1 = 0.0220,$	$R_1 = 0.0627,$
	$wR_2 = 0.0673$	$wR_2 = 0.1095$	$wR_2 = 0.0559$	$wR_2 = 0.1119$

Table 2

Selected bond lengths (Å) and angles (°) for the complexes 1b, 4a, 5a, and 6 with estimated standard deviations in parentheses

	1b	4a	5a	6
Bond lengths				
Pt-P(1)	2.2936(8)	2.3151(12)	2.2997(6)	2.3058(16)
Pt-P(2)	2.2857(8)	2.3247(12)	2.2947(6)	2.3058(16)
Pt–N	2.038(4)-N', 2.106(7)-N"	2.107(4)	2.038(2)	2.044(10)
Pt–Cl(1)	2.2875(9)			
Pt-N(1)			2.043(2)	2.061(7)
Pt-N(2)			2.526(2)	2.625(7)
Pt-P(3)		2.2688(13)		
N-C(1)	1.301(6)-A, 1.242(8)-B	1.290(6)	1.295(3)	1.297(15)
Bond angles				
P(1) - Pt - P(2)	174.84(3)	160.96(5)	161.34(2)	175.30(8)
N–Pt–Cl(1)	169.83(10)-A, 168.20(14)-B			
N-Pt-P(3)		175.68(12)		
N-Pt-N(1)			172.52(8)	170.3(2)
P(1)-Pt-N	80.85(10)-A, 98.08(16)-B	82.23(11)	84.66(6)	80.3(2)
P(2)–Pt–N	95.13(10)-A, 77.34(16)-B	83.37(11)	86.84(6)	99.4(2)
P(1)-Pt-Cl(1)	93.14(3)			
P(2)-Pt-Cl(1)	91.29(3)			
P(1) - Pt - P(3)		98.80(5)		
P(2)–Pt–P(3)		96.49(5)		
P(1) - Pt - N(1)			91.98(6)	90.07(4)
P(2)-Pt-N(1)			98.25(6)	90.07(4)
P(1) - Pt - N(2)			94.69(5)	92.26(4)
P(2)-Pt-N(2)			103.04(5)	92.26(4)
N(1)-Pt-N(2)			74.54(8)	72.6(3)
N-Pt-N(2)			99.03(8)	109.1(3)

found in $[Pt(PNCHP-\kappa^3P, N, P)(phen)]^{2+}$. Again, the platinum atom is square pyramidal with the two phosphorus atoms [P(1) and P(2)] and one nitrogen atom (N) of PNCHP occupying three equatorial sites, with the fourth site occupied by one of the terminal nitrogen

atoms [N(1)] of the 2,2',6'2"-terpyridine ligand. The central nitrogen atom [N(2)] of the terpy occupies the axial site with the axial Pt–N(2) distance at 2.625(7) Å being longer than the equatorial Pt–N(1) distance of 2.061(7) Å. The Pt–N(2) distance is considered to cor-

respond to a bonding interaction since the same arguments put forth to describe the nature of the axial Pt-N(2) bond in [Pt(PNCHP)(phen- $\kappa^2 N, N$]²⁺ (5a) also hold for 6, although the interaction is weaker: the platinum atom is displaced from the basal donor atom plane by only 0.0349(8) Å towards the N(2) atom, the axial/equatorial ratio is slightly larger at 1.27 and difference between the M-N(1)-C(105) and M-N(1)-C(101) angles is also slightly larger at +5.0°. In addition, unlike the phen ligand in 5a, the pyridyl ring containing the axial bound nitrogen atom is free to rotate around the C(105)-C(106) axis and therefore is not required to orientate itself for bonding with the metal, as it does. The two rings containing the N(1) and N(2) atoms lie in one plane. In contrast, the mean plane of the pyridyl ring containing the non-bonding nitrogen atom N(3) is tilted 47.7° relative to the mean plane of the middle pyridyl ring.

2.3. NMR spectroscopy

The ³¹P NMR data for selected compounds are collected in Table 3. All the platinum(II) compounds displayed similar spectra, showing two doublets with platinum-195 satellites which are assigned to the two phosphorus atoms of the PNCHP ligand with ${}^{2}J(P,P)$ coupling between the two inequivalent phosphorus nuclei and ${}^{1}J(Pt,P)$ coupling due to the spin 1/2 nucleus ${}^{195}Pt$, found in 33% abundance. In general, for all the platinum(II) compounds discussed here, one of the

Table 3 NMR data for selected compounds

phosphorus atoms gives rise to a high frequency resonance (δ 45.9–28.7) and the other to a low frequency resonance (δ 19.5–12.3). The former resonances can reasonably assigned to the phosphorus atoms involved in the five-membered ring, due to the ring contribution (ΔR) effect [16,17]. The ²J(P,P) coupling constants ranged from 306 to 422 Hz which is indicative of a trans arrangement of inequivalent phosphorus atoms [18]. Coupling constants of larger magnitude were exhibited by the monocationic complexes, whilst those of smaller magnitude were displayed by the dicationic complexes. ${}^{1}J(P,Pt)$ coupling constants ranged from 2353 to 2789 Hz and were typical of trans-platinum(II) complexes [18]. The ${}^{1}J(\mathbf{P},\mathbf{Pt})$ coupling constants associated with the higher frequency resonances, i.e. those from δ 45.9–28.7, were on average 30 Hz higher than their lower frequency counterparts at δ 19.5–12.3, further supporting the assignment of the signals at high frequency to the phosphorus atoms involved in the five-membered ring, again due to the ring contribution (ΔR) effect [18].

The spectra of the two complexes, [Pt(PNCHP- $\kappa^3 P, N, P$)(PPh₃)](BF₄)₂ (**4a**) and [Pt(PNCHP- $\kappa^3 P, N, P$)-(diphos)](BF₄)₂ (**5c**) contain additional phosphorus signals due to their phosphine co-ligands. For **4a**, where the ancillary ligand is triphenylphosphine, an additional resonance at δ 5.1, with ²J(P,P) coupling constants of 18 and 21 Hz and a ¹J(P,Pt) of 3397 Hz, was observed. The relatively large ¹J(P,Pt) coupling constant for the triphenylphosphine ligand, relative to those observed for PNCHP, is due to the poorer *trans* influence of the ni-

Compound	³¹ P { ¹ H}NMR ^a			¹ H NMR ^b	
	δ	$^{2}J(\text{PP})/\text{Hz}$	¹ J(PPt)/Hz	$\delta (CH=N)^{c}$	³ J(HPt)/Hz
[Pd(PNCHP)Cl]Cl (1a)	37.3, 22.6	478		10.61	
[Pt(PNCHP)Cl]Cl (1b)	32.0, 18.8	421	2542, 2495	10.87	106.5
$[Pt(PNCHP)(PPh_3)](BF_4)_2$ (4a)	38.5, 19.5, 5.1 ^e	337, 21, 18	2496, 2367, 3397	8.62(dd) ^d	63.9 [⁴ J(HP) 11.6, 1.1]
$[Pt(PNCHP)(2-pico)](BF_4)_2$ (4b)	33.4, 18.5 ^g	363	2493, 2490	9.48 ^f	92.2
$[Pt(PNCHP)(3-pico)](BF_4)_2$ (4c)	34.4, 19.3 ^g	366	2499, 2505	9.46 ^f	90.3
$[Pt(PNCHP)(phen)](BF_4)_2$ (5a)	29.9, 14.4	354	2789, 2757	9.42 ^h	91.6
$[Pt(PNCHP)(bipy)](BF_4)_2$ (5b)	29.7, 15.2	363	2731, 2722	8.95	90.9
$[Pt(PNCHP)(diphos)](BF_4)_2$ (5c)	45.9, 12.3	396	2435, 2353	i	
	42.6 ^j , 38.3 ^j	k	^k 3088		
$[Pt(PNCHP)(terpy)](BF_4)_2$ (6)	28.7, 13.6	306	2698, 2669	9.04 ^h	95.7
[Pd(PNCHP)Me]Cl (7)	33.6, 27.5	392		10.29	

^a Recorded at 109 MHz, chemical shifts are in ppm relative to 85% H₃PO₄, solvent CDCl₃ unless stated otherwise.

^b Recorded at 270 MHz, chemical shifts are in ppm relative to Si(CH₃)₄, solvent CDCl₃ unless stated otherwise.

^c In addition, compounds **4b**, **4c** and **7** show CH_3 -resonances at δ 2.24, 1.97 and 0.56, respectively. **5c** shows Ph₂PCH₂CH₂PPh₂resonances at δ 3.02.

^d In CD₃CN.

^e Ph₃P resonance.

^fIn (CD₃)₂CO

^g In CH₃CN.

^h In CD₂Cl₂.

ⁱObscured by aromatic CH resonances in the range δ 7.95 – 5.94.

^jPh₂PCH₂CH₂PPh ₂resonance.

^k Not resolved.

rangement [18]. Free diphos contains equivalent phosphorus atoms but on coordination in **5c**, these become inequivalent, exhibiting one resonance at 42.6 and the other at δ 38.3, values which support both diphos phosphorus atoms being coordinated to the platinum atom. The ¹*J*(P,Pt) coupling constant of 3088 Hz is typical of diphos coordinated in square planar platinum(II) complexes [20,21] and consistent with P *trans* to N. The expected second ¹*J*(P,Pt) coupling constant could not be resolved.

The phosphorus-31 NMR spectra of the palladium complexes are similar to those of the platinum compounds, but with the expected absence of phosphorusto-metal coupling. All spectra displayed two doublet signals, which are assigned to the inequivalent phosphorus atoms of PNCHP. As for the platinum compounds, chemical shifts are indicative of phosphorus-transition metal coordination. The ${}^{2}J(P,P)$ coupling constants were typical of the PNCHP ligand bound to palladium(II) with its two phosphorus atoms *trans* to one another. As previously reported [18], chemical shifts and coupling constants for the palladium complexes were significantly larger than those for their platinum analogues.

All the compounds listed in Table 3 displayed a signal in the range δ 10.9–8.6 which can be assigned to the imine proton of coordinated PNCHP with coupling to 195 Pt (60 – 110 Hz) being observed for the platinum complexes. As the ancillary ligand is changed from a halogen to a nitrogen to a phosphorus donor ligand, the chemical shift of the imine proton moves to lower frequency and the ${}^{3}J(H,Pt)$ coupling constant decreases. The shift to lower frequency can be explained using the relative trans influence of the donor atom of the ancillary ligand. For example, when the ancillary donor atom is phosphorus (high in the *trans* influence series), as it is $[Pt(PNCHP-\kappa^{3}P, N, P)(PPh_{3})](BF_{4})_{2}$ (**4**a) in and $[Pt(PNCHP-\kappa^{3}P, N, P)(diphos)](BF_{4})_{2}$ (5c), the imine proton exhibits its lowest frequency shifts.

3. Conclusions

For the d⁸ metals, platinum(II) and palladium(II), the PNCHP ligand coordinates to three sites of the square-plane, using the two phosphorus atoms and the imino-nitrogen atom. In the compound [Pt(PNCHP- $\kappa^3 P, N, P$)(MeCN)](BF₄)₂ (**3**), the acetonitrile ancillary ligand, which occupies the fourth site of the square-plane, can be substituted with monodentate ligands, such as 2- and 3-picoline and triphenylphosphine. Reaction of **3** with the bidentate ligands 2,2'-bipyridine,

1,10-phenanthroline and bis(diphenylphosphino)ethane, does not result in any observable competition with the PNCHP ligand for coordination sites. Instead, these ligands act in a bidentate fashion, with one of their donor atoms occupying the fourth site of the square-plane, and the second donor atom the apical site of a square pyramid to give five-coordinate dicationic complexes. The potentially tridentate ligand, 2,2',6',2''-terpyridine, also behaves as a bidentate, forming the five-coordinate complex [Pt(PNCHP- $\kappa^3 P, N, P$)(terpy- $\kappa^2 N, N$)]²⁺ (6).

4. Experimental

4.1. Materials and instrumentation

Spectral measurements were performed as previously described [7]. Microanalyses were performed by the Campbell Microanalytical Laboratory, University of Otago. Many of the compounds contained solvated CH₂Cl₂ which was readily lost and the analytical data reflect this. The PNCHP ligand [4], [Pt(COD)Cl₂], [Pd(COD)Cl₂] and [Pd(COD)(Me)Cl] [22] were prepared according to literature preparations. All reactions were carried out under an inert atmosphere. Solvents were dried by standard procedures [23].

4.2. Preparation of the complexes

4.2.1. $[Pd(PNCHP-\kappa^{3}P, N, P)Cl]Cl$ (1a)

A mixture of $[Pd(COD)Cl_2]$ (0.100 g, 0.350 mmol) and PNCHP (0.193 g, 0.351 mmol) in benzene (12 mL) was heated to reflux for 1 h. The resulting yellow precipitate was isolated by filtration, washed with *N*-pentane and air dried to yield **1a** (0.235 g, 86.9%) as a yellow powder. *Anal.* Calc. for C₃₇H₂₉Cl₂NP₂Pd · 0.5 CH₂Cl₂: C, 58.54; H, 3.93; N, 1.82. Found: C, 58.41; H, 3.99; N, 1.78%.

4.2.2. $[Pt(PNCHP-\kappa^{3}P, N, P)Cl]Cl$ (1b)

A mixture of [Pt(COD)Cl₂] (0.100 g, 0.267 mmol) and PNCHP (0.147g, 0.267 mmol) in benzene (12 mL) was stirred at room temperature for 40 min, giving a yellow precipitate. The mixture was heated to reflux for 30 min and allowed to cool. The resulting yellow precipitate was isolated by filtration, washed with diethylether and air dried to yield **1b** (0.146 g, 60.7%) as a yellow powder. The compound can be crystallised from dichloromethane/*N*-hexane. M.p: 294-296 °C (dec). *Anal.* Calc. for $C_{37}H_{29}Cl_2NP_2Pt \cdot 1.5CH_2Cl_2$: C, 49.04; H, 3.42; N, 1.49. Found: C, 48.78; H, 2.75; N, 1.52%.

4.2.3. $[Pd(PNCHP-\kappa^{3}P, N, P)Cl]BF_{4}$ (2a)

A mixture of 1a (0.202 g, 0.263 mmol) and AgBF₄ (0.054 g, 0.277 mmol) in dichloromethane (12 mL) was

exposed to ultrasound for 1 h resulting in yellow and white precipitates. This mixture was filtered through kieselguhr and the trapped yellow precipitate dissolved and washed through into the filtrate with acetonitrile, leaving the insoluble white precipitate behind. The filtrate was taken to dryness in vacuo and the resulting yellow residue crystallised from dichloromethane/*n*-hexane. Compound **2a** (0.169 g, 82.6%) was isolated as large yellow crystals, washed with a dichloromethane/*N*-pentane mixture and air-dried. *Anal.* Calc. for $C_{37}H_{29}BClF_4NP_2Pd$: C, 57.10; H, 3.76; N, 1.80. Found: C, 56.68; H, 3.70; N, 1.90%.

4.2.4. $[Pt(PNCHP-\kappa^{3}P, N, P)Cl]BF_{4}$ (2b)

A mixture of **1b** (0.300 g, 0.333 mmol) and AgBF₄ (0.071 g, 365 mmol) in dichloromethane (12 mL) was exposed to ultrasound for 1 h, resulting in yellow and white precipitates. The mixture was filtered through kieselguhr and the trapped yellow precipitate dissolved and washed through into the filtrate using acetonitrile, leaving the insoluble white precipitate behind. The filtrate was taken to dryness in vacuo and the resulting yellow residue crystallised from dichloromethane/*N*-hexane overnight. Compound **2b** (0.248 g, 79.9%) was isolated as orange crystals, washed with a dichloromethane/*N*-pentane mixture and air-dried. M.p. 198–200 °C. *Anal.* Calc. for C₃₇H₂₉BClF₄NP₂Pt \cdot 0.75CH₂Cl₂: C, 48.72; H, 3.30; N, 1.51. Found: C, 48.55; H, 3.29; N, 1.56%.

4.2.5. $[Pt(PNCHP-\kappa^{3}P, N, P)(MeCN)](BF_{4})_{2}$ (3)

A mixture of **2b** (0.401 g, 0.431 mmol) and AgBF₄ (0.0899 g, 401 mmol) in acetonitrile (c.a. 15 mL) was heated to reflux for 27 h, giving a dark-orange solution. The solvent was removed in vacuo and the resulting orange residue crystallised from dichloromethane/*N*-hexane to yield **3** (0.369 g, 96.0%). *Anal.* Calc. for $C_{39}H_{32}B_2F_8N_2P_2Pt \cdot 0.5CH_2Cl_2$: C, 47.36; H, 3.32; N, 2.80. Found: C, 47.89; H, 3.45; N, 2.81%.

4.2.6. $[Pt(PNCHP-\kappa^{3}P, N, P)(PPh_{3})](BF_{4})_{2}$ (4a)

A mixture **2b** (0.101 g, 0.108 mmol) and AgBF₄ (0.0226 g, 0.116 mmol) in acetonitrile (12 mL) was heated to reflux for ca. 25 min, giving a white precipitate. PPh₃ (0.0306 g, 0.117 mmol) was added to the reaction mixture and refluxing continued for a further 30 min. This mixture was filtered through kieselguhr and the trapped yellow precipitate dissolved and washed through into the filtrate with dichloromethane, leaving the original white precipitate behind. The filtrate solvent was evaporated in vacuo and the resulting yellow residue precipitated from dichloromethane/*N*-hexane overnight. Compound **4a** (0.103 g, 80.8%) was isolated as a very pale yellow powder, washed with *N*-pentane and airdried. The powder can be recrystallised from a CH₂Cl₂/*N*-hexane vapour diffusion to yield colourless crystals.

Anal. Calc. for C₅₅H₄₄B₂F₈NP₃Pt · CH₂Cl₂: C, 53.15; H, 3.66; N, 1.11. Found: C, 53.36; H, 3.80; N, 1.18%.

4.2.7. $[Pt(PNCHP-\kappa^{3}P, N, P)(2-pico)](BF_{4})_{2}$ (4b)

A mixture of **2b** (0.162 g, 0.174 mmol) and $AgBF_4$ (0.0360 g, 0.185 mmol) in acetonitrile (12 mL) was heated to reflux for 30 min, giving a white precipitate. 2-Picoline (2-pico) (0.0183 mL, 0.185 mmol) was added to the reaction mixture and refluxing continued for a further 30 min. The white precipitate was removed by filtration through kieselguhr and the filtrate taken to dryness in vacuo. The resulting yellow residue converted to a white and brown mixture over two days. The white product was separated from the insoluble brown product by dissolving in dichloromethane, followed by filtration. Crystallisation was initiated by addition of Nhexane to the filtrate. Compound 4b (0.1354 g, 72.4%) was isolated as white microcrystals, washed with diethylether and dried in vacuo. Anal. Calc. for C₄₃H₃₆B₂F₈N₂P₂Pt: C, 51.06; H, 3.59; N, 2.78. Found: C, 51.04; H, 3.48; N, 2.79%.

4.2.8. $[Pt(PNCHP-\kappa^{3}P, N, P)(3-pico)](BF_{4})_{2}$ (4c)

A mixture of **2b** (0.154 g, 0.165 mmol) and AgBF₄ (0.0343 g, 0.176 mmol) in acetonitrile (12 mL) was heated to reflux for ca. 25 min, giving a white precipitate. 3-Picoline (3-pico) (0.016 mL, 0.18 mmol) was added to the reaction mixture and refluxing continued for a further 30 min. The white precipitate was removed by filtration through kieselguhr and the filtrate taken to dryness in vacuo. The resulting yellow residue was taken into solution with acetonitrile, followed by addition of diethylether to precipitate out the desired product. Compound **4c** (0.101 g, 56.5%) was isolated as a very pale yellow powder, washed with diethylether and air-dried. *Anal.* Calc. for C₄₃H₃₆B₂F₈N₂P₂Pt · CH₂Cl₂: C, 48.20; H, 3.49; N, 2.56. Found: C, 47.88; H, 3.31; N, 3.05%.

4.2.9. $[Pt(PNCHP-\kappa^{3}P, N, P)(phen)](BF_{4})_{2}$ (5a)

A mixture of **3** (0.114 g, 0.119 mmol) and 1,10-phenanthroline (phen) (0.024 g, 0.133 mmol) in benzene (15 mL) was heated to reflux for 1 h, giving an orange toffeelike solid. The solvent was removed in vacuo and the resulting orange residue taken up into dichloromethane and heated to reflux overnight. The orange solution was subject to vapour diffusion using *N*-hexane giving **5a** (0.126 g, 96.4%) as chunky orange crystals. *Anal.* Calc. for C₄₉H₃₇B₂F₈N₃P₂Pt · CH₂Cl₂: C, 50.75; H, 3.32; N, 3.55. Found: C, 51.05; H, 2.95; N, 3.52%.

4.2.10. $[Pt(PNCHP-\kappa^{3}P, N, P)(bipy)](BF_{4})_{2}$ (5b)

A yellow solution of **2b** (0.194 g, 0.209 mmol) and $AgBF_4$ (0.0436 g, 0.224 mmol) in acetonitrile (12 mL) was heated to reflux for 20 h. The resulting orange solution was filtered through kieselguhr. 2,2'-Bipyridine

(bipy) (0.033 g, 0.21 mmol), dissolved in acetonitrile, was added to the filtrate and refluxing continued for a further 1 h, giving an intense orange solution. The solution was allowed to cool, followed by solvent removal in vacuo. Additional white precipitate was removed by filtration through kieselguhr and washed with acetonitrile, and the filtrate plus washings were taken to dryness in vacuo. The resulting yellow residue was recrystallised from dichloromethane/*N*-hexane. Compound **5b** (0.141 g, 62.7%) was isolated as orange crystals, washed with *N*-pentane and air-dried. M.p: 259-260 °C. *Anal.* Calc. for $C_{47}H_{37}B_2F_8N_3P_2Pt \cdot 0.5CH_2Cl_2$: C, 51.08; H, 3.43; N, 3.76. Found: C, 51.22; H, 3.26; N, 3.85%.

4.2.11. $[Pt(PNCHP-\kappa^{3}P, N, P)(diphos)](BF_{4})_{2}$ (5c)

Compound 3 (0.100 g, 0.104 mmol) and bis(diphenvlphosphino)ethane (diphos) (0.0420 g, 0.105 mmol) were dissolved together in dichloromethane (12 mL) and heated to reflux for 3 h. A small amount of the byproduct [Pt(diphos)₂](BF₄)₂ (0.015 g, 24.5%), as a yellow precipitate, was removed by filtration and the filtrate set up for vapour diffusion with N-hexane. Compound 5c was isolated as a yellow powder which on exposure to air. slowly turns green. Anal. Calc. for C₆₃H₅₃B₂F₈NP₄Pt · 2CH₂Cl₂: C, 52.52; H, 3.86; N, 0.94. Found: C, 52.60; H, 3.79; N, 0.58%.

4.2.12. $[Pt(PNCHP-\kappa^{3}P, N, P)(terpy)](BF_{4})_{2}$ (6)

Compound **3** (0.100 g, 0.105 mmol) and 2,2',6',2"terpyridine (terpy) (0.0244 g, 0.105 mmol) were dissolved together in dichloromethane (c.a. 12 mL) and heated to reflux for ca. 3 h. The reaction mixture was filtered and set up for vapour diffusion in *N*-hexane. Compound **6** (0.0919 g, 76.9%) was isolated as orange crystals, washed with *N*-pentane and air dried. *Anal.* Calc. for $C_{52}H_{40}B_2F_8N_3P_2Pt$: C, 54.24; H, 3.50; N, 4.87. Found: C, 53.97; H, 3.50; N, 4.85%

4.2.13. $[Pd(PNCHP-\kappa^{3}P, N, P)(CH_{3})]Cl(7)$

A mixture of [Pd(COD)(CH₃)Cl] (0.101 g, 0.381 mmol) and PNCHP (0.208 g, 0.378 mmol) in dichloromethane (12 mL) was stirred at room temperature for 1 h, giving a yellow solution. *N*-Hexane was added until a slight cloudiness was observed. Very pale yellow microcrystals resulted after standing overnight. These were isolated by filtration, washed with *N*-pentane and air dried to yield **7** (0.239 g, 89.4%). *Anal.* Calc. for $C_{38}H_{32}ClNP_2Pd$: C, 64.60; H, 4.57; N, 1.98. Found: C, 64.30; H, 4.64; N, 2.01%.

4.2.14. $[Pd(PNCHP-\kappa^{3}P, N, P)(CH_{3})]BF_{4}$ (8)

Compound 7 (164 g, 0.232 mmol) and $AgBF_4$ (0.0447 g, 0.230 mmol) were combined in dichloromethane (ca.

12 mL) and heated to reflux for 1 h. The reaction mixture was filtered through kieselguhr. *N*-Pentane was vapour diffused into the filtrate over a weekend. Compound **8** (0.114 g, 61.9%) was isolated as pale yellow microcrystals, washed with *N*-pentane and dried in vacuo. *Anal.* Calc. for $C_{38}H_{32}BF_4NP_2Pd \cdot 0.5CH_2Cl_2$: C, 57.78; H, 4.16; N, 1.75. Found: C, 58.15; H, 4.18; N, 1.83%.

4.3. Crystallography

Single crystals of the compounds, 1b, 4a, 5a and 6, were grown as described under their respective syntheses and attached to the ends of glass fibres with cyanoacrylate glue. Data collection and refinement were performed as previously described [24]. Table 1 lists the crystal data for the compounds. For 1b, the imine bond of the PNCHP ligand and contiguous phenyl rings are disordered over two sites, A and B, and were refined with a free variable giving the occupancy of these as 0.67 and 0.33, respectively. In the case of 6, the platinum atom and the two pyridyl rings of the terpy ligand lie on a mirror plane and were refined with special position constraints. The PNCHP ligand is disordered about this mirror plane and the two single phenyl rings and the phosphorus are assigned with occupancies of 1. When the imine link between the two phosphorus atoms was refined with an occupancy of 0.5 (as this was indicated by the large temperature factors in this part of the molecule in the initial refinement) with the N constrained to lie on the mirror plane, unreasonable C=N bond distances resulted. Removing the special position constraint allowed the imine nitrogen, N, and carbon, C(1), to take their respective disordered positions slightly above and below the mirror plane, hence giving bond distances in the usual range.

5. Supplementary material

CCDC 213469 (1b), 213470 (5a), 213471 (4a) and 213472 (6) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; or data_request@ccdc.cam.ac.uk).

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