

# Synthesis of new heterotridentate ligands comprising mixed hard–soft donor sets, and their complexation with Group 10 metals

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The new phosphorus-containing heterotridentate ligands 2-(2-(Ph<sub>2</sub>P)C<sub>6</sub>H<sub>4</sub>CH=NCH(Me)CH(OH)Ph)-1*S*,2*R* (HL<sup>1</sup>) and 2-(2-(Ph<sub>2</sub>P)C<sub>6</sub>H<sub>4</sub>N=CHC<sub>6</sub>H<sub>4</sub>OH) (HL<sup>2</sup>) were prepared by the condensation of 2-(diphenylphosphino)benzaldehyde with 1*S*,2*R*-norephedrine (HL<sup>1</sup>) and 2-(diphenylphosphino)aniline with salicylaldehyde (HL<sup>2</sup>). The co-ordination chemistry of HL<sup>1</sup> and HL<sup>2</sup> with Group 10 metals was explored, together with that of the previously reported ligand 2-(2-(Ph<sub>2</sub>P)C<sub>6</sub>H<sub>4</sub>CH=NC<sub>6</sub>H<sub>4</sub>OH) (HL<sup>3</sup>) which is isomeric with (HL<sup>2</sup>). Compound HL<sup>1</sup> affords cationic complexes of general formula [M(HL<sup>1</sup>)Cl]Cl, where M = Ni (**1**), Pd (**2**) or Pt (**3**). Spectroscopic, microanalytical and crystallographic data for **1–3** confirm that deprotonation of the hydroxyl group does not occur on complexation. In contrast, both HL<sup>2</sup> and HL<sup>3</sup> deprotonate on complexation to form neutral species of general formula [MLCl] where L = L<sup>2</sup>, M = Ni (**4**), Pd (**5**) or Pt (**6**); L = L<sup>3</sup>, M = Ni (**7**), Pd (**8**) or Pt (**9**). The crystal structures of **4**, **5**, **7** and **9** confirm tridentate PNO co-ordination of the deprotonated ligands to the metal centres, forming 5- and 6-membered rings.

Over the past fifteen years or so there has been a growing interest in bidentate ligands which combine both hard and soft donor atoms. Typically these are heterofunctionalised phosphines, where the phosphorus is the soft donor, and the hard donor is either an oxygen or nitrogen atom.<sup>1</sup> These ligands can exhibit partial lability, where the co-ordination mode alternates between bidentate and monodentate, leading to co-ordinative unsaturation at the metal centre. This is a particularly desirable characteristic for complexes which might have applications in homogeneous catalysis, and since the majority of metals used in such systems are late or middle transition metals it is usually the soft donor which is continually bound to the metal. The incorporation of a chiral centre into such ligands allows enantioselectivity in catalytic transformations mediated by complexes of these ligands.<sup>1*c,i*</sup> Furthermore, the unco-ordinated donor atom may be used to bind to a second metal centre, affording bimetallic species.<sup>1*e,f*</sup> There are, however, few tridentate PNE (E = N', O or S) donor ligands which have been prepared or studied in this regard. For E = O, the known examples can be subdivided into monobasic ligands containing ionisable (OH or NH) groups<sup>2–6</sup> and those comprising ether donor groups.<sup>7–10</sup> Ruthenium(II) complexes containing ligands in this second category have been shown to be active catalysts for the transfer hydrogenation of ketones in the presence of Pr<sup>t</sup>OH.<sup>9,10</sup> There are in the literature even fewer examples reported of such ligands where E = N' or S.<sup>11–13</sup>

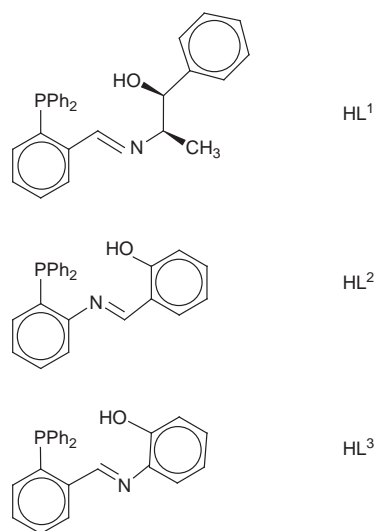
We report here new tridentate ligands providing PNO donor sets which are readily accessible from simple condensation reactions and outline their complexation behaviour with the Group 10 metals.

## Results and discussion

### Ligand synthesis

Condensation reactions of 2-(diphenylphosphino)benzaldehyde and 1*S*,2*R*-norephedrine [PhCH(OH)CH(Me)NH<sub>2</sub>] or of 2-(diphenylphosphino)aniline with salicylaldehyde, both performed in refluxing thf, lead to new functionalised heterotridentate ligands HL<sup>1</sup> and HL<sup>2</sup> in good yield. These have been characterised by mass spectrometry, NMR and IR spectroscopies; HL<sup>2</sup> is isomeric with the known compound HL<sup>3</sup>,

available from the condensation of 2-(diphenylphosphino)benzaldehyde and 2-aminophenol, the relative positions of the phosphine and aryloxy substituents of the C=N bonds being reversed.<sup>6</sup> Compounds HL<sup>1</sup> and HL<sup>2</sup> are, in common with HL<sup>3</sup>, soluble in a range of organic solvents and stable to both aerial oxidation and hydrolysis under ambient conditions. While HL<sup>1</sup> is amenable to further reaction without purification, it is necessary to recrystallise HL<sup>2</sup> from chloroform–diethyl ether to free the compound from the traces of salicylaldehyde which inevitably persist. In the <sup>1</sup>H NMR spectrum of HL<sup>1</sup> the imine proton is coupled to the <sup>31</sup>P nucleus, *J*(<sup>31</sup>P–<sup>1</sup>H) 4 Hz, which is comparable with the value of 5.5 Hz seen for HL<sup>3</sup>. In the case of HL<sup>2</sup> there is no observed (<sup>31</sup>P–<sup>1</sup>H) coupling for the corresponding imine proton. The molecular structure of HL<sup>2</sup> has been determined using a crystal grown from chloroform–diethyl ether.



### Complexation reactions of HL<sup>1–3</sup>

The stoichiometric reaction of HL<sup>1</sup> with either NiCl<sub>2</sub>·6H<sub>2</sub>O in ethanol or [M(cod)Cl<sub>2</sub>], where M = Pd or Pt, in dichloro-

**Table 1** Selected spectroscopic ( $^{31}\text{P}$ - $\{^1\text{H}\}$  and  $^1\text{H}$  NMR, IR and MS) and microanalytical data (calc. values in parentheses) for 1–9. Data for  $\text{HL}^{1-3}$  included for comparison

Compound	Analysis (%)			$\delta(^{31}\text{P}) [J(\text{PtP})/\text{Hz}]^a$	$\nu(\text{CN})/\text{cm}^{-1}$	$m/z^b$	$\delta(\text{CH}=\text{N})^a$	$[\alpha]_{589}^c/\text{deg cm}^3 \text{g}^{-1} \text{dm}^{-1}$
	C	H	N					
( $\text{HL}^1$ )				-10.5	1638		8.62	+1.1)
1 [Ni( $\text{HL}^1$ )Cl]Cl	60.4 (60.6)	5.1 (4.9)	2.2 (2.5) <sup>c</sup>	—	1631s	516	—	+20.0
2 [Pd( $\text{HL}^1$ )Cl]Cl	55.9 (55.8)	4.8 (5.7)	2.1 (2.2) <sup>d</sup>	45.6	1640m	564	8.36	+67.0
3 [Pt( $\text{HL}^1$ )Cl]Cl	48.6 (48.8)	4.0 (4.1)	1.8 (2.0) <sup>d</sup>	9.7 [4042]	1631m	654	8.66	+52.7
( $\text{HL}^2$ )				-14.6	1614		8.40)	
4 [NiL <sup>2</sup> Cl]	63.2 (63.3)	4.0 (4.0)	3.0 (2.9)	—	1608s	489	—	
5 [PdL <sup>2</sup> Cl]	57.3 (57.4)	3.5 (3.7)	2.8 (2.7)	47.1	1606s	536	8.65	
6 [PtL <sup>2</sup> Cl]	48.8 (49.1)	2.9 (3.1)	2.3 (2.3)	12.9 [3814]	1607s	626	9.03	
( $\text{HL}^3$ )				-9.0	1624		8.92)	
7 [NiL <sup>3</sup> Cl]	63.1 (63.3)	4.4 (4.0)	3.3 (2.9)	—	1582m	474	—	
8 [PdL <sup>3</sup> Cl]	57.8 (57.4)	3.8 (3.7)	2.6 (2.7)	32.6	1579m	522	8.44	
9 [PtL <sup>3</sup> Cl]	48.7 (49.1)	3.3 (3.1)	2.2 (2.3)	3.2 [3559]	1580m	611	8.75	

<sup>a</sup> No NMR observed for nickel complexes 1, 4 and 7. <sup>b</sup>  $\text{M}^+ - \text{HCl}$  for complexes 1–3,  $\text{M}^+$  for 4–9. <sup>c</sup> As 0.25 EtOH solvate. <sup>d</sup> As 0.5 EtOH solvate. <sup>e</sup> In 0.01 M solution in MeOH at 28 °C.

methane gives the cationic complexes  $[\text{ML}^1\text{Cl}]\text{Cl}$  1–3 respectively in high yield. These complexes are all soluble in ethanol but largely insoluble in other common organic solvents. The equivalent reactions of  $\text{HL}^2$  and  $\text{HL}^3$  give the neutral complexes  $[\text{MLCl}]$  4–9 which are all highly soluble in chlorinated solvents, thf and acetone. This is supported by elemental analysis and  $\text{FAB}^+$  mass spectrometry (Table 1), where the parent molecular ions give rise to the most prominent peak in the observed mass spectra.

### IR spectroscopy

Selected IR data for the complexes 1–9 and the ligands  $\text{HL}^{1-3}$  are presented in Table 1. For 1–3 the most salient features are the broad bands of medium intensity seen at 2400–2500  $\text{cm}^{-1}$ , assigned to  $\nu(\text{OH})$ , which are absent from the spectra of 4–9. The bands due to  $\nu(\text{C}=\text{N})$  are also readily identified, and are found to vary little from the free HL values for 1–6. For 7–9, however, there is a consistent and significant bathochromic shift of ca. 40  $\text{cm}^{-1}$  compared to the value for free  $\text{HL}^3$ .

### NMR spectroscopy

Selected NMR data for complexes 1–9 are collected in Table 1. For the complexes of  $\text{Ni}^{\text{II}}$ , 1, 4 and 7, there were no NMR spectra observed, indicating that in solution these samples are paramagnetic. Since complexes of  $\text{Ni}^{\text{II}}$  which have a square planar geometry are expected to be diamagnetic, this observation indicates that these complexes are distorted somewhat from their expected geometry.

The  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR spectra show singlets for the palladium(II) and platinum(II) complexes, with resolved coupling to  $^{195}\text{Pt}$  for 3, 6 and 9. The  $^1J(^{195}\text{Pt}-^{31}\text{P})$  couplings are consistent with a phosphine ligand disposed *trans* to oxygen, with the  $^1J$  values decreasing in the order 3 > 6 > 9. Interestingly there is a ca. 7% increase in  $^1J$  for  $[\text{PtL}^2\text{Cl}]$  6 over its isomeric form  $[\text{PtL}^3\text{Cl}]$  9. In the  $^1\text{H}$  NMR spectra of the palladium(II) and platinum(II) complexes no coupling of the imine proton with the  $^{31}\text{P}$  or  $^{195}\text{Pt}$  (in the case of 3, 6 and 9) nuclei was observed. The hydroxyl protons of 2 and 3 are not observed in spectra recorded in  $\text{C}_2\text{D}_5\text{OD}$ , which is perhaps unsurprising since there is likely to be rapid exchange of this hydroxyl proton with the (OD) deuteron.

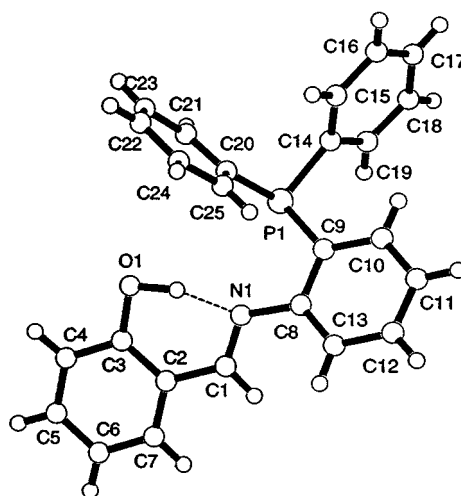


Fig. 1 Crystal structure of  $\text{HL}^2$ .

### Single crystal X-ray diffraction studies

The crystal structure of  $\text{HL}^2$  (Fig. 1) reveals that in the solid state the molecule exhibits the same *trans* planar configuration of the central C(2)–C(1)–N(1)–C(8) backbone and orientation of P(1) towards O(1) [ $\text{P}(1)\cdots\text{O}(1)$  4.06 Å], which is consistent with that observed in the structure of  $\text{HL}^3$ .<sup>6</sup> Additionally for  $\text{HL}^2$  there is an intramolecular hydrogen-bonding interaction between the imine nitrogen atom N(1) and the phenolic hydrogen H(1o) of O(1) [ $\text{N}(1)\cdots\text{H}(1\text{o})$  1.59 Å,  $\text{O}(1)\text{--H}(1\text{o})\text{--N}(1)$  155°] to form a pseudo six membered ring, a feature not observed in  $\text{HL}^3$  but common in other related imine–phenol compounds.<sup>14</sup> There are small distortions in the pyramidal geometry at P(1), with C–P–C angles between 100.6(1) and 103.1(2)°. The C(1)–N(1) length of 1.282(3) Å in  $\text{HL}^2$  is marginally longer than the corresponding distance in  $\text{HL}^3$  [1.269(3) Å],<sup>6</sup> in which the substituents on the C=N bond are reversed.

The crystal structures of the Group 10 metal complexes 1–5, 7 and 9 (Figs. 2–4; selected bond lengths and angles are presented in Table 2) reveal in general a square planar geometry at the

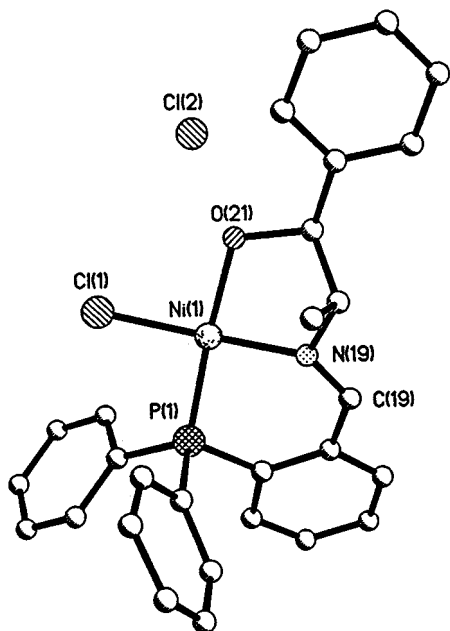


Fig. 2 Crystal structure of  $[\text{Ni}(\text{HL}^1)\text{Cl}]\text{Cl}$  **1** (hydrogen atoms omitted for clarity);  $[\text{Pd}(\text{HL}^1)\text{Cl}]\text{Cl}$  **2** and  $[\text{Pt}(\text{HL}^1)\text{Cl}]\text{Cl}$  **3** have the same geometry.

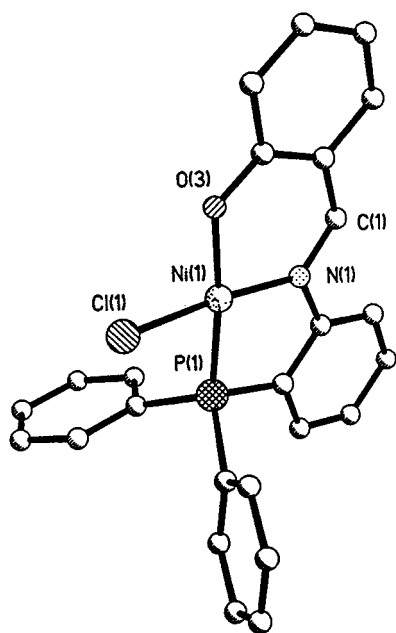


Fig. 3 Crystal structure of  $[\text{NiL}^2\text{Cl}]$  **4** (hydrogen atoms omitted for clarity);  $[\text{PdL}^2\text{Cl}]$  **5** has the same geometry.

metal atom with tridentate PNO co-ordination of the ligand, where the remaining bound chloride ligand is obligatorily disposed *trans* to N(1). The complexes **1–3** are cations and the proximity of the unbound chloride Cl(2) to the innocent alcohol oxygen O(21) [ $\text{Cl}(2)\cdots\text{O}(21)$  2.88–2.93 Å,  $\text{O}(21)\text{—H}(21)\cdots\text{Cl}(2)$  147–164°] in the crystal lattices suggests a strong hydrogen-bonding interaction with the undissociated hydroxyl proton H(21), corroborating the IR spectral assignments.

The complexes **4–9** are neutral owing to deprotonation of the oxygen atom of the tridentate ligand upon complexation, presumably due to the greater acidity of the phenolate protons compared to that of the alcohol. The ligand in complexes **4–6** is isomeric with that in **7–9** in that the relative positions of the six- and five-membered P,N and N,O chelate rings formed on complexation are reversed.

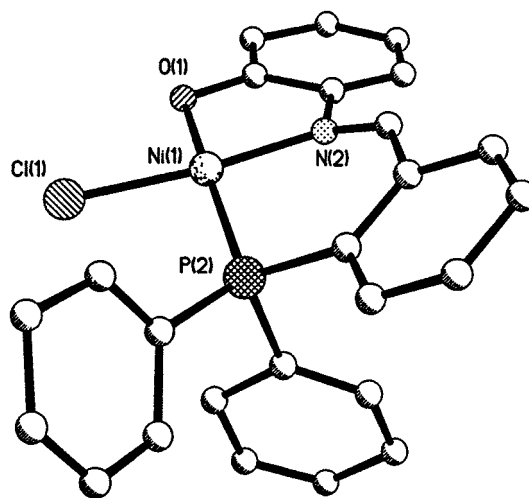


Fig. 4 Crystal structure of  $[\text{NiL}^3\text{Cl}]$  **7** (hydrogen atoms omitted for clarity);  $[\text{PtL}^3\text{Cl}]$  **9** has the same geometry.

All of the crystal structures exhibit distortions from idealised square-planar geometry at the metal, due to the bulk of the phosphine group and to the bite angle of the N,O chelate; the *trans* O–M–P [ $168.3(2)$ – $176.14(8)^\circ$ ] and *trans* N–M–Cl [ $171.15(11)$ – $176.63(6)^\circ$ ] axes are less than  $180^\circ$  in all of the complexes. The *cis* P–M–N and *cis* N–M–O angles vary between the complexes and are seemingly dependent upon the sizes of the P,N and N,O chelate rings. Thus *cis* N–M–O for the  $\text{HL}^1$  and  $(\text{L}^3)^-$  complexes **1–3**, **7** and **9**, which all have five-membered N,O chelate rings, are in the range  $81.6(3)$ – $86.6(3)^\circ$ , considerably smaller than those seen for **4** and **5**,  $96.09(7)$  and  $94.02(8)^\circ$ , which both contain a six-membered N,O ring. Conversely, the *cis* N–M–P angles exceed  $90^\circ$  for **1–3**, **7** and **9**, with six membered P,N chelate rings, as compared to  $87.92(6)$  and  $86.03(6)^\circ$  for **4** and **5**.

The structures of the nickel complexes **1**, **4** and **7** allow comparisons between the bonding parameters for the tridentate ligands  $\text{HL}^1$ ,  $(\text{L}^2)^-$  and  $(\text{L}^3)^-$ . In **1**, **4** and **7** there is little variation among the Ni–N and Ni–P distances (Table 2), suggesting similar basicities for the nitrogen and phosphorus atoms in all of these PNO ligands, although the Ni–Cl distance in **4** is *ca.* 0.04 Å longer than in either **1** or **7**. In  $[\text{Ni}(\text{HL}^1)\text{Cl}]\text{Cl}$  **1** there is an elongation of the Ni–O distance by *ca.* 0.1 Å compared with **4** and **7** which reflects the combined effects of O-protonation and the non-phenolic nature of the hydroxyl group in  $\text{HL}^1$ . Similar lengthening by *ca.* 0.12 Å of the M–O distances in the  $\text{HL}^1$  complexes compared with those of  $(\text{L}^2)^-$  and  $(\text{L}^3)^-$  is observed with palladium and platinum [Pd–O 2.155(6) in **2**, 2.030(2) Å in **5**; Pt–O 2.147(6) Å in **3**, 2.038(3) Å in **9**]. The M–N and M–P bond lengths in the palladium and platinum complexes, as seen for nickel, vary little with the phosphine employed, the Pd–N distance in  $[\text{Pd}(\text{HL}^1)\text{Cl}]\text{Cl}$  **2** exceptionally being *ca.* 0.03 Å shorter than in  $[\text{PdL}^2\text{Cl}]$  **5**. The complex  $[\text{NiL}^2\text{Cl}]$  **4** has the smallest *cis* O–M–Cl, *cis* N–M–P and *cis* P–M–Cl angles of all the nickel complexes [ $88.54(5)$ ,  $87.92(6)$  and  $87.65(2)^\circ$  respectively], whereas the corresponding values for **1** and **7** are all greater than  $90^\circ$ .

## Conclusion

New tridentate PNO donor ligands are readily synthesized from condensation reactions of 2-(diphenylphosphino)-aniline or -benzaldehyde, leading to stable complexes with the Group 10 metals. Differences in the acidity of the hydroxyl group and the sizes of the P,N and N,O chelate rings formed upon co-ordination dramatically affect the co-ordination behaviour and spectroscopic parameters for complexes of  $\text{HL}^1\text{—HL}^3$ .

**Table 2** Selected bond lengths (Å) and angles (°) for complexes **1–5**, **7** and **9** (estimated standard deviations in parentheses)

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>7</b>	<b>9</b>
M–P	2.138(1)	2.190(2)	2.185(2)	2.132(1)	2.194(1)	2.142(2)	2.198(1)
M–N	1.877(3)	1.985(7)	2.005(2)	1.892(2)	2.016(2)	1.900(7)	2.003(3)
M–O	1.975(2)	2.155(6)	2.147((6)	1.863(2)	2.030(2)	1.875(5)	2.038(3)
M–Cl(1)	2.144(1)	2.267(3)	2.278(3)	2.187(1)	2.306(1)	2.148(3)	2.282(1)
C=N	1.297(4)	1.323(9)	1.270(12)	1.311(3)	1.442(3)	1.260(11)	1.289(5)
C–O	1.441(4)	1.441(10)	1.469(10)	1.301(3)	1.293(3)	1.324(10)	1.322(5)
O···Cl(2)	2.93	2.89	2.88	—	—	—	—
N–M–O	84.67(11)	81.6(3)	82.0(3)	96.09(7)	94.02(8)	86.3(3)	83.02(13)
N–M–P	91.48(9)	90.8(2)	91.3(2)	87.92(6)	86.03(6)	91.7(2)	96.66(11)
O–M–Cl(1)	91.98(8)	94.3(2)	92.2(2)	88.54(5)	88.70(5)	90.4(2)	89.07(9)
P–M–Cl(1)	91.80(4)	93.11(9)	94.50(9)	87.65(2)	91.40(3)	92.25(10)	91.65(4)
O–M–P	176.14(8)	172.3(2)	173.2(2)	174.16(5)	176.00(6)	168.3(2)	173.37(8)
N–M–Cl(1)	171.70(10)	172.5(2)	172.9(2)	174.75(6)	176.63(6)	175.1(2)	171.15(11)
C–N–M	134.1(3)	109.1(5)	106.7(6)	121.1(2)	119.1(2)	131.0(5)	128.1(3)
C–O–M	111.0(2)	108.7(5)	109.6(5)	111.2(6)	125.4(2)	111.2(6)	110.7(3)
O–H···Cl(2)	164	147	160	—	—	—	—

## Experimental

Ligand syntheses and complexation reactions were performed under an atmosphere of oxygen-free nitrogen; thf and dichloromethane were distilled under nitrogen from sodium-benzophenone and calcium hydride respectively, all other solvents were analytical grade and used without further purification. The compounds [M(cod)Cl<sub>2</sub>] (M = Pt or Pd, cod = cycloocta-1,5-diene),<sup>15</sup> 2-(diphenylphosphino)aniline<sup>16</sup> and 2-(2-Ph<sub>2</sub>P)C<sub>6</sub>H<sub>4</sub>CH=NC<sub>6</sub>H<sub>4</sub>OH (HL<sup>3</sup>)<sup>6</sup> were prepared by literature methods; 2-(diphenylphosphino)benzaldehyde (Aldrich) was used as received. The <sup>1</sup>H (250.13) and <sup>31</sup>P-<sup>1</sup>H} (36.21 MHz) NMR spectra, recorded as C<sub>2</sub>D<sub>5</sub>OD (**1–3**) or CDCl<sub>3</sub> (**4–9**) solutions on Bruker AM250 and JEOL FX-90Q spectrometers, and were referenced to external tetramethylsilane (δ 0) and 85% phosphoric acid (δ 0) respectively using the high-frequency positive convention. Infrared spectra (pressed KBr discs) were recorded on a Perkin-Elmer System 2000 NIR FT-Raman spectrometer. Elemental analyses (Perkin-Elmer 2400 CHN elemental analyser) were performed by the University of Loughborough Analytical Service. Electron impact and fast atom bombardment (positive ionisation mode, 3-nitrobenzyl alcohol matrix) mass spectra were performed by the EPSRC National Mass Spectrometry Service Centre, Swansea, UK.

## Ligand syntheses

**2-(2-Ph<sub>2</sub>P)C<sub>6</sub>H<sub>4</sub>CH=NCH(Me)CH(OH)Ph-R,S HL<sup>1</sup>.** A thf (20 cm<sup>3</sup>) solution of 2-(diphenylphosphino)benzaldehyde (0.51 g, 1.75 mmol) and 1*S*,2*R*-norephedrine (0.27 g, 1.75 mmol) was heated at reflux for 3 h, giving an orange solution. The solvent was removed under reduced pressure and the resulting oil pumped *in vacuo* for 30 min to give 0.53 g of HL<sup>1</sup> as a pale pink solid. Yield 68% [Found (Calc. for C<sub>28</sub>H<sub>26</sub>NOP): C, 79.4 (79.4); H, 6.2 (6.2); N, 3.4 (3.3)%]. δ(<sup>31</sup>P) –10.5 (s). δ(<sup>1</sup>H) 8.62 [1 H, d, *J*(PH) 4, CH=N], 7.7–6.7 (m, aryl H), 4.53 [1 H, d, *J*(HH) 4, CHOH], 3.40 (1 H, m, CHMe), 0.7 [3 H, d, *J*(HH) 6 Hz, CH<sub>3</sub>]. IR (cm<sup>-1</sup>): ν(CN) 1638s. EI: *m/z* 424 (M<sup>+</sup>).

**2-(2-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>N=CH)C<sub>6</sub>H<sub>4</sub>OH HL<sup>2</sup>.** A thf solution (30 cm<sup>3</sup>) of 2-(diphenylphosphino)aniline (0.7 g, 2.5 mmol) and salicylaldehyde (0.33 g, 2.7 mmol) was heated at reflux for 12 h, during which time it became orange. The solvent was removed *in vacuo* and the solid product obtained recrystallised from chloroform-diethyl ether as 0.69 g of yellow crystals. Yield 67% [Found (Calc. for C<sub>25</sub>H<sub>20</sub>NOP): C, 78.4 (78.8); H, 5.2 (5.3); N, 3.3 (3.7)%]. δ(<sup>31</sup>P) –14.6 (s). δ(<sup>1</sup>H) 12.50 (1 H, br, OH), 8.40 (1 H,

s, CH=N) and 7.5–6.8 (m, aryl H). IR (cm<sup>-1</sup>): ν(CN) 1614s. EI: *m/z* 381 (M<sup>+</sup>).

## Metal complexes 1–9

Complexes **1**, **4** and **7** were all prepared according to a general method. An ethanolic (15 cm<sup>3</sup>) solution of HL (0.1 mmol) and NiCl<sub>2</sub>·6H<sub>2</sub>O (0.1 mmol) was stirred for 2 h to give a dark red solution. The solvent was removed *in vacuo*, the crude product extracted into dichloromethane (*ca.* 2–3 cm<sup>3</sup>) and precipitated with hexanes (25 cm<sup>3</sup>). Complex **1** was recrystallised from ethanol-diethyl ether, **4** and **7** from dichloromethane-diethyl ether.

Complexes **2**, **3**, **5**, **6**, **8** and **9** were all prepared according to a general method. A dichloromethane (15 cm<sup>3</sup>) solution of HL (0.1 mmol) and [M(cod)Cl<sub>2</sub>] (M = Pd or Pt; 0.1 mmol) was stirred for 2 h to give an intensely coloured (yellow to red) solution. The solvent was removed *in vacuo*, the crude product extracted into dichloromethane (*ca.* 2–3 cm<sup>3</sup>) and precipitated with hexanes (25 cm<sup>3</sup>). Complexes **2** and **3** were recrystallised from ethanol-diethyl ether, **5**, **6**, **8** and **9** from dichloromethane-hexanes.

Isolated yields of microcrystalline complexes **1–9** were typically in the range 25–60%; characterisation data are given in Table 1.

## X-Ray crystallography

The crystal structures of complexes **1–5**, **7** and **9** were determined at 298 K using a Siemens SMART diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structure of HL<sup>2</sup> was recorded on a Rigaku AFC7S instrument with Cu-Kα radiation (λ = 1.54178 Å) and ω scans. The crystal data, a summary of the data collections and the structure refinements are given in Table 3. All structures were solved by direct methods and all of the non-hydrogen atoms refined with anisotropic displacement parameters; the hydrogen atoms bound to carbon were included in calculated positions (C–H 0.95 Å) with a fixed isotropic displacement parameter. The hydrogen atom H(21) associated with O(21) in **1–3** and H(1o) associated with O(1) in HL<sup>2</sup> were located using the difference maps and allowed to refine isotropically with no distance restraint. Structural refinements were by full-matrix least-squares methods on *F*<sup>2</sup>, calculations being performed using the program SHELXTL PC;<sup>17</sup> for HL<sup>2</sup>, calculations were performed using TEXSAN<sup>18</sup> and empirical absorption corrections (DIFABS)<sup>19</sup> applied.

CCDC reference number 186/1141.

**Table 3** Details of the X-ray data collections and refinements for compounds HL<sup>2</sup>, 1–5, 7 and 9

	HL <sup>2</sup>	1·0.25EtOH	2·0.5EtOH	3·0.5EtOH	4	5	7	9
Empirical formula	C <sub>25</sub> H <sub>20</sub> NOP	C <sub>28.5</sub> H <sub>27.5</sub> Cl <sub>2</sub> NNiO <sub>1.25</sub> P	C <sub>29</sub> H <sub>29</sub> Cl <sub>2</sub> NO <sub>1.5</sub> PPd	C <sub>29</sub> H <sub>29</sub> Cl <sub>2</sub> NO <sub>1.5</sub> PPt	C <sub>25</sub> H <sub>19</sub> CINNiOP	C <sub>25</sub> H <sub>19</sub> CINOPPd	C <sub>25</sub> H <sub>19</sub> CINNiOP	C <sub>25</sub> H <sub>19</sub> CINOPPt
<i>M</i>	381.41	564.60	623.80	712.49	474.54	522.23	474.54	610.92
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 1	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> /Å	11.038(5)	10.513(1)	10.534(1)	10.573(1)	9.702(1)	9.784(1)	10.326(1)	9.085(1)
<i>b</i> /Å	10.589(4)	15.023(1)	15.194(1)	15.220(1)	13.006(1)	13.054(1)	10.518(1)	16.349(1)
<i>c</i> /Å	16.919(5)	19.019(1)	18.805(1)	18.695(1)	17.296(1)	17.284(1)	12.144(1)	14.091(1)
<i>α</i> <sup>o</sup>							83.06(1)	
<i>β</i> <sup>o</sup>	92.97(3)				96.14(1)	96.81(1)	73.58(1)	92.36(1)
<i>γ</i> <sup>o</sup>							71.52(1)	
<i>U</i> /Å <sup>3</sup>	1975(1)	3003.75(10)	3010.0(3)	3008.34(12)	2169.9(2)	2191.91(8)	1199.31(3)	2091.18(3)
<i>Z</i>	4	4	4	4	4	4	2	4
<i>μ</i> /mm <sup>-1</sup>	1.327	0.898	0.870	4.918	1.108	1.058	1.002	6.932
Total data	3390	18041	17938	18619	13043	12916	5161	9057
Unique data ( <i>R</i> <sub>int</sub> )	3136 (0.326)	6916 (0.1031)	7080 (0.1756)	7083 (0.0710)	5157 (0.0286)	5131 (0.0331)	3353 (0.0745)	3009 (0.0843)
No. of parameters	254	324	324	323	272	272	272	272
Goodness of fit on <i>F</i> <sup>2</sup>	2.87	0.635	0.818	0.879	0.655	0.914	0.837	0.602
<i>R</i> 1, <i>wR</i> 2 [ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup>	0.041, 0.026 <sup>b</sup>	0.0427, 0.0996	0.0664, 0.1085	0.0503, 0.0895	0.0298, 0.0793	0.0302, 0.0581	0.0849, 0.2390	0.0238, 0.0423

<sup>a</sup> *R*1 = Σ(|*F*<sub>o</sub>| - |*F*<sub>c</sub>|)/Σ|*F*<sub>o</sub>|, *wR*2 = [Σ*w*(*F*<sub>o</sub><sup>2</sup> - *F*<sub>c</sub><sup>2</sup>)<sup>2</sup>/Σ*w*(*F*<sub>o</sub><sup>2</sup>)<sup>2</sup>]<sup>1/2</sup>; *I* > 3σ(*I*) for HL<sup>2</sup>. <sup>b</sup> *wR*2 for HL<sup>2</sup> as defined by TEXSAN.

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