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# Synthesis, coordination chemistry and reactivity of cyano-functionalised *N*-pyrrolyl phosphines

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Dedicated to Professor Pierre Braunstein.

#### Abstract

The cyano-functionalised *N*-pyrrolyl phosphines PPh<sub>2</sub>(NC<sub>4</sub>H<sub>3</sub>CN-2) (L<sup>1</sup>) and P(NC<sub>4</sub>H<sub>3</sub>)(NC<sub>4</sub>H<sub>3</sub>CN-2) (L<sup>2</sup>) have been prepared from the reaction of PCIR<sub>2</sub> (R = Ph, NC<sub>4</sub>H<sub>4</sub>) with lithium 2-cyanopyrrolide, itself generated in situ from 2-cyanopyrrole and BuLi. The reaction of L<sup>1</sup> or L<sup>2</sup> with [MCl<sub>2</sub>(cod)] gives [MCl<sub>2</sub>(L- $\kappa^1 P$ )<sub>2</sub>] (1, M = Pt, L = L<sup>1</sup>; 2, M = Pd, L = L<sup>1</sup>; 3, M = Pt, L = L<sup>2</sup>; 4, M = Pd, L = L<sup>2</sup>) and both *cis*-1 and *trans*-4 have been structurally characterised. The crystal structure of *cis*-1 reveals the presence of an unusually wide P–Pt–P angle [107.22(5)°], which has its origin in an intramolecular interaction between the two 2-cyanopyrrole rings. The reaction of L<sup>1</sup> with [M(dmba)(µ-Cl)]<sub>2</sub> (Hdmba = *N*,*N*-dimethylbenzylamine) results in formation of [MCl(dmba)(L<sup>1</sup>- $\kappa^1 P$ )] (5, M = Pt; 6, M = Pd). Compounds 5 and 6 react with TIPF<sub>6</sub> to give oligomeric *P*,*N*-coordinated compounds of empirical formula [M(dmba)(L<sup>1</sup>)][PF<sub>6</sub>]. The dimeric compound [Pt(dmba)(µ-L<sup>1</sup>- $\kappa^1 P$ , $\kappa^1 N$ )]<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub> (7), has been isolated and structurally characterised, and coordination of the cyano groups leads to formation of a 12-membered ring. Compound 6 reacts with PhCH<sub>2</sub>CH(NH<sub>2</sub>)CH<sub>2</sub>OH in the presence of TIPF<sub>6</sub> to yield [Pd(dmba)(PPh<sub>2</sub>NC<sub>4</sub>H<sub>3</sub>{C=NCH(CH<sub>2</sub>Ph)CH<sub>2</sub>O-2})]PF<sub>6</sub> (8) in which the cyano group has been transformed into an oxazoline group. The molybdenum complex [MoCl(CO)<sub>3</sub>( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)] reacts with L<sup>1</sup> to give [MoCl(CO)<sub>2</sub>(L<sup>1</sup>- $\kappa^1 P$ )( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)] (9) which has been structurally characterised. In contrast to the reaction of 5 or 6, compound 9 does not react with TIPF<sub>6</sub> or AgBF<sub>4</sub> to give tractable oligomeric products. Reaction of the rhodium complex [Rh(acac)(CO)<sub>2</sub>] with L<sup>1</sup> occurs to give [Rh(acac)(CO)(L<sup>1</sup>- $\kappa^1 P$ )] (10). The infrared spectrum of 10 indicates the electronic properties of L<sup>1</sup> are very similar to those for PPh<sub>2</sub>(NC<sub>4</sub>H<sub>4</sub>).

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#### 1. Introduction

*N*-pyrrolyl phosphines have been known for over 25 years [1], but it is only recently that interest in these ligands has taken off due to recognition of their behaviour as good  $\pi$ -acceptors [2] and the catalytic implications of this electronic character [3]. As a consequence of involvement of the filled nitrogen porbital in the aromatic pyrrole ring, the P–N bond has no double bond character. This is in contrast to most ligands containing P–N bonds, which are typically good  $\sigma$ -donors due to the enhanced electron density this partial delocalisation imparts on the phosphorus atom

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[4]. For *N*-pyrrolyl phosphines, the nitrogen merely acts as an electronegative substituent, making the ligand a poor  $\sigma$ -donor. The  $\pi$ -acidity of the ligands has been demonstrated structurally [2], computationally [5] and through quantitative analysis of ligand effects [6] and is primarily a consequence of the LUMO energy.

While functionalities have been added with a view to enhancing the electronic properties of *N*-pyrrolyl phosphines [7], very little use has been made of the pyrrolyl ring as a skeleton for phosphines bearing additional donor groups [8]. Recently we reported the synthesis of the ketophosphine ligands (2-acetyl-*N*-pyrrolyl)diphenylphosphine ( $\mathbf{L}^3$ ) [9] and (2-acetyl-*N*-pyrrolyl)di-*N*pyrrolylphosphine ( $\mathbf{L}^4$ ) [10] and showed they could act as either *P*-donor or *P*,*O*-donor ligands, with the coordination modes readily interconverted. In this paper we report the synthesis of (2-cyano-*N*-pyrrolyl)diphe-

nylphosphine  $(L^1)$  and (2-cyano-*N*-pyrrolyl)di-*N*-pyrrolylphosphine  $(L^2)$ , and the coordination of these ligands to palladium, platinum, molybdenum and rhodium centres.

#### 2. Experimental

Reactions were routinely carried out using Schlenkline techniques under pure dry dinitrogen using dry dioxygen-free solvents. Microanalyses (C, H and N) were carried out by Mr. Alan Carver (University of Bath Microanalytical Service). Infrared spectra were recorded on a Nicolet 510P spectrometer as KBr pellets or solutions. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on JEOL EX270, Bruker Avance 300 or Varian Mercury 400 spectrometers referenced to TMS or 85% H<sub>3</sub>PO<sub>4</sub>. Coupling constants are reported in Hz. The complexes  $[PtCl_2(cod)]$  [31],  $[PdCl_2(cod)]$  [32],  $[M(dmba)(\mu-Cl)]_2$  (M = Pt, Pd) [33],  $[MoCl(CO)_3(\eta^5 C_5H_5$ ] [34] and [Rh(acac)(CO)<sub>2</sub>] [35] were prepared by standard literature methods. 2-Cyanopyrrole (Lancaster) was dried over molecular sieves and distilled prior to use.

#### 2.1. Syntheses

#### 2.1.1. $PPh_2(NC_4H_3CN-2)$ ( $L^1$ )

A 2.5 M hexane solution of BuLi (4.3 cm<sup>3</sup>, 10.8 mmol) was added dropwise to a solution of 2-cyanopyrrole (1.00 g, 10.8 mmol) in THF (10 cm<sup>3</sup>) at -78 °C. The reaction mixture was allowed to warm to ambient temperature and added to a solution of PClPh<sub>2</sub> (2.40 g, 10.8 mmol) in THF (5 cm<sup>3</sup>). After stirring for 4 h, the solvent was removed in vacuo to give a yellow oil, which was triturated with cold hexane to give a white powder. Recrystallisation from THF-hexane at -25 °C afforded  $L^1$  as colourless needles. Yield 1.88 g (63%). Found: C, 73.9; H, 4.80; N, 10.2. C<sub>17</sub>H<sub>13</sub>N<sub>2</sub>P requires C, 73.9; H, 4.74; N, 10.1%. δ (<sup>1</sup>H) (ppm) (CDCl<sub>3</sub>, 399.8 MHz) 7.48-7.40 (m, 6H, Ph), 7.34-7.30 (m, 4H, Ph), 6.99 (m, 1H, pyr), 6.75 (m, 1H, pyr), 6.34 (m, 1H, pyr).  $\delta$ (<sup>13</sup>C) (ppm) (CDCl<sub>3</sub>, 100.5 MHz): 133.8 (d, J<sub>CP</sub> 12), 132.1 (d, J<sub>CP</sub> 21), 132.2 (s), 130.7 (s), 129.0 (d, J<sub>CP</sub> 8), 126.5 (s), 114.3 (s), 113.6 (s), 106.7 (d,  $J_{CP}$  23).  $\delta$  (<sup>31</sup>P) (ppm) (CDCl<sub>3</sub>, 161.8 MHz) 51.8 (s). v(CN) (cm<sup>-1</sup>) (KBr) 2218m.

# 2.1.2. $P(NC_4H_4)_2(NC_4H_3CN-2)$ ( $L^2$ )

A 2.5 M hexane solution of BuLi (5.3 cm<sup>3</sup>, 13.2 mmol) was added dropwise to a solution of 2-cyanopyrrole (1.22 g, 13.2 mmol) in THF at -78 °C. The reaction mixture was allowed to warm to ambient temperature and added to a THF-hexane solution of PCl(NC<sub>4</sub>H<sub>4</sub>)<sub>2</sub> (2.62 g, 13.2 mmol). After 3 h stirring, the solution was filtered and the solvent removed in vacuo. The residue

was dissolved in toluene, filtered and stored at -25 °C for 24 h after which a colourless oil separated out. The oil was washed with small amounts of cold hexane and dried in vacuo. Yield 2.03 g (60%).  $\delta$  (<sup>1</sup>H) (ppm) (C<sub>6</sub>D<sub>6</sub>, 270.2 MHz) 6.43 (ps.qn, 4H, NC<sub>4</sub>H<sub>4</sub>), 6.35 (m, 1H, pyr), 6.17 (ps.t, 4H, NC<sub>4</sub>H<sub>4</sub>), 6.05 (m, 1H, pyr), 5.71 (m, 1H, pyr).  $\delta$  (<sup>13</sup>C) (ppm) (C<sub>6</sub>D<sub>6</sub>, 67.9 MHz) 124.7 (s), 122.9 (d, *J*<sub>CP</sub> 15), 122.5 (s), 114.2 (d, *J*<sub>CP</sub> 5), 114.0 (d, *J*<sub>CP</sub> 5), 113.2 (s), 112.3 (s).  $\delta$  (<sup>31</sup>P) (ppm) (C<sub>6</sub>D<sub>6</sub>, 109.4 MHz) 80.1 (s).  $\nu$ (CN) (cm<sup>-1</sup>) (CH<sub>2</sub>Cl<sub>2</sub>) 2221m.

# 2.1.3. $cis-[PtCl_2(L^1-\kappa^1 P)_2]$ (1)

[PtCl<sub>2</sub>(cod)] (0.272 g, 0.7 mmol) was added to a stirred solution of L<sup>1</sup> (0.386 g, 1.5 mmol) in dichloromethane (20 cm<sup>3</sup>), and the mixture stirred overnight. The volume of the solution was reduced by two-thirds and hexane added to precipitate **1** as a colourless powder. This was washed with hexane, dried in vacuo and crystallised from dichloromethane–hexane. Yield 0.50 g (87%). Found: C, 43.7; H, 3.00; N, 5.52. C<sub>34</sub>H<sub>26</sub>Cl<sub>2</sub>N<sub>4</sub>P<sub>2</sub>Pt·2CH<sub>2</sub>Cl<sub>2</sub> requires C, 43.7; H, 3.06; N, 5.67%.  $\delta$  (<sup>1</sup>H) (ppm) (CD<sub>2</sub>Cl<sub>2</sub>, 399.8 MHz) 7.70–7.65 (4H, m, Ph), 7.57–7.53 (2H, m, Ph), 7.43–7.38 (4H, m, Ph), 7.00 (1H, m, pyr), 6.66 (1H, m, pyr) and 6.16 (1H, m, pyr).  $\delta$  (<sup>31</sup>P) (ppm) (CD<sub>2</sub>Cl<sub>2</sub>, 109.4 MHz) 54.3 (s, <sup>1</sup>J<sub>PtP</sub> 4021).  $\nu$ (CN) (cm<sup>-1</sup>) (KBr) 2215m.

2.1.4. trans- $[PdCl_2(L^1 - \kappa^1 P)_2]$  (2)

[PdCl<sub>2</sub>(cod)] (0.100 g, 0.35 mmol) was added to a stirred solution of  $L^1$  (0.193 g, 0.70 mmol) in dichloromethane (10 cm<sup>3</sup>), and the mixture stirred overnight. The resulting yellow precipitate was isolated by filtration, washed with hexane and dichloromethane and dried in vacuo. Yield 0.150 g (59%). Found: C, 56.2; H, 3.75; N, 7.52. C<sub>34</sub>H<sub>26</sub>Cl<sub>2</sub>N<sub>4</sub>P<sub>2</sub>Pd requires C, 56.0; H, 3.59; N, 7.68%.  $\delta$  (<sup>1</sup>H) (ppm) (CD<sub>2</sub>Cl<sub>2</sub>, 399.8 MHz) 7.76 (m, 4H, Ph), 7.65 (m, 2H, Ph), 7.53 (m, 4H, Ph), 7.08 (m, 1H, pyr), 6.95 (m, 1H, pyr), 6.33 (m, 1H, pyr).  $\delta$  (<sup>31</sup>P) (ppm) (CD<sub>2</sub>Cl<sub>2</sub>, 109.4 MHz) 68.0 (s).  $\nu$ (CN) (cm<sup>-1</sup>) (KBr) 2211m.

# 2.1.5. $cis-[PtCl_2(L^2-\kappa^1 P)_2]$ (3)

[PtCl<sub>2</sub>(cod)] (0.334 g, 0.89 mmol) was added to a solution of  $L^2$  (0.504 g, 1.98 mmol) in dichloromethane and the mixture stirred overnight. Addition of hexane led to the formation of a colourless powder, which was separated by filtration, washed with hexane and dried in vacuo. Yield 0.605 g (88%). Found: C, 37.6; H, 2.85; N, 13.0. C<sub>26</sub>H<sub>22</sub>Cl<sub>2</sub>N<sub>8</sub>P<sub>2</sub>Pt·CH<sub>2</sub>Cl<sub>2</sub> requires C, 37.7; H, 2.81; N, 13.0%.  $\delta$  (<sup>1</sup>H) (ppm) (CD<sub>2</sub>Cl<sub>2</sub>, 270.2 MHz) 7.39 (m, 4H, NC<sub>4</sub>H<sub>4</sub>), 7.04 (m, 1H, pyr), 6.54 (m, 4H, NC<sub>4</sub>H<sub>4</sub>), 6.33 (m, 1H, pyr), 6.19 (m, 1H, pyr).  $\delta$  (<sup>31</sup>P) (ppm) (CD<sub>2</sub>Cl<sub>2</sub>, 109.4 MHz) 69.2 (s, <sup>1</sup>J<sub>PtP</sub> 3915). *v*(CN) (cm<sup>-1</sup>) (KBr) 2227m.

# 2.1.6. trans- $[PdCl_2(L^2-\kappa^1 P)_2]$ (4)

[PdCl<sub>2</sub>(cod)] (0.314 g, 1.1 mmol) was added to a solution of  $L^2$  (0.550 g, 2.2 mmol) in dichloromethane and the mixture stirred overnight. Addition of hexane led to the formation of a yellow powder which was separated by filtration, washed with hexane, dried in vacuo and crystallised from dichloromethane–hexane. Yield 0.445 g (59%). Found: C, 45.3; H, 3.14; N, 16.3. C<sub>26</sub>H<sub>22</sub>Cl<sub>2</sub>N<sub>8</sub>P<sub>2</sub>Pd requires C, 45.5; H, 3.23; N, 16.3%.  $\delta$  (<sup>1</sup>H) (ppm) (CD<sub>2</sub>Cl<sub>2</sub>, 270.2 MHz) 7.31 (m, 4H, NC<sub>4</sub>H<sub>4</sub>), 7.06 (m, 1H, pyr), 6.53 (m, 4H, NC<sub>4</sub>H<sub>4</sub>), 6.34 (m, 1H, pyr), 6.20 (m, 1H, pyr).  $\delta$  (<sup>31</sup>P) (ppm) (CD<sub>2</sub>Cl<sub>2</sub>, 109.4 MHz) 74.4 (s).  $\nu$ (CN) (cm<sup>-1</sup>) (KBr) 2226m.

# 2.1.7. $[PtCl(dmba)(L^{1}-\kappa^{1}P)]$ (5)

A solution of L<sup>1</sup> (0.176 g, 0.6 mmol) in dichloromethane (5 cm<sup>3</sup>) was added with stirring to a solution of [Pt(dmba)( $\mu$ -Cl)]<sub>2</sub> (0.220 g, 0.30 mmol) in dichloromethane (5 cm<sup>3</sup>). After 2 h, the volume of the solution was reduced in vacuo and hexane added to give **5** as a colourless powder. Yield 0.272 g (71%). Found: C, 48.5; H, 3.95; N, 6.55. C<sub>26</sub>H<sub>25</sub>ClN<sub>3</sub>PPt requires C, 48.7; H, 3.93; N, 6.56%.  $\delta$  (<sup>1</sup>H) (ppm) (CDCl<sub>3</sub>, 399.8 MHz) 7.86–7.84 (m, 4H, Ph), 7.62–7.58 (m, 2H, Ph), 7.48– 7.43 (m, 4H, Ph), 7.09–7.04 (m, 1H, Ar), 6.95–6.88 (m, 2H, Ar), 6.86–6.80 (m, 1H, pyr), 6.48–6.42 (m, 1H, pyr), 6.32–6.28 (m, 1H, Ar), 6.24–6.22 (m, 1H, pyr), 4.14 (d, 2H, <sup>4</sup>*J*<sub>PH</sub> 3.2, <sup>3</sup>*J*<sub>PtH</sub> 30, CH<sub>2</sub>), 2.96 (d, 6H, <sup>4</sup>*J*<sub>PH</sub> 3.6, <sup>3</sup>*J*<sub>PtH</sub> 24, CH<sub>3</sub>).  $\delta$  (<sup>31</sup>P) (ppm) (CDCl<sub>3</sub>, 161.8 MHz) 64.1 (s, <sup>1</sup>*J*<sub>PtP</sub> 4752).  $\nu$ (CN) (cm<sup>-1</sup>) (KBr) 2220m.

# 2.1.8. $[Pd(dmba)Cl(L^{1}-\kappa^{1}P)]$ (6)

A dichloromethane solution of  $L^1$  (0.370 g, 1.34 mmol) was added with stirring to a solution of  $[Pd(dmba)(\mu-Cl)]_2$  (0.370 mg, 0.67 mmol) in dichloromethane. After 2 h, the volume of the solution was reduced in vacuo and hexane added. The product separated as a vellow oil that was recrystallised from dichloromethane-hexane. Yield 0.526 g (71%). Found: C, 56.3; H, 4.57; N, 7.63. C<sub>26</sub>H<sub>25</sub>ClN<sub>3</sub>PPd requires C, 56.6; H, 4.56; N, 7.61%. δ (<sup>1</sup>H) (ppm) (CDCl<sub>3</sub>, 399.8 MHz) 7.91-7.86 (m, 4H, Ph), 7.60-7.56 (m, 2H, Ph), 7.51-7.39 (m, 4H, Ph), 7.05-7.03 (m, 1H, Ar), 6.91-6.87 (m, 1H, Ar), 6.85 (m, 1H, pyr), 6.75 (m, 1H, Ar), 6.49 (m, 1H, pyr), 6.21–6.15 (m, 2H, Ar+pyr), 4.15 (d, 2H,  ${}^{4}J_{PH}$  2.0, CH<sub>2</sub>), 2.87 (d, 6H,  ${}^{4}J_{PH}$  2.4, CH<sub>3</sub>).  $\delta$  (<sup>13</sup>C) (ppm) (CDCl<sub>3</sub>, 100.5 MHz) 152.4 (s), 149.1 (s), 135.5 (s), 133.2 (s), 131.0 (d, J<sub>CP</sub> 10), 129.5 (d, J<sub>CP</sub> 11), 129.0 (s), 126.0 (m), 125.1 (m), 123.5 (m), 114.1 (s), 112.2 (m), 110.3 (d, J<sub>CP</sub> 7.7), 73.8 (d, J<sub>CP</sub> 3.8, CH<sub>2</sub>), 51.2 (s, CH<sub>3</sub>).  $\delta$  (<sup>31</sup>P) (ppm) (CDCl<sub>3</sub>, 161.8 MHz) 88.2 (s). v(CN)  $(cm^{-1})$  (KBr) 2220m.

# 2.1.9. $[Pt(dmba)(\mu - L^{1} - \kappa^{1}P, \kappa^{1}N)]_{2}(PF_{6})_{2}$ (7)

Thallium hexafluorophosphate (0.048 g, 0.1 mmol) was added to a stirred solution of complex 5 (0.080 g,

0.1 mmol) in dichloromethane. After stirring for 24 h, TlCl was removed by filtration and the filtrate recrystallised from dichloromethane–hexane to give colourless crystals of **7**. Yield 0.056 g (80%). Found: C, 40.0; H, 3.30; N, 5.30. C<sub>52</sub>H<sub>50</sub>F<sub>12</sub>N<sub>6</sub>P<sub>4</sub>Pt<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub> requires C, 40.1; H, 3.30; N, 5.30%.  $\delta$  (<sup>1</sup>H) (ppm) (CD<sub>2</sub>Cl<sub>2</sub>, 399.8 MHz) 7.91–7.76 (m, 12H, Ph), 7.58–7.40 (m, 8H, Ph), 7.11 (m, 2H, pyr), 7.05 (m, 2H, Ar), 6.85 (m, 2H, Ar), 6.41 (m, 2H, pyr) 6.36 (m, 2H, pyr), 6.31 (m, 2H, Ar), 6.14 (m, 2H, Ar), 4.10 (d, 4H, <sup>4</sup>J<sub>PH</sub> 2.4, CH<sub>2</sub>), 2.94 (d, 12H, <sup>4</sup>J<sub>PH</sub> 3.2, CH<sub>3</sub>).  $\delta$  (<sup>31</sup>P) (ppm) (CD<sub>2</sub>Cl<sub>2</sub>, 161.8 MHz) 70.9 (s, <sup>1</sup>J<sub>PtP</sub> 4363), -141.6 (sept., PF<sub>6</sub>). *v*(CN) (cm<sup>-1</sup>) (KBr) 2258m.

# 2.1.10. $[Pd(dmba)(\mu - L^{1})](PF_{6})$

Thallium hexafluorophosphate (0.070 g, 0.20 mmol) was added to a stirred solution of complex **6** (0.111 mg, 0.20 mmol) in dichloromethane. After stirring for 24 h, TlCl was removed by filtration. The product slowly precipitated out of solution as a pale yellow powder, which was washed with dichloromethane and dried in vacuo. Yield 0.95 g (72%). Found: C, 46.2; H, 3.66; N, 6.26. C<sub>52</sub>H<sub>50</sub>F<sub>12</sub>N<sub>6</sub>P<sub>4</sub>Pd<sub>2</sub>·1/2CH<sub>2</sub>Cl<sub>2</sub> requires C, 46.2; H, 3.76; N, 6.15%.  $\delta$  (<sup>1</sup>H) (ppm) (CD<sub>2</sub>Cl<sub>2</sub>, 270.2 MHz) 7.66 (br, 6H), 7.51 (br, 4H), 6.96 (br, 3H), 6.93 (br, 1H), 6.50 (br, 1H), 6.30 (br, 1H) 6.19 (br, 1H), 4.08 (br, 2H), 2.77 (br, 6H).  $\delta$  (<sup>31</sup>P) (ppm) (CD<sub>2</sub>Cl<sub>2</sub>, 109.4 MHz) 89.8 (s, br), -141.6 (sept., PF<sub>6</sub>). v(CN) (cm<sup>-1</sup>) (KBr) 2248m.

# 2.1.11. $[Pd(dmba)(PPh_2NC_4H_3\{C=NCH(CH_2Ph)CH_2O-2\})]PF_6$ (8)

Thallium hexafluorophosphate (0.080 g, 0.23 mmol) was added to a stirred dichloromethane solution of 6 (0.130 g, 0.23 mmol). After 2 h (S)-2-amino-3-phenyl-1propanol (0.035 g, 0.23 mmol) was added and the suspension was refluxed for 24 h. The solution was filtered and the solvent removed in vacuo. The resulting oil was washed with hexane and diethyl ether, then dried in vacuo to give a glassy white solid. Yield 0.130 g (74%).  $\delta$  (<sup>1</sup>H) (ppm) (CDCl<sub>3</sub>, 399.8 MHz) 7.63–7.37 (m, 10H, Ph), 7.18-7.11 (m, 5H, Ph), 7.02 (d, 1H, J 6.8), 6.88-6.85 (m, 1H), 6.47-6.43 (m, 1H), 6.28-6.26 (m, 1H), 6.20-6.17 (m, 1H), 5.86 (br.s, 1H), 5.75 (d, 1H, J 8.4), 4.07 (d, 1H, <sup>2</sup>J<sub>HH</sub> 13.2, CH<sub>2</sub>N), 3.89 (dd/m, 2H,  ${}^{2}J_{\text{HH}}$  13.2,  ${}^{4}J_{\text{PH}}$  2.7, CH<sub>2</sub>N/CHN), 3.80 (dd, 1H,  ${}^{2}J_{\text{HH}}$  11.4,  ${}^{3}J_{\text{HH}}$  3.9, CH<sub>2</sub>O), 3.64 (dd, 1H,  ${}^{2}J_{\text{HH}}$  11.4,  ${}^{3}J_{\text{HH}}$ 7.2, CH<sub>2</sub>O), 2.99 (dd, 1H, <sup>2</sup>J<sub>HH</sub> 13.9, <sup>3</sup>J<sub>HH</sub> 3.9, CH<sub>2</sub>Ph), 2.74 (d, 3H,  ${}^{4}J_{HP}$  2.4, CH<sub>3</sub>), 2.69 (dd, 1H,  ${}^{2}J_{HH}$  13.9,  ${}^{3}J_{\rm HH}$  3.9, CH<sub>2</sub>Ph), 2.64 (d, 3H,  ${}^{4}J_{\rm HP}$  2.4, CH<sub>3</sub>).  $\delta$  ( ${}^{13}$ C) (ppm) (CDCl<sub>3</sub>, 75.5 MHz) 138.9 (d, J 8), 138.1 (s), 134.1–133.6 (m), 130.5 (d, J 6), 130.5–129.6 (m), 129.3 (d, J 15), 128.3 (d, J 5), 127.6 (d, J 4), 127.1 (s), 126.0 (d, J 6), 125.1 (s), 123.4 (s), 119.5 (d, J 3), 113.8 (d, J 4), 73.1 (d,  ${}^{3}J_{PC}$  3, CH<sub>2</sub>N), 66.1 (s, CH<sub>2</sub>O), 57.1 (s, CH), 50.4 (d,  ${}^{3}J_{PC}$  2, CH<sub>3</sub>), 50.3 (d,  ${}^{3}J_{PC}$  2, CH<sub>3</sub>), 37.7 (s, CH<sub>2</sub>Ph).  $\delta$  ( ${}^{31}P$ ) (ppm) (CDCl<sub>3</sub>, 161.8 MHz) 86.1 (s),

-141.6 (sept. PF<sub>6</sub>). v(C=N) (cm<sup>-1</sup>) (CH<sub>2</sub>Cl<sub>2</sub>) 1607s, 1555s.

# 2.1.12. $[MoCl(CO)_2(L^1-\kappa^1 P)(\eta^5-C_5H_5)]$ (9)

[MoCl(CO)<sub>3</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)] (0.299 g, 0.82 mmol) was added to a hexane solution of L<sup>1</sup> (0.229 g, 0.82 mmol) with stirring. The mixture was refluxed for 10 h after which the resulting red precipitate was separated by filtration, washed with hexane and dried in vacuo. Yield 0.394 g (91%). Found: C, 54.1; H, 3.58; N, 5.10. C<sub>24</sub>H<sub>18</sub>ClN<sub>2</sub>O<sub>2</sub>PMo requires C, 54.5; H, 3.43; N, 5.30%. δ (<sup>1</sup>H) (ppm) (CDCl<sub>3</sub>, 399.8 MHz) 7.66–7.45 (m, 10H, Ph), 7.10 (m, 1H, pyr), 6.65 (m, 1H, pyr), 6.23 (m, 1H, pyr), 5.63 (s, 5H, Cp). δ (<sup>31</sup>P) (ppm) (CDCl<sub>3</sub>, 161.8 MHz) 114.5 (s).  $\nu$ (CN) (cm<sup>-1</sup>) (KBr) 2217m;  $\nu$ (CO) (cm<sup>-1</sup>) (KBr) 1979s, 1901s.

# 2.1.13. $[Rh(acac)(CO)(L^{1}-\kappa^{1}P)]$ (10)

[Rh(acac)(CO)<sub>2</sub>] (0.116 g, 0.45 mmol) was added to a stirred solution of L<sup>1</sup> (0.125 g, 0.45 mmol) in dichloromethane. After 2 h, the volume of solvent was reduced in vacuo and diethyl ether added to precipitate **10** as a yellow powder. This was separated by filtration, washed with diethyl ether and dried in vacuo. Yield 0.181 g (79%). Found: C, 52.9; H, 3.83; N, 5.30. C<sub>23</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>PRh·1/4CH<sub>2</sub>Cl<sub>2</sub> requires 52.9; H, 3.92; N, 5.31%.  $\delta$  (<sup>1</sup>H) (ppm) (CD<sub>2</sub>Cl<sub>2</sub>, 399.8 MHz) 7.69–7.64 (m, 4H, Ph), 7.56–7.46 (m, 7H, Ph and pyr), 7.08 (m, 1H, pyr), 6.34 (m, 1H, pyr), 5.50 (s, 1H, CH), 2.11 (s, 3H, CH<sub>3</sub>), 1.70 (s, 3H, CH<sub>3</sub>).  $\delta$  (<sup>31</sup>P) (ppm) (CD<sub>2</sub>Cl<sub>2</sub>, 161.8 MHz):  $\delta$  98.1 (d, <sup>1</sup>J<sub>PRh</sub> 197).  $\nu$ (CN) (cm<sup>-1</sup>) (CH<sub>2</sub>Cl<sub>2</sub>) 2218m;  $\nu$ (CO) (cm<sup>-1</sup>) (CH<sub>2</sub>Cl<sub>2</sub>) 1992s.

#### 2.2. Crystallography

X-ray data for compound *cis*-1·2CH<sub>2</sub>Cl<sub>2</sub> was collected on an Enraf–Nonius CAD4 automatic four-circle diffractometer using Mo K $\alpha$  radiation ( $\lambda = 0.71069$  Å), and corrected for Lorentz, polarisation and absorption (DIFABS, max and min transmission factors 1.000 and 0.476). X-ray data for compounds **4**, 7·CH<sub>2</sub>Cl<sub>2</sub> and **9** were collected on a Nonius Kappa CCD diffractometer using Mo K $\alpha$  radiation ( $\lambda = 0.71070$  Å), and corrected for Lorentz, polarisation and absorption (multiscan, max and min corrections 1.055 and 0.963 for 7·CH<sub>2</sub>Cl<sub>2</sub>). The crystal data, data collection and refinements are summarised in Table 4. The refinements were all full-matrix least-squares based on  $F^2$ .

#### 3. Results and discussion

#### 3.1. Ligand synthesis

Since NH bonds are typically more acidic than CH bonds, the formation of N-P bonds generally requires

milder conditions than the formation of C–P bonds. This fact has been exploited in the synthesis of tri(N-pyrrolyl)phosphine [2] and of aminophosphines such as PPh<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub> [11], PPh<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>N-(CH<sub>3</sub>)<sub>2</sub> [12] and PPh<sub>2</sub>NHC<sub>5</sub>H<sub>4</sub>N-2 [13] which have all been prepared from the reaction of PClPh<sub>2</sub> with the appropriate pyrrole or amine in the presence of triethyl-amine. This synthesis is also successful for the N-pyrrolyl-based ketophosphine PPh<sub>2</sub>{NC<sub>4</sub>H<sub>3</sub>C(O)CH<sub>3</sub>-2} (L<sup>3</sup>), though in this case the yield is improved by use of the base DBU instead of NEt<sub>3</sub> [9]. The stronger base also increases the rate of formation of the product.

Despite the precedence of these syntheses, the reaction of PClPh<sub>2</sub>, 2-cyanopyrrole and triethylamine did not provide a good route to  $PPh_2(NC_4H_3CN-2)$  (L<sup>1</sup>). Compound  $L^1$  was the major product observed in <sup>31</sup>P{<sup>1</sup>H} NMR spectra of crude reaction mixtures, but other products were also invariably present, and it proved difficult to isolate  $L^1$  from these mixtures. However, it did prove possible to generate  $L^1$  as a pure compound in good yield from a two-step process. In this method, 2-cyanopyrrole was reacted with BuLi to give lithium 2-cyanopyrrolide, and this intermediate was reacted, without isolation, with  $Ph_2PCl$  to give  $L^1$  as colourless crystals following recrystallisation from THF-hexane.  $L^1$  was characterised on the basis of NMR and IR spectroscopy. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum shows a singlet at  $\delta$  51.8, which is close to value observed previously for  $L^3$  ( $\delta$  55.8). The CN stretching frequency is observed in the IR spectrum at  $2218 \text{ cm}^{-1}$ .

The functionalised tri-*N*-pyrrolylphosphine P(NC<sub>4</sub>-H<sub>4</sub>)<sub>2</sub>(NC<sub>4</sub>H<sub>3</sub>CN-2) (L<sup>2</sup>) was prepared by the reaction of PCl(NC<sub>4</sub>H<sub>4</sub>)<sub>2</sub> [10] with lithium 2-cyanopyrrolide in an analogous manner. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum for L<sup>2</sup> shows a singlet at  $\delta$  80.1, whereas the CN stretching frequency is observed in the IR spectrum at 2221 cm<sup>-1</sup>. The higher value for the chemical shift of L<sup>2</sup> with respect to L<sup>1</sup> is consistent with the reduced  $\sigma$ -basicity of this ligand.

The cyanophosphine  $L^1$  is more sensitive to hydrolysis and alcoholysis than the ketophosphine  $L^3$ , with the reaction with methanol to give Ph<sub>2</sub>POMe reaching completion within minutes rather than hours. Substitution of the two phenyl groups for *N*-pyrrolyl groups did not affect the stability, which is surprising given the stability to alcoholysis of tri-*N*-pyrrolylphosphine [2]. In contrast to  $L^3$ , the cyanophosphines  $L^1$  and  $L^2$  are also somewhat light sensitive, slowly decomposing with a progressive darkening in colour to deep red.

# 3.2. Reactions of $[MCl_2(cod)]$ with $L^1$ and $L^2$

The reactions of  $[MCl_2(cod)]$  (M = Pt, Pd) with 2 equiv. of L<sup>1</sup> or L<sup>2</sup> gave rise to complexes of the general formula  $[MCl_2L_2]$  in good yields. The complex  $[PtCl_2(L^1-\kappa^1P)_2]$  (1) was formed initially as a mixture of the *cis* and *trans* isomers (  $\sim 10:1$ ) as witnessed in the <sup>31</sup>P{<sup>1</sup>H} NMR spectra by singlets with <sup>195</sup>Pt satellites at  $\delta$  54.3 (<sup>1</sup>J<sub>PtP</sub> 4021 Hz) and  $\delta$  63.3 (<sup>1</sup>J<sub>PtP</sub> 2972 Hz), respectively. Both the chemical shift and coupling constant values allow the major product to be assigned as the cis-isomer. The IR spectrum shows v(CN) at 2215  $cm^{-1}$ , which is virtually unchanged from the free ligand. The cis isomer of complex 1 was purified by recrystallisation from dichloromethane-hexane, and a singlecrystal X-ray analysis confirmed its identity. The complex  $[PdCl_2(L^1-\kappa^1 P)_2]$  (2) proved to be only sparingly soluble in dichloromethane, precipitating during the reaction between [PdCl<sub>2</sub>(cod)] and L<sup>1</sup>. The  ${}^{31}P{}^{1}H{}$ NMR spectrum of the powder, dissolved in CD<sub>2</sub>Cl<sub>2</sub>, consisted of a singlet at  $\delta$  68.0, whereas that of the filtrate contained in addition to this a singlet at  $\delta$  79.3. On the basis of the chemical shift data and solubilities the isolated compound can be characterised as the trans isomer, with the more soluble minor compound being the *cis* isomer. As with 1, v(CN) is virtually unchanged from L<sup>1</sup>.

In contrast to the reactions with  $L^1$ , only single isomers were observed in the reactions with  $L^2$ . The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the compound *cis*-[PtCl<sub>2</sub>( $L^2-\kappa^1 P$ )<sub>2</sub>] (3) consists of a singlet with <sup>195</sup>Pt satellites at  $\delta$  69.2 (<sup>1</sup>J<sub>PtP</sub> 3915 Hz) whereas that of the compound *trans*-[PdCl<sub>2</sub>( $L^2-\kappa^1 P$ )<sub>2</sub>] (4) consists of a singlet at  $\delta$  74.4. The IR spectra of 3 and 4 both show v(CN) as being virtually unchanged from the free phosphine. The identity of 4 as the *trans* isomer was confirmed by a single crystal analysis.

The crystal structure determination of the platinum complex cis-1·2CH<sub>2</sub>Cl<sub>2</sub> revealed the metal coordination geometry to be distorted square-planar (Fig. 1) with Pt-Cl and Pt-P distances within the expected ranges.

Table 1 Selected bond lengths (Å) and angles (°) for complexes cis-1·2CH<sub>2</sub>Cl<sub>2</sub> and 4

cis-1·2CH <sub>2</sub> Cl <sub>2</sub>		4	
Bond lengths			
Pt(1) - P(1)'	2.2451(10)	Pd(1) - P(1)	2.2924(6)
Pt(1)-Cl(1)'	2.3408(11)	Pd(1)-Cl(1)	2.2854(6)
P(1) - N(1)'	1.729(3)	P(1) - N(1)	1.679(2)
N(1)-C(13)	1.386(4)	P(1) - N(2)	1.670(2)
N(1)-C(16)	1.393(5)	P(1) - N(3)	1.703(2)
N(2)-C(17)	1.143(6)	C(12)-C(13)	1.423(3)
C(13)-C(14)	1.339(6)	N(4) - C(13)	1.145(3)
C(14) - C(15)	1.404(6)		
C(15)-C(16)	1.356(5)		
C(16)-C(17)	1.413(5)		
Bond angles			
P(1) - Pt(1) - P(1)	107.22(5)	P(1)-Pd(1)-P(1)''	180.0
P(1) - Pt(1) - Cl(1)	169.99(4)	Cl(1) - Pd(1) - Cl(1)''	180.0
P(1)-Pt(1)-Cl(1)	82.48(4)	Cl(1) - Pd(1) - P(1)	88.59(2)
Cl(1) - Pt(1) - Cl(1)	87.95(6)	Cl(1) - Pd(1) - P(1)''	91.41(2)
N(2)-C(17)-C(16)	177.7(5)	N(4)-C(13)-C(12)	178.5(3)

Primed atoms generated by the symmetry transformation -x, y, -z+2 and double primed atoms by the transformation -x, -y, -z+2.

Selected bond lengths and angles are given in Table 1. The most striking feature of this structure is the P–Pt–P angle which at  $107.22(5)^{\circ}$  is one of the largest observed for a *cis*-dichlorobis(phosphine)platinum(II) complex. Indeed, a search of the Cambridge Structural Database [14] revealed a mean value of  $97.2^{\circ}$  for this angle in complexes of the general formula *cis*-[PtCl<sub>2</sub>P<sub>2</sub>] in which the phosphorus donors are located on different ligands. Only one other complex has a P–Pt–P angle as wide as that observed for *cis*-1: this is *cis*-[PtCl<sub>2</sub>(PPhBu<sub>2</sub><sup>t</sup>)<sub>2</sub>], where the angle at  $107.3(4)^{\circ}$  is similar to that in *cis*-1 [15]. In *cis*-[PtCl<sub>2</sub>(PPhBu<sub>2</sub><sup>t</sup>)<sub>2</sub>] the wide angle is clearly a consequence of the steric bulk of the phosphines, but in



Fig. 1. Molecular structure of complex cis-1·2CH<sub>2</sub>Cl<sub>2</sub> with thermal ellipsoids shown at the 30% probability level. Included CH<sub>2</sub>Cl<sub>2</sub> molecules have been omitted for clarity.

cis-1 the cause is not so straightforward. Indeed, the orientation adopted by the ligand in the solid state reveals that the 2-cyano-N-pyrrolyl group is not exceptionally sterically demanding. The crystallographic cone angle [16] for  $L^1$  in the structure of complex *cis*-1 is 169°, with the 2-cyano-N-pyrrolyl ring less sterically demanding than the two phenyl rings ( $\theta/2$  82.5, vs. 85.8 and  $84.9^{\circ}$ )<sup>1</sup>. Examination of the crystal structure reveals the wide P-Pt-P angle has its origin in an intramolecular offset  $\pi \cdots \pi$  interaction between the two 2-cyano-N-pyrrolyl groups. The angle between the two mean planes defined by the carbon and nitrogen atoms in the pyrrolyl rings is  $4^\circ$ , with the shortest inter-plane distance being that between C(15) and C(15)' (3.18 Å). If the P-Pt-P angle were more acute, this interaction between pyrrolyl rings would be prevented on steric grounds. Another noteworthy point is that the sum of angles around N(1) is close to  $360^{\circ}$  reflecting no change in the sp<sup>2</sup> hybridisation of the pyrrolyl nitrogen atom on coordination.

Structural analysis of 4 revealed the palladium atom lies on an inversion centre with half site occupancy. The geometry around the metal centre is distorted squareplanar, with cis angles of 88.59(2) and 91.41(2)°. The molecular structure of 4 is shown in Fig. 2(a), and selected bond lengths and angles are given in Table 1. Analysis of the conformation of the phosphine ligands revealed that  $L^2$  in 4 has the same crystallographic cone angle (169°) as  $L^1$  in *cis*-1, reflecting the similar steric requirements of phenyl and pyrrolyl groups [17]. The sum of angles around each of the pyrrolyl nitrogen atoms is close to 360°. Obviously the trans orientation of the ligands in the structure prevents any intramolecular interaction between the cyanopyrrolyl groups. The supramolecular structure of 4 reveals no intermolecular  $\pi \cdots \pi$  interaction to be present either—instead, the molecules are linked into chains via the formation of  $C-H \cdots N$  hydrogen bonds involving a cyanopyrrolyl CH group and the cyano nitrogen atom  $[C(10) \cdots N(4)]$ 3.392(4) Å, H(10)···N(4) 2.51 Å, C(10)–H(10)···N(4) 155°]. These chains are cross-linked by  $C-H\cdots Cl$ hydrogen bonds [C(6)···Cl(1) 3.659(3) Å, H(6)···Cl(1) 2.76 Å, C(6)–H(6)···Cl(1) 162°]. These interactions are shown in Fig. 2(b).

The P–N distances in **4** and *cis*-**1** are longer than those in platinum(II) complexes of PPh<sub>2</sub>NHR [7] and tri(*N*-pyrrolyl)phosphine [18]. The non-involvement of the nitrogen lone pair in an aromatic ring in aminophosphines allows for greater P–N double bond character than in *N*-pyrrolyl phosphines, whereas the increase in P–N distances on going from tri(*N*-pyrrolyl)phosphine through di(*N*-pyrrolyl)phenylphosphine to (*N*-pyrrolyl)diphenylphosphine has been previously observed [19].

# 3.3. Reactions of $[M(dmba)(\mu-Cl)]_2$ with $L^1$

Although (cyanoethyl)phosphines have been well studied [20,21], ligands with rigid spacers between the phosphino and cyano groups, such as Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>CN-2 [22], have received far less attention. There is some spectroscopic evidence [23] for  $\eta^2$ -coordination of the cyano groups in rhenium(I) and manganese(I) complexes of Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>CN-2, but these compounds have not been crystallographically characterised, and it is more likely that the ligands bridge between metal centres with a  $\sigma$ -bonded cyano group [24]. In order to assess the coordination ability of the cyano group in L<sup>1</sup>, the complexes [MCl(dmba)(L<sup>1</sup>- $\kappa^1 P$ )] (5, M = Pt; 6, M = Pd; Hdmba = N,N-dimethylbenzylamine) were prepared and reacted with TlPF<sub>6</sub>.

Complex 5 was prepared from the reaction of  $[Pt(dmba)(\mu-Cl)]_2$  with L<sup>1</sup> and characterised on the basis of NMR and IR spectroscopy. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of 5 gave a singlet with <sup>195</sup>Pt satellites at  $\delta$  64.1  $[^{1}J_{PtP} 4752 \text{ Hz}]$  demonstrating that only one of the two potential geometric isomers was formed. The high value of  ${}^{1}J_{PtP}$  together with observation of  ${}^{4}J_{PH}$  coupling in the <sup>1</sup>H NMR spectrum indicates that the phosphorus atom is coordinated trans to the dmba nitrogen atom [20]. In the IR spectrum v(CN) was observed at 2220  $cm^{-1}$  consistent with non-coordination of the cyano group. Complex 6 was prepared from the analogous reaction of  $[Pd(dmba)(\mu-Cl)]_2$  with L<sup>1</sup> and also characterised on the basis of NMR and IR spectroscopy. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **6** gave a singlet at  $\delta$ 88.2, again demonstrating formation of a single isomer. As for complex 5, the observation of  ${}^{4}J_{\rm PH}$  in the  ${}^{1}{\rm H}$ NMR spectrum confirmed the trans arrangement of the phosphorus and nitrogen atoms. In the IR spectrum of 6, v(CN) was observed at 2220 cm<sup>-1</sup>.

Reaction of complex 5 with  $TlPF_6$  gave a precipitate of TlCl and the initial formation of three compounds, observed in the  ${}^{31}P{}^{1}H$  NMR spectrum with similar values for  ${}^{1}J_{PtP}$  [ $\delta$  70.9 ( ${}^{1}J_{PtP}$  4363 Hz, 55%),  $\delta$  66.8  $({}^{1}J_{PtP}$  4654 Hz, 15%),  $\delta$  58.2  $({}^{1}J_{PtP}$  4448 Hz, 30%)] together with a septet at  $\delta$  -141.6 for the PF<sub>6</sub><sup>-</sup> ion. On standing for several hours, the signal for one of these compounds [ $\delta$  70.9] increased in intensity at the expense of the other two, and after recrystallisation from dichloromethane-hexane only this product was observed in the spectrum of both the solid and the mother liquor, demonstrating it to be the thermodynamic product of the reaction. The IR spectrum of this compound shows v(CN) at 2258 cm<sup>-1</sup>. The shift to a higher wavenumber relative to 5 ( $\Delta v = 38$  cm<sup>-1</sup>) is consistent with coordination of the cyano group through the nitrogen atom [25]. This compound has

<sup>&</sup>lt;sup>1</sup> van der Waals' radius of 1.55 Å used for N(1).



Fig. 2. (a) Molecular structure of complex 4 with thermal ellipsoids shown at the 30% probability level. (b) Formation of chains in the crystal structure of 4 through  $C-H\cdots N$  hydrogen bonds.

been characterised crystallographically as the dimer  $[Pt(dmba)(\mu-L^1-\kappa^1P,\kappa^1N)]_2(PF_6)_2$  (7). The two other compounds observed in the initial NMR spectra have yet to be characterised. Although it is tempting to assign these to higher cyclic oligomers on the basis of their similar coupling constants to 7, there is no evidence in the FAB MS of the crude reaction mixture for such species.

The X-ray crystal structure analysis of  $7 \cdot CH_2Cl_2$ revealed that the cationic complex is dimeric (Fig. 3), with coordination of the cyano nitrogen atom to a second platinum atom leading to the formation of a 12membered ring. Selected bond lengths and angles are given in Table 2. The geometry around each of the two independent platinum centres is distorted square-planar, with *cis* angles in the range  $81.7(2)-94.51(14)^\circ$  for Pt(1)



Fig. 3. Structure of the cation in complex  $7 \cdot CH_2Cl_2$  with thermal ellipsoids shown at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Table 2	
Selected bond lengths (Å) and angl	les (°) for complex $7 \cdot CH_2Cl_2$

Selected cond lengths (1) and t	
Bond lengths	
Pt(1)-C(18)	2.024(6)
Pt(1)-N(5)	2.055(5)
Pt(1)-N(3)	2.125(5)
Pt(1) - P(1)	2.2186(14)
Pt(2)-C(44)	2.017(5)
Pt(2)-N(2)	2.047(4)
Pt(2)–N(6)	2.124(4)
Pt(2)-P(2)	2.2188(14)
P(1)-N(1)	1.751(5)
P(2)-N(4)	1.766(5)
N(2)-C(17)	1.148(7)
N(5)-C(43)	1.151(7)
Bond angles	
C(18) - Pt(1) - N(5)	172.1(2)
C(18) - Pt(1) - N(3)	81.7(2)
N(5)-Pt(1)-N(3)	91.0(2)
C(18) - Pt(1) - P(1)	92.83(18)
N(5)-Pt(1)-P(1)	94.51(14)
N(3)-Pt(1)-P(1)	174.51(15)
C(44) - Pt(2) - N(2)	173.2(2)
C(44) - Pt(2) - N(6)	81.73(19)
N(2)-Pt(2)-N(6)	92.09(17)
C(44) - Pt(2) - P(2)	92.16(16)
N(2)-Pt(2)-P(2)	93.99(12)
N(6)-Pt(2)-P(2)	173.86(13)
C(17)-N(2)-Pt(2)	170.8(4)
C(43)-N(5)-Pt(1)	170.4(5)
N(2)-C(17)-C(16)	172.7(6)
N(5)-C(43)-C(42)	174.5(6)

and  $81.73(19)-93.96(12)^{\circ}$  for Pt(2). The angle between the two coordination planes is  $80.5^{\circ}$ . There is only one previously reported crystal structure of a cyanophosphine complex in which the ligand is acting in a bridging manner, which is the octahedral nickel(II) complex [NiBr<sub>2</sub>{P(CH<sub>2</sub>CH<sub>2</sub>CN)<sub>3</sub>}<sub>2</sub>] [26]. Reaction of complex **6** with TIPF<sub>6</sub> also gave a precipitate of TICl. A compound of empirical formula  $[Pd(dmba)(\mu-L^{1}-\kappa^{1}P,\kappa^{1}N)](PF_{6})$  was isolated, though the low solubility and consequently the broad nature of the NMR spectra mean it is not possible to say whether the product is a dimer, directly analogous to 7, or a mixture of higher oligomers. As with 7, the shift of  $\nu(CN)$  to a higher wavenumber ( $\nu = 2248 \text{ cm}^{-1}, \Delta \nu = 30 \text{ cm}^{-1}$ ) is indicative of coordination of the cyano group through the nitrogen atom. Similar observations were reported by Braunstein and co-workers following the reaction of  $[PdCl(dmba)(PPh_2CH_2CN)]$  with AgPF<sub>6</sub> [20].

#### 3.4. Preparation of phosphino-oxazolines

An important reaction of cyano groups is their conversion, on reaction with an amino alcohol, to oxazoline groups. Phosphino-oxazolines have been used as chiral P,N-donor ligands in a number of catalytic reactions [27] and have also been shown to act as hemilabile ligands [28]. Recently Pfaltz and co-workers demonstrated that N-pyrrolyl phosphines containing oxazoline groups could be prepared from a oxazoline-functionalised pyrrole [29].

Our approach, contemporary with this, involved preformation of a P,N-coordinated complex of the cyanophosphine and reaction of it with an amino alcohol. Coordination of the phosphorus atom should improve the stability of the P–N bond towards alcoholysis, whereas coordination of the nitrogen atom should activate the carbon atom of the nitrile group. Initial reactions using ZnCl<sub>2</sub>, [PdCl<sub>2</sub>(cod)] and [PdCl(CH<sub>3</sub>)-(cod)] with 2-methyl-2-aminopropanol were all promising, as indicated by the NMR and IR spectra of the crude reaction mixtures. However, satisfactory analytical results could not be obtained due to difficulties in purification. In contrast, the cyanophosphine complex [PdCl(dmba)( $L^{1}-\kappa^{1}P$ )] (6) reacts with the amino alcohol (S)-(-)-2-amino-3-phenyl-1-propanol under reflux in the presence of TlPF<sub>6</sub> to give the compound [Pd(dmba)(PPh<sub>2</sub>NC<sub>4</sub>H<sub>3</sub>{C=NCH(CH<sub>2</sub>Ph)CH<sub>2</sub>O-2})]PF<sub>6</sub> (8), which can be isolated in good yield after work up as a glassy colourless solid (Scheme 1). The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum for 8 showed a singlet at  $\delta$  86.1 in addition to the septet for the hexafluorophosphate. The <sup>13</sup>C{<sup>1</sup>H}, <sup>1</sup>H and <sup>13</sup>C-<sup>1</sup>H correlation NMR spectra confirmed that the cyano group had been converted into an oxazoline group. The IR spectrum confirmed the absence of  $\nu$ (C=N) and the presence of  $\nu$ (C=N) at 1607 cm<sup>-1</sup>.

# 3.5. Molybdenum complexes of $L^1$

In order to investigate the coordination behaviour of  $L^1$  on an earlier transition metal the complex  $[MoCl(CO)_2(L^1-\kappa^1 P)(\eta^5-C_5H_5)]$  (9) was prepared from the reaction of  $[MoCl(CO)_3(\eta^5-C_5H_5)]$  with L<sup>1</sup> in refluxing hexane. In the  ${}^{31}P{}^{1}H{}$  NMR spectrum a singlet was observed at  $\delta$  114.5, in a similar position to the resonance observed for  $[MoCl(CO)_2(L^3-\kappa^1 P)(\eta^5 C_5H_5$ ] ( $\delta$  112.2) [9]. In the IR spectrum two carbonyl resonances reflect the cis geometry of the carbonyls and v(CN) is observed at 2217 cm<sup>-1</sup>, close to the frequency observed for free ligand. Further confirmation of the identity of 9 was obtained by a single crystal X-ray analysis. Suitable single crystals were grown by diffusion of hexane into a dichloromethane solution. The molecular structure of 9 is shown in Fig. 4, and selected bond lengths and angles are given in Table 3. The compound adopts a pseudo square-pyramidal geometry, with the cis carbonyls and the phosphorus and chlorine atoms forming the base of the pyramid and the cyclopentadienyl ligand the apex. The bond lengths and angles are unremarkable, though since the Mo-P distance is longer than the M-P distances in cis-1, trans-4 and 7, the crystallographic cone angle for the ligand is less (155°).

Compound 9 was treated with both TlPF<sub>6</sub> and AgBF<sub>4</sub> in attempts to abstract the chloride. On stirring for 24 h in the presence of TlPF<sub>6</sub> no reaction was observed, the  ${}^{31}P{}^{1}H{}$  NMR spectrum being essentially unchanged



Fig. 4. Molecular structure of complex 9 with thermal ellipsoids shown at the 30% probability level.

Table 3 Selected bond lengths (Å) and angles (°) for complex  ${\bf 9}$ 

Bond lengths		
Mo(1) - C(1)	1.987(3)	
Mo(1)-C(2)	1.970(3)	
Mo(1)-P(1)	2.4842(6)	
Mo(1)-Cl(1)	2.5171(7)	
P(1) - N(1)	1.758(2)	
N(2)-C(3)	1.151(4)	
Bond angles		
C(2)-Mo(1)-C(1)	76.97(11)	
C(1)-Mo(1)-P(1)	118.77(8)	
C(2)-Mo(1)-P(1)	80.04(8)	
C(1)-Mo(1)-Cl(1)	77.64(8)	
C(2)-Mo(1)-Cl(1)	131.70(8)	
P(1)-Mo(1)-Cl(1)	77.28(2)	
N(2)-C(3)-C(4)	175.2(3)	

after this time. In contrast, stirring with  $AgBF_4$  led to a precipitate of AgCl, showing abstraction had taken place. However, the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum contained a large number of peaks suggesting decomposition had occurred.



Scheme 1.

Table 4 Crystal data for compounds  $cis-1.2CH_2Cl_2$ , 4,  $7.CH_2Cl_2$  and 9

Complex	$cis-1 \cdot 2CH_2Cl_2$	4	$7 \cdot CH_2Cl_2$	9
Empirical formula	$C_{36}H_{30}Cl_6N_4P_2Pt$	$C_{26}H_{22}Cl_2N_8P_2Pd$	$C_{53}H_{52}Cl_2F_{12}N_6P_4Pt_2$	C24H18ClMoN2O2P
$M^{-}$	988.37	685.76	1585.97	528.76
Temperature	293(2)	150(2)	170(2)	150(2)
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	C2/c	$P2_1/c$	$P2_{1}2_{1}2_{1}$	$P2_1/n$
a	17.714(4)	8.1320(2)	14.1900(1)	9.4160(3)
b	10.435(2)	19.3020(5)	16.5460(1)	14.2570(5)
с	21.233(3)	9.1750(2)	24.7970(3)	16.6620(6)
β	100.91(2)	95.2340(10)	90	104.9120(18)
U	3853.9(13)	1434.14(6)	5822.03(9)	2161.44(13)
Ζ	4	2	4	4
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	4.172	0.977	5.082	0.829
Reflections collected	4729	17 059	99 327	24188
Independent reflections	4179	3266	13 319	4936
R <sub>int</sub>		0.0609	0.0774	0.0497
$R_1, wR_2 [I > 2\sigma(I)]$	0.0290, 0.0732	0.0306, 0.0735	0.0317, 0.0780	0.0341, 0.0846
R indices (all data)	0.0360, 0.0753	0.0459, 0.0805	0.0425, 0.0859	0.0451, 0.0919

# 3.6. Synthesis of $[Rh(acac)(CO)(L^{1}-\kappa^{1}P)]$

Carbonyl stretching frequencies can be useful indicators in determining the electronic properties of a phosphine co-ligand. A considerable body of data has been compiled for complexes of the general formula [Rh(acac)(CO)L], which can usually be prepared in a straightforward manner from the reaction of [Rh(a $cac)(CO)_2$  with L. Reaction of L<sup>1</sup> with [Rh(acac)(CO)\_2] in dichloromethane gave, as anticipated, [Rh(a $cac)(CO)(L^{1}-\kappa^{1}P)$ ] (10) in good yield. The carbonyl stretching frequency for 10 was observed at 1992  $cm^{-1}$ , which is very similar to the value previously reported for  $[Rh(acac)(CO){PPh_2(NC_4H_4)}]$  (1990)  $cm^{-1}$ ) [30]. This suggests that introduction of the cyano functionality into the pyrrolyl ring has little effect on the electronic properties of the phosphine. In the  ${}^{31}P{}^{1}H{}$ NMR spectrum of 10 a doublet was observed at  $\delta$  98.1  $({}^{1}J_{PRh}$  197 Hz), and in the IR spectrum v(CN) was observed at 2218 cm $^{-1}$ .

# 4. Conclusions

In this paper we have demonstrated that cyanofunctionalised N-pyrrolyl phosphines can be readily prepared, and that they can act as either P-donor or bridging P,N-donor ligands. Infrared spectroscopic data indicates that the 2-cyano-N-pyrrolyl group is as electron-withdrawing as the N-pyrrolyl group, demonstrating that functionalised N-pyrrolyl phosphines can be prepared without destroying the useful electronic properties of the N-pyrrolyl phosphine core. The cyano group can also be readily converted into an oxazoline group. Both intra- and intermolecular interactions, involving offset  $\pi \cdots \pi$  interactions and C-H $\cdots$ N hydrogen bonds respectively, have been shown to be important in the solid state with the former leading to an unusually large P-Pt-P angle in *cis*-1.

#### 5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as CCDC Nos. 186630–186633. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac. uk or www: http://www.ccdc.cam.ac.uk).

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