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Synthesis and coordination of 2-diphenylphosphinopicolinamide

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Abstract

The synthesis and coordination of 2-diphenylphosphinopicolinamide (dpppa **1**) is reported. Coordination complexes with Pd, Pt, Ru, Rh, Ir and Au are described. The ligand behaves as a monodentate *P* donor in complexes such as $[PtCl_2(dpppa\text{-}P_2)]$, [PdCl(allyl)(dpppa-*P*)], $[RuCl_2(p\text{-Cymene})(dpppa\text{-}P)]$, *cis*-$[PtCl_2(dpppa\text{-}P)(PR_3)]$ and [AuCl(dpppa-*P*)]. Bidentate *P,* O coordination was accomplished by reaction of BuLi with $[RuCl_2(p\text{-Cymene})(dpppa\text{-}P)]$, to give [RuCl(*p*-Cymene)(dpppa-*P*,*O*). *P*,*N* donor behaviour was achieved by reaction of a monodentate complex with a halide abstractor $[AgBF_4]$ generating [RuCl(*p*-Cymene)(dpppa-*P*,*N*)][ClO_4] and$[RhCl(\eta^5\text{-}C_5Me_5)(dpppa\text{-}P,N)][BF_4]$. The X-ray structures of dpppa, dpppaO, dpppaS, four monodentate complexes and [RuCl(*p*-Cymene)(dpppa-*P*,*O*) are reported. All of the structures contain intramolecular N–H···N hydrogen bonding.

Keywords: 2-Diphenylphosphinopicolinamide (dpppa **1**); Coordination chemistry; Monodentate donors; Bidentate donors

1. Introduction

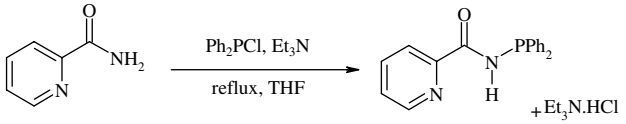
There is widespread interest in hemilabile phosphorus–nitrogen ligands, which has focused on the presence of both 'hard' (nitrogen) and soft (phosphorus) donor atoms on one ligand. One aspect of the hemilabile nature of these ligands is based around the presence of spacer atoms between the phosphorus nitrogen donor atom which can influence electronic properties as well as flexibility. For example in pyridine based systems, N–H (**A**) [1–3], CH_2–CH_2 (**B**) [4–7], NH–NH (**C**) [8–10] have been used as spacer atoms/groups (see Fig. 1).

There has also been considerable interest in phosphorus–oxygen ligands, with oxygen acting as the 'hard' donor atom. There are numerous examples where oxygen has been incorporated into a ligand, examples include etherphosphines (**D**) [11], 1,3-dioxolane derivatives (**E**) [12], aldehyde functionlised phosphines (**F**) [13–15] and furylphosphines (**G**) [16] systems (see Fig. 2).

Here, we will describe our investigations into an amalgamation of two of these aspects of coordination chemistry; aminopyridylphosphines and phosphino-enolates in the synthesis and coordination of 2-diphenylphosphinopicolinamide (dpppa **1**). We report a range of coordination modes incorporating both the pyridylphosphine and phosphino-enolate character of dpppa. The ligand, its derivatives and the complexes generated have been principally characterised by multi-element NMR spectroscopy and X-ray crystallography.

2. Results and discussion

The synthesis of dpppa is straightforward



dpppa **1**

(1)

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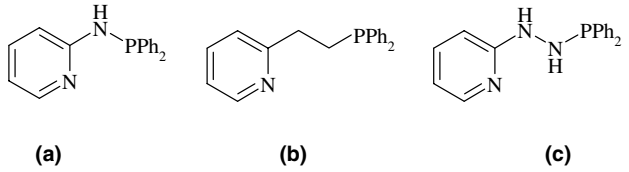


Fig. 1. Pyridylphosphines.

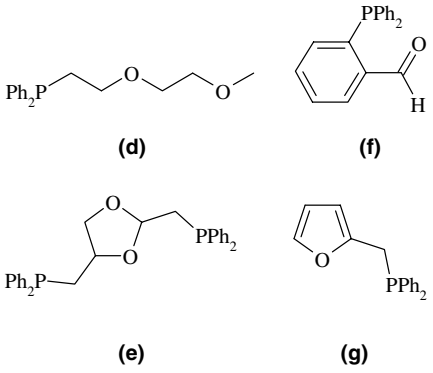


Fig. 2. Phosphorus–oxygen ligands.

Dpppa was recrystallised from boiling methanol to give a colourless crystalline solid in a tolerable yield (55%) and is relatively air stable; however exposure to air for prolonged periods resulted in degradation. It is readily soluble in chlorinated solvents, acetone, thf, somewhat less so in toluene, methanol and diethyl ether. A singlet is observed in the ^{31}P spectra of dpppa (in $CDCl_3$) at δ(P) 22.0 ppm. The ^{1}H NMR clearly shows the presence of an amide proton at δ(H) 8.65 ppm, as a doublet $^2J_{P-H} = 4$ Hz. The IR spectra shows a weak ν(N–H) band at 3297 cm^{-1}, and bands attributable to ν(pyCN) and ν(P–N) at 1452 and 996 cm^{-1} respectively. The expected ν(C=O) signature is visible at 1691 cm^{-1}. Satisfactory microanalysis was also obtained. The crystal structure of dpppa (Table 1 and Fig. 3) reveals that the P(1)–N(2)–C(3)–O(3) backbone is essentially planar

Table 1
Selected bond lengths (Å) and angles (°) for dpppa, dppaO and dppaS

	Dpppa **1**	DpppaO **2**	DpppaS **3**
Bond lengths			
P–O/S		1.478(2)	1.9475(9)
P(1)–N(2)	1.702(3)	1.683(2)	1.699(2)
N(2)–C(3)	1.355(5)	1.370(4)	1.378(3)
C(3)–C(4)	1.500(6)	1.506(4)	!.502(5)
C(3)–O(3)	1.221(5)	1.217(3)	1.219(3)
N(2)···N(5)	2.67(5)	2.65(5)	2.65
Bond angles			
C(3)–N(2)–P(1)	126.1(3)	124.09(19)	125.33(18)
N(2)–C(3)–C(4)	116.2(4)	114.4(2)	114.1(2)
O(3)–C(3)–N(2)	122.1(4)	123.1(3)	123.4(2)
O(3)–C(3)–C(4)	121.7(4)	122.6(3)	122.6(2)
N(2)–H(2)···N(5)	129(3)	109(3)	111(2)

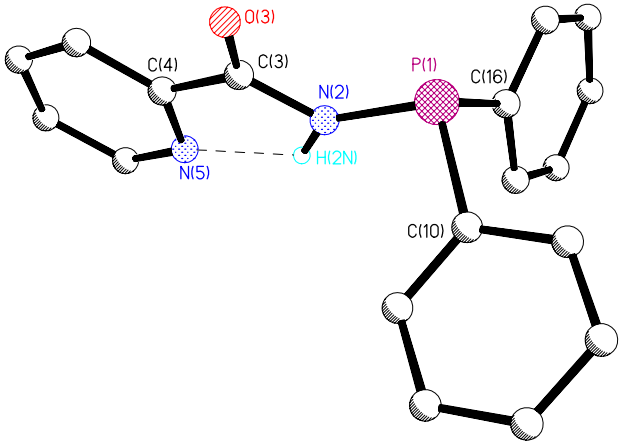
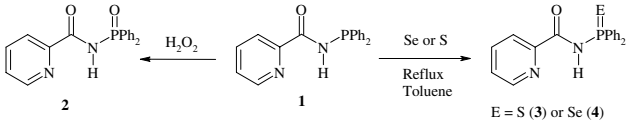


Fig. 3. The crystal structure of dpppa (**1**).

with an intramolecular hydrogen bond between the amide proton and the pyridyl nitrogen, generating an effective five-membered ring that is almost planar [N(2)–N(5) 2.67 Å] The phosphorus–nitrogen bond length of 1.702(3) Å is well within acceptable boundaries previously established in aminophosphine chemistry.



(2)

The oxide, sulfide and selenide of dpppa were also synthesised as seen in Eq. (2). The expected downfield shift is found in the ^{31}P NMR spectra of all three compounds (Table 2), the $^1J_{P-Se}$ is 788 Hz which is typical for a phosphorus–selenium double bond.

In **2**, the P–N bond is somewhat shorter than in dpppa (Table 1 and Fig. 4), the C(4)–C(3)–N(2)–P(1) backbone is essentially planar [mean deviation of 0.0391 Å] and as in **1** there is an H-bonded five-membered ring linking N(5) and H(2) [N(2)–N(5) is 2.653 Å, N(2)–H(2)···N(5) 109°]. It has been shown that the oxides and sulfides of phosphorus(III) ligands can display different solid state motifs [17]. We found that the sulfide **3** crystallises in a dimer arrangement rather than favouring the internal bonding seen in the oxide. The backbone of the molecule remains mostly planar, with the N(2) and N(5) distance [2.65 Å] indicating that the N(2)–H(2)···N(5) hydrogen bond interaction is retained (Table 1 and Fig. 5).

We formed a number of monodentate complexes, thus dpppa reacts with [$PtCl_2$(cod)] in dichloromethane to give *cis*-[$PtCl_2$(dpppa-P_2)] (**5**) as a white crystalline solid in good yield [80%] which is in marked contrast to 2-(diphenylphosphino)aminopyridine (dppap) which is reported to give [PtX(Ph_2PNHpy-*P*,*N*)(Ph_2 PNHpy-*P*)][Cl] (X = Cl or Me) [1–3]. The ^{31}P NMR ($CDCl_3$) of **5** is a singlet at δ(P) 31.2 ppm [$^1J_{Pt-P} = 3984$ Hz],

Table 2
Spectroscopic data for $Ph_2P(E)C(O)NHpy$

Compound	$\delta(^1H)$		$\delta(^{31}P)$	IR (cm^{-1})			
	NH	Aromatics	P	P=E	C=O	NH	CN(py)
1	8.7	8.5–7.2	22.0	N/A	1691	3297	1452
2	9.4	8.5–7.3	22.1	1215	1694	3302	1451
3	9.3	8.6–7.4	54.4	837	1689	3268	1447
4	9.3	8.6–7.1	48.7[a]	Obscured	1698	3288	1391

[a] $^1J_{P-Se}$ = 788 Hz.

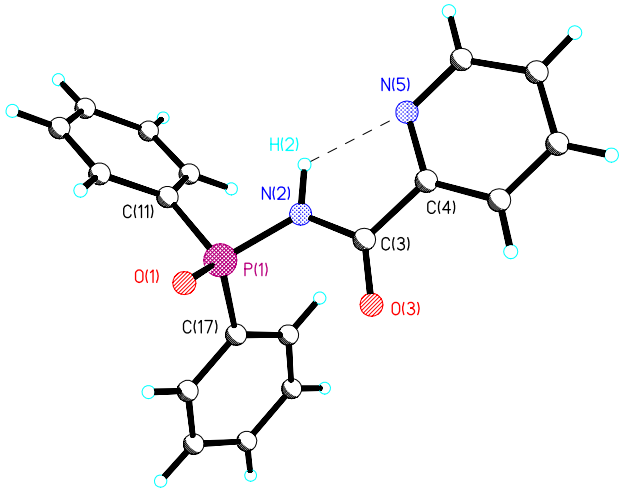


Fig. 4. The crystal structure of dpppaO (**2**).

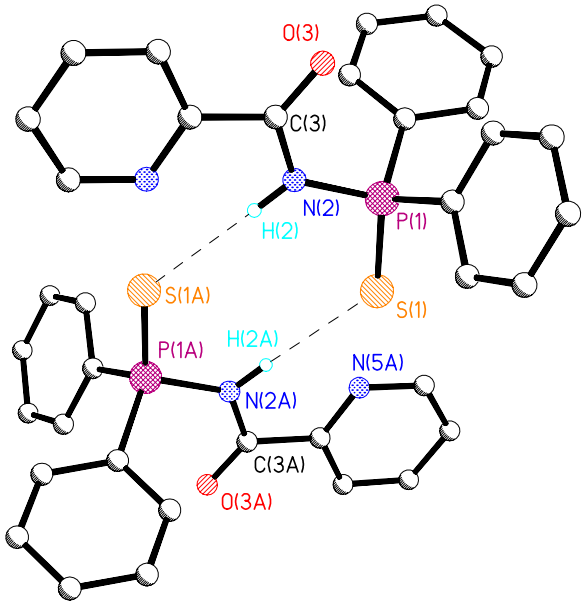


Fig. 5. Crystal structure of dpppaS (**3**).

whilst in the ^1H NMR it displays some significant changes from the free ligand. The amine proton is shifted to δ(H) 10.7 ppm, and $^2J_{P-H}$ at 15 Hz is significantly increased Two Pt–Cl stretches are visible in the IR spectrum (320 and 302 cm^{-1}), further evidence of a *cis*-conformation for **5**. In contrast, reaction of $[PdCl_2(cod)]$ with dpppa gives $[PdCl_2(dpppa\text{-}P)_2]$ (**6**), which is insoluble and displays only one Pd–Cl stretch (310 cm^{-1}), suggesting a *trans*-arrangement, the other expected IR peaks are observed clearly, ν(N–H) at 3232, ν(C=O) at 1694, ν(P–N) at 997 cm^{-1}. This *trans*-arrangement is consistent with previous examples of pyridylaminophosphines found in the literature [1–3].

A series of palladium complexes were synthesised bearing only one dpppa monodentate bound via the phosphorus (Fig. 6). Complexes $[PdCl(allyl)(dpppa\text{-}P)]$ (**7**), $[PdCl(C_{10}H_6NO)(dpppa\text{-}P)]$ (**8**), $[PdCl(C_9H_{12}N)(dpppa\text{-}P)]$ (**9**), $[PdCl(C_{12}H_{12}N)(dpppa\text{-}P)]$ (**10**), were all synthesised via bridge cleavage reactions of the respective dimer starting materials. Complex **7** is a yellow solid which shows the expected singlet at δ(P) 54.5 ppm. The amide proton is shifted downfield in the ^1H NMR spectra ($CDCl_3$), to δ(H) 10.7 ppm, this mirrors the shift of the amide proton in **5**, and also in common with **5** the $^2J_{P-H}$ coupling constant is enlarged, stretching to 22 Hz. The IR spectrum shows the ν(N–H) stretch has shifted to a much greater extent than seen in **5**, this could be due to much stronger hydrogen bonding interaction being present in **7**, and once again the ν(C=O) is relatively unmoved in comparison with the free ligand being found at 1686 cm^{-1}. In the solid state (Table 3 and Fig. 7), complex **7** has a hydrogen-bonds between H(2)–N(5) and H(2)–Cl(1) [N(2)–Cl(1) 3.204 Å and N(2)–N(5) 2.67(8) Å]. The interaction with Cl(1) causes the five-membered ring to distort with a N(5)–C(4)–C(3)–N(2) torsion angle of −15.08°.

Complexes **8**, **9** and **10** are similar and display the expected spectroscopic properties.

Complexes of ruthenium, rhodium and iridium were synthesised to further investigate the coordination of dpppa. $[RuCl_2(p\text{-Cymene})(dpppa\text{-}P)]$ (**11**) was generated by reaction of $[RuCl(\mu\text{-}Cl)(p\text{-Cymene})]_2$ with dpppa and isolated as a red solid. The rhodium and iridium complexes were synthesised by reaction with $[MCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)]_2$ (where M = Rh or Ir), and dpppa, to give complexes of the type $[MCl_2(\eta^5\text{-}C_5\ Me_5)(dpppa\text{-}P)]$ (where M = Rh (**12**) or Ir (**13**)). Crystals of **12** and **13** proved to be isomorphous; here we will only consider **13** (Table 3 and Fig. 8). On inspection of the ligand

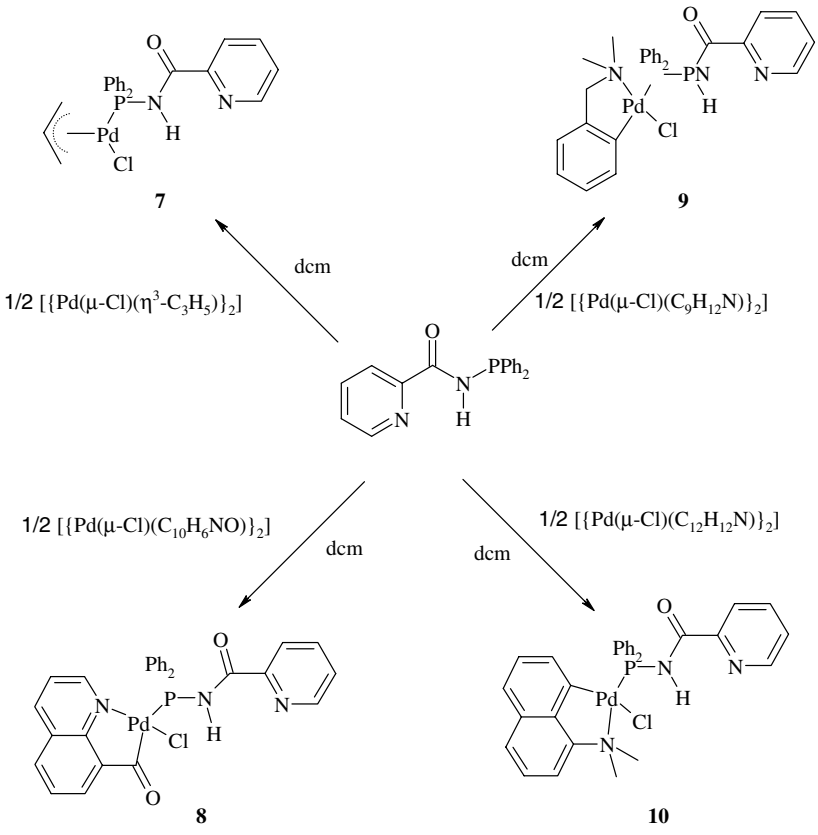


Fig. 6. Reaction of dpppa with palladium dimers.

Table 3
Selected bond lengths (Å) and angles (°) for monodentate complexes of dpppa: [PdCl(allyl)(dpppa-*P*)] (**7**), [$IrCl_2(\eta^5\text{-}C_5Me_5)$(dpppa-*P*)] (**13**), [$PtCl_2$(dpppa-*P*)($PEt_3$)] (**15**) and [AuCl(dpppa-*P*)] (**17**)

	7	13	15	17
Bond lengths				
P(1)–M(1)	2.2786(8)	2.287(2)	2.2389(14)	2.2168(18)
M(1)–Cl(1)	2.3800(8)	2.4126(19)	2.3446(14)	2.2993(17)
M(1)–Cl(2)		2.4034(18)	2.3554(13)	
P(1)–N(2)	1.703(3)	1.699(7)	1.693(4)	1.694(5)
N(2)–C(3)	1.366(4)	1.379(10)	1.377(7)	1.395(8)
C(3)–C(4)	1.512(4)	1.494(11)	1.507(8)	1.495(9)
O(3)–C(3)	1.216(4)	1.233(9)	1.211(6)	1.215(8)
N(2)···Cl	3.204(7)	3.403(6)	3.011(5)	
N(2)···N(5)	2.67(8)	2.71(1)	2.64(7)	2.64(7)
Bond angles				
P(1)–M(1)–Cl(1)	96.52(3)	88.49(7)	175.94(5)	177.82(6)
P(1)–M(1)–Cl(2)		87.72(7)	91.05(5)	
Cl(1)–M(1)–Cl(2)		87.57(7)		
C(3)–N(2)–P(1)	130.3(2)	129.0(5)	126.6(4)	125.6(4)
O(3)–C(3)–N(2)	124.5(3)	123.3(7)	124.3(5)	124.1(6)
O(3)–C(3)–C(4)	121.4(3)	122.1(7)	122.6(5)	122.6(6)
N(2)–C(3)–C(4)	114.1(3)	114.6(6)	113.1(5)	113.3(6)

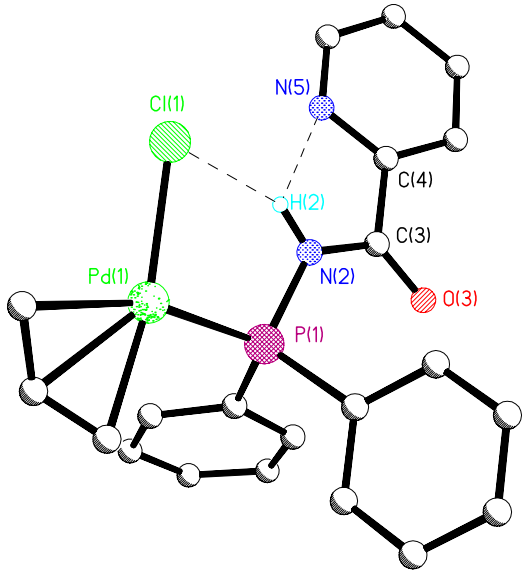


Fig. 7. Crystal structure of [PdCl(allyl)(dpppa-*P*)] (**7**).

backbone, we observe a modest shift out of plane, with the mean deviation of C(3)–N(2)–P(1)–Ir(1) being 0.1160Å, this is the highest deviation seen so far with monodentate dpppa complexes but is not unexpected the analogous complex formed with 2-(diphenylphosphino)hydrazinopyridine displays a similar deviation [18]. Also as seen with the 2-(diphenylphosphino)hydrazinopyridine example there are two types of hydrogen bonding displayed, the first is between the amine proton and one of the chlorides [N(2)···Cl(2) 3.403 Å]. The second type of hydrogen bonding observed in the complex is of

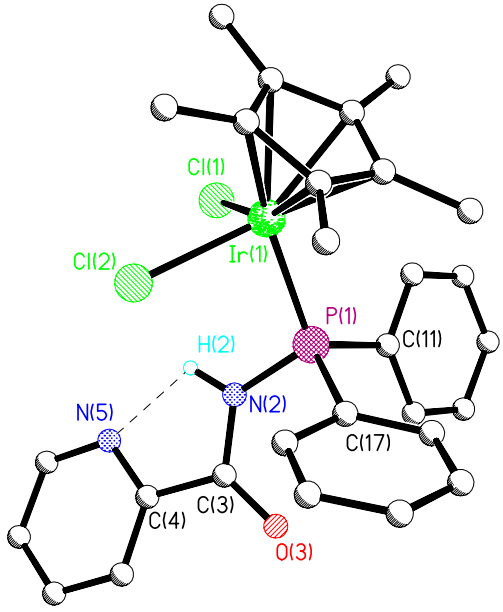


Fig. 8. Crystal structure of [IrCl2(η^5-C_5Me_5)(dpppa-*P*)] (**13**).

a similar motif to that found in the free ligand, oxide and sulfide [N(2)–N(5) 2.71(1) Å].

Dpppa reacts with [{PtCl(μ-Cl)(PR_3)}$_2$](PR_3=PMe_2Ph or PEt_3), to give complexes of the type *cis*-[$PtCl_2$(dpppa-*P*)(PR_3)](PR_3=PMe_2Ph (**14**) or PEt_3 (**15**)). Monodentate binding was the only observed mode of coordination in both instances. The ^{31}P NMR shows the expected AM spectra and the large $^1J_{Pt-P}$ coupling constants and the small $^2J_{P-P}$ couplings are consistent with a *cis*-arrangement of phosphorus around the platinum centre.

In **15** (Table 3 and Fig. 9), the C(3)–N(2)–P(1)–Pt(1) backbone is essentially planar, with a mean deviation of 0.0334 Å, which is consistent with the other structures

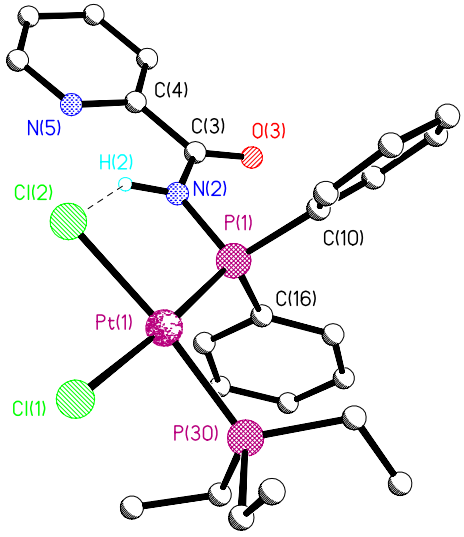
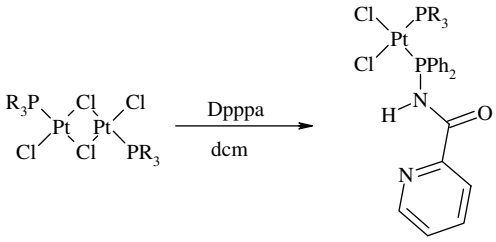


Fig. 9. Crystal structure of [$PtCl_2$(dpppa-*P*)(PEt_3)] (**15**).

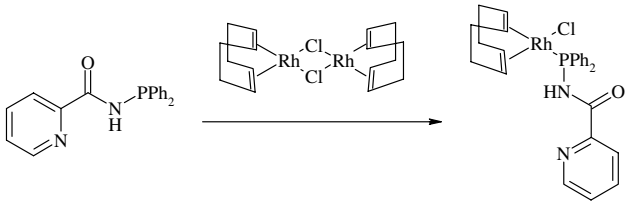
described above. Two different hydrogen bonding motifs are again observed within the complex [N(2)–Cl(2) 3.011, N(2)–N(5) 2.64(7) Å]



(3)

PR_3 = Me_2PhP (**14**) or Et_3 (**15**)

Reaction of dpppa with [RhCl(cod)]$_2$ in dichloromethane gave [RhCl(cod)(dpppa-*P*)] (**16**) as a yellow solid in average yield (63%), (P) 58.3 $^1J_{Rh-P}$ = 162 Hz.



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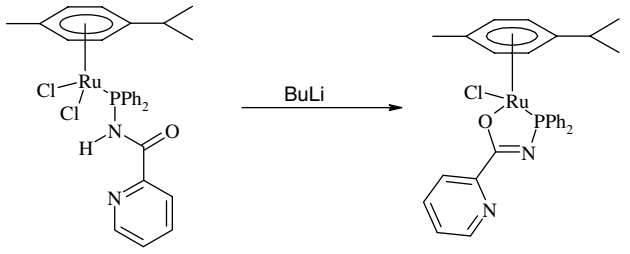
(4)

When dpppa was reacted with [AuCl(tht)] in dichloromethane the anticipated monodentate [AuCl(dpppa-*P*)] (**17**) complex was generated as a colourless solid, δ(P) 53.5 ppm, On inspection of the crystal data (Table 3 and Fig. 10), we see the now familiar hydrogen-bonding pattern [N(2)···N(5) 2.64 Å, N(2)–H(2)–N(5) 114°].

Chelation of dpppa was achieved by reaction of a chloride containing monodentate complex with BuLi



11 **18**

(5)

As can be seen this generates a five-membered 'true' heterocycle, with the oxygen binding to the metal centre. The ^{31}P NMR shows a downfield shift in the complex, to δ(P) 101.5 ppm, indicating chelation. As expected the amide proton disappears from the ^{1}H spectrum, and the pyC[6]H shift and coupling constant is relatively unchanged. The IR spectrum also confirms the loss of the amide proton, and shows a ν(C–O) stretch at 1351 cm^{-1}, confirming C–O is present and not C=O. Acceptable microanalytical data was obtained. The five-membered

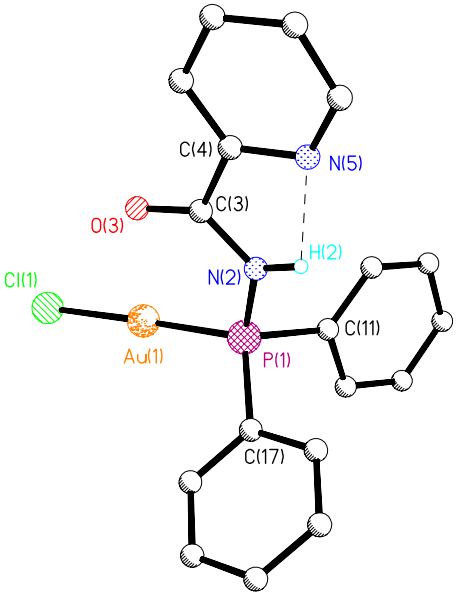


Fig. 10. Crystal structure of [AuCl(dpppa-*P*)] (**17**).

ring that is formed is essentially planar (Fig. 11 and Table 4), the Ru–O and Ru–P bond lengths within the ring are normal whilst the angles are typical for a five membered ring.

A second mode of chelation [via the pyridyl nitrogen] is possible for dpppa. This was facilitated by reaction of the appropriate monodentate complex with a halide abstractor [$AgBF_4$ or $AgClO_4$] generating the cationic species [RuCl(*p*-Cymene)(dpppa-*P*,*N*)][ClO_4] (**19**) and [RhCl(η^5-C_5Me_5)(dpppa-*P*,*N*)][BF_4] (**20**) in good yield (93% and 74%, respectively). The ^{31}P NMR shows the downfield shift generated by chelate ring formation with δ(P) 98.1 and 85.2 ppm for **19** and **20**, respectively, also the amine proton is shifted back toward the free ligand

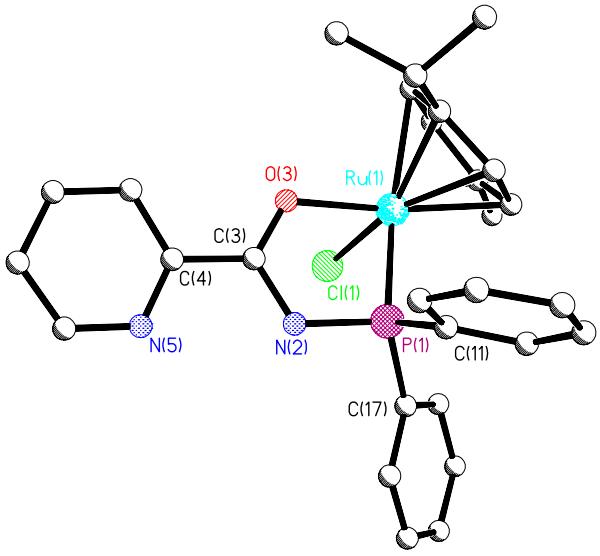
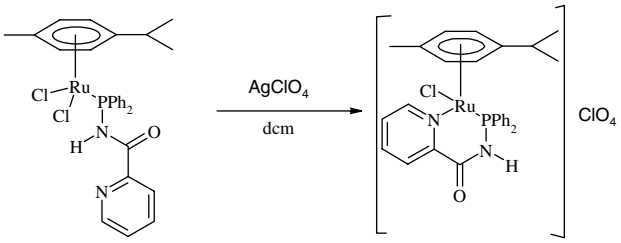


Fig. 11. Crystal structure of [RuCl(p-Cymene)(dpppa-*P*,*O*)] (**18**).

Table 4
Selected bond lengths (Å) and angles (°) for *P*, *O* bidentate [RuCl(*p*-Cymene)(dpppa-*P*,*O*)] (**18**)

Bond lengths			
P(1)–Ru(1)	2.2812(19)	Ru(1)–O(3)	2.097(5)
P(1)–N(2)	1.715(6)	N(2)–C(3)	1.380(10)
C(3)–O(3)	1.276(9)	C(3)–C(4)	1.465(10)
C(4)–C(9)	1.423(10)	C(4)–N(5)	1.315(9)
Ru(1)–Cl(1)	2.3910(18)		
Bond angles			
P(1)–Ru(1)–O(3)	80.28(14)	P(1)–Ru(1)–Cl(1)	86.32(6)
O(3)–Ru(1)–Cl(1)	81.53(14)		
Ru(1)–P(1)–N(2)	101.2(2)	P(1)–N(2)–C(3)	116.3(5)
N(2)–C(3)–O(3)	120.6(6)	C(3)–O(3)–Ru(1)	120.0(5)
N(2)–C(3)–C(4)	117.5(7)	O(3)–C(3)–C(4)	121.9(7)
C(3)-C(4)–C(9)	119.2(7)	C(3)–C(4)–N(5)	117.0(7)
C(9)–C(4)–N(5)	123.8(7)		

value at δ(H) 8.6 ppm in both cases [$^2J_{P-H}$ of 5 and 4 Hz, respectively].



11 **19**

(6)

3. Experimental

3.1. General conditions

All manipulations were carried out in an atmosphere of nitrogen, unless stated otherwise. All solvents were either freshly distilled from an appropriate drying agent (thf, Et_2O from sodium, CH_2Cl_2 from calcium hydride) or obtained as anhydrous grade from Aldrich. ^{1}H and ^{31}P NMR spectra were recorded using a Jeol Delta FT (270 MHz) spectrometer. IR spectra were recorded as KBr discs (prepared in air) on a Perkin–Elmer 2000 FTIR/Raman spectrometer. All significant peaks (>800 cm^{-1}) are quoted to serve as a fingerprint. Silver salts, 2-picolinamide (Aldrich Chemical Co.) and BuLi (2.5 M, Lancaster) were purchased and used as received. Triethylamine and chlorodiphenylphosphine were distilled prior to use. Dimethylaminopyridine (DMAP) was sublimed before use. The various metal starting materials were made by the appropriate literature methods; [AuCl(tht)] [19], [MCl_2(cod)] (M = Pt or Pd; cod = cycloocta-1,5-diene) [20,21], [PdCl(L–L)]$_2$ dimers [22], [{PtCl(μ-Cl)(PMe_2 Ph)}$_2$] [23], [{MCl(μ-Cl)-(Cp*)}$_2$] (M = Rh or Ir) [24], [{Rh(μ-Cl)(cod)}$_2$] [25],

$[\{RuCl(\mu\text{-}Cl)(\eta^6 p\text{-}MeC_6H_4^iPr)\}_2]$ [26], $[\{PdCl(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)\}_2]$ [27].

3.1.1. 2-Diphenylphosphinopicolinamide (*1*)

Chlorodiphenylphosphine (3.7 cm^3, 20 mmol) was added to a solution of 2-picolinamide (2.5 g, 20 mmol), triethylamine (3.0 cm^3, 21 mmol) and DMAP (240 mg, 2.0 mmol) in thf (100 cm^3) and refluxed overnight. The reaction mixture was filtered to remove a white solid (Et_3NHCl) and washed with thf (50 cm^3). The solvent was removed in vacuo leaving a pale yellow solid. This solid was recrystallised by cooling a concentrated methanol solution at 4 °C overnight (yield: 3.38 g, 55%). *Anal.* Calc. for $C_{18}H_{15}N_2OP$: C, 70.6; H, 4.9; N, 9.1. Found: C, 70.29; H, 4.58; N, 8.95%. ν_{max}/cm^{-1}: 3297, 1691, 1452, 1412, 996. ^{31}P NMR δ 22.0 ppm ^1H NMR ($CDCl_3$), 8.65 (1H, d, $J = 4$ Hz, N–H), 8.54 (1H, d, $J = 5$ Hz, pyC[6]H), 8.26 (1H, d, $J = 8$ Hz, pyC[3]H), 7.85 (1H, t, $J = 8$ Hz, pyC[5]H), 7.6–7.2 (11H, m, aromatic).

3.1.2. 2-Diphenylphosphinopicolinamide oxide (*2*)

Aqueous H_2O_2 (30% w/w, 0.0071 cm^3, 0.065 mol) was added dropwise over 5 min to a solution of dpppa (200 mg, 0.065 mol) in thf (10 cm^3) and the mixture stirred for 30 min and then reduced to dryness. The residue was dissolved in CH_2Cl_2, and filtered while hot and subsequently dried over $MgSO_4$. The filtrate was stored at −4 °C during which time a crystalline solid was deposited and filtered and dried. Yield: 85 mg, 41%. *Anal.* Calc. for $C_{18}H_{15}N_2O_2P$: C, 67.1; H, 4.69; N, 8.69. Found: C, 66.7; H, 4.26; N, 8.41%. ν_{max}/cm^{-1}: 3302, 1694, 1451, 1403, 1215, 998. ^{31}P NMR δ 22.1 ppm. ^1H NMR ($CDCl_3$), δ 9.46 (1H, d, $J = 9$ Hz, N–H), 8.58 (1H, d, $J = 4$ Hz, pyC[6]H), 8.1–7.7 (6H, m, aromatic), 7.5–7.2 (7H, m, aromatic).

3.1.3. 2-Diphenylphosphinopicolinamide sulfide (*3*)

Sulfur (105 mg, 3.3 mmol) was added to a solution of 2-diphenylphosphinopicolinamde (1 g, 3.3 mmol) in toluene (100 cm^3) and refluxed overnight. The solvent was removed in vacuo leaving an off-white solid. This solid was recrystallised by cooling a concentrated toluene solution at 4 °C overnight (yield: 900 mg, 82%). *Anal.* Calc. for $C_{18}H_{15}N_2OPS$: C, 63.9; H, 4.47; N, 8.28. Found: C, 63.6; H, 4.22; N, 8.26%. ν_{max}/cm^{-1}: 3268, 1689, 1387, 997. ^{31}P NMR δ 54.4 ppm. ^1H NMR ($CDCl_3$), δ 9.3 (1H, d, $J = 11$ Hz, N–H), 8.6 (1H, d, $J = 1$ Hz, pyC[6]H), 8.1–7.8 (6H, m, aromatic), 7.6–7.4 (7H, m, aromatic).

3.1.4. 2-Diphenylphosphinopicolinamide selenide (*4*)

Selenium (52 mg, 0.65 mmol) was added to a solution of 2-diphenylphosphinopicolinamde (200 mg, 0.65 mmol) in toluene (5 cm^3) and refluxed overnight. The solvent was removed in vacuo leaving an off-white solid. This solid was recrystallised by cooling a concentrated toluene solution at 4 °C overnight (yield: 105 mg, 48%). *Anal.* Calc. for $C_{18}H_{15}N_2OPSe$: C, 56.1; H, 3.92; N, 7.27. Found: C, 56.4; H, 3.77; N, 7.05%. ν_{max}/cm^{-1}: 3288, 1698, 1391, 998. ^{31}P NMR ($CDCl_3$) δ 47.8, $^1J_{P-Se} = 788$ Hz. ^1H NMR ($CDCl_3$), δ 9.3 (1H, d, $J = 13$ Hz, N–H), 8.6 (1H, d, $J = 1$ Hz, pyC[6]H), 8.2–7.7 (6H, m, aromatic), 7.5–7.3 (7H, m, aromatic).

3.1.5. $[PtCl_2(dpppa\text{-}P)_2]$ (*5*)

Dpppa (50 mg, 0.16 mmol) and $[PtCl_2(cod)]$ (30 mg, 0.08 mmol) were weighed into a schlenk type flask and CH_2Cl_2 (5 cm^3) added. The solution was stirred for 10 min and the majority of the solvent removed in vacuo. A white solid was precipitated after addition of Et_2O (20 cm^3) then isolated by filtration and washed with further ether (10 cm^3) (yield: 57 mg, 80%). *Anal.* Calc. for $C_{36}H_{30}N_4O_2P_2Cl_2Pt(CH_2Cl_2)_{0.5}$: C, 47.6; H, 3.39; N, 6.08. Found: C, 47.5; H, 3.20; N, 5.81%. ν_{max}/cm^{-1}: 3251, 1692, 1446, 1391, 998, 320, 302. ^{31}P NMR ($CDCl_3$) δ 31.2 ppm, $^1J_{Pt-P} = 3984$ Hz. ^1H NMR ($CDCl_3$), 10.7 (2H, d, $J = 15$ Hz, N–H), 8.5 ((2H, d, $J = 4$ Hz), pyC[6]H), 7.7–7.2 (26H, m, aromatic).

3.1.6. $[PdCl_2(dpppa\text{-}P)_2]$ (*6*)

Dpppa (258 mg, 0.86 mmol) and $[PdCl_2(cod)]$ (120 mg, 0.43 mmol) were weighed into a schlenk type flask and CH_2Cl_2 (10 cm^3) added. The solution was stirred for 10 min. This resulted in precipitation of the desired product, which was filtered and washed with ether (10 cm^3). Yield: 307 mg, 92%. *Anal.* Calc. for $C_{36}H_{30}N_4O_2P_2Cl_2Pd$: C, 54.6; H, 3.83; N, 7.09. Found: C, 53.9; H, 3.64; N, 6.85%. ν_{max}/cm^{-1}: 3232, 1694, 1446, 1392, 997, 310.

3.1.7. $[PdCl(allyl)(dpppa\text{-}P)]$ (*7*)

Reaction followed as for **5**. Dpppa (84 mg, 0.27 mmol) and $[\{Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)\}_2]$ (50 mg, 0.13 mmol) gave a pale yellow solid, (yield: 117 mg, 87%). *Anal.* Calc. for $C_{21}H_{20}N_2OPClPd$: C, 51.5; H, 4.12; N, 5,72. Found: C, 51.8; H, 3.93; N, 5.61%. ν_{max}/cm^{-1}: 3193, 1686, 1446, 1396, 1103, 998. ^{31}P NMR ($CDCl_3$) δ 54.5 ppm. ^1H NMR ($CDCl_3$), 10.5 (1H, d, $J = 22$ Hz, N–H), 8.7 (1H, d, $J = 4$ Hz, pyC[6]H), 7.8–7.4 (12H, m, aromatic), 5.5 (1H, m, allyl), 4.7 (1H, t, $J = 7$ Hz, allyl), 3.7 (1H, t, $J = 13$ Hz, allyl), 3.3 (1H, d, $J = 7$ Hz, allyl), 2.6 (1H, d, $J = 13$ Hz, allyl).

3.1.8. $[PdCl(C_{10}H_6NO)(dpppa\text{-}P)]$ (*8*)

Dpppa (205 mg, 0.66 mmol) and $[Pd(\mu\text{-}Cl)(C_{10}H_6NO)]_2$ (200 mg, 0.33 mmol) were weighed into a schlenk type flask and CH_2Cl_2 (10 cm^3) added. The solution was stirred for 10 min. This resulted in precipitation of the desired product, which was filtered and washed with ether (10 cm^3) (yield: 371 mg, 95%). *Anal.* Calc. for $C_{28}H_{21}N_3O_2PClPd$: C, 55.6; H, 3.50; N, 6.95.

Found: C, 55.7; H, 3.18; N, 6.04%. ν_{max}/cm^{-1}: 3231, 1673, 1446, 1394, 996, 322. FAB MS: *m/z* 568 ($[M - Cl]^+$).

3.1.9. [PdCl(C9H12N)(dpppa-P)] (9)

Dpppa (223 mg, 0.72 mmol) and $[Pd(\mu\text{-}Cl)(C_9H_{12}N)]_2$ (200 mg, 0.36 mmol) gave a yellow solid, (yield: 136 mg, 64%). *Anal.* Calc. for $C_{27}H_{25}N_3OPClPd(CH_2Cl_2)_{0.5}$: C, 52.9; H, 4.51; N, 6.73. Found: C, 54.3; H, 4.46; N, 6.07%. ν_{max}/cm^{-1}: 3187, 1683, 1449, 1391, 997. ^{31}P NMR ($CDCl_3$) δ 63.3 ppm. ^1H NMR ($CDCl_3$) δ 10.9 (1H, d, $J = 19$ Hz, N–H), 8.6 (1H, d, $J = 4$ Hz, pyC[6]H), 8.1 (1H, m, aromatic), 8.0 (1H, m, aromatic), 7.8 (1H, m, aromatic), 7.4 (8H, m, aromatic) 7.0, (1H, m, aromatic), 6.8 (1H, m, aromatic), 6.4 (1H, m, aromatic), 3.4 (2H, d $J = 3$ Hz, CH_2) 2.8 (6H, d, $J = 3$ Hz, NMe–H). FAB MS: *m/z* 546 ($[M - Cl]^+$).

3.1.10. [PdCl(C12H12N)(dpppa-P)] (10)

Reaction followed as for **5**. Dpppa (197 mg, 0.64 mmol) and $[Pd(\mu\text{-}Cl)(C_{12}H_{12}N)]_2$ (200 mg, 0.32 mmol) gave a yellow/green solid, (yield: 176 mg, 44%). *Anal.* Calc. for $C_{30}H_{27}N_3OPClPd$: C, 58.2; H, 3.40; N, 6.80. Found: C, 58.09; H, 2.92; N, 6.62%. ν_{max}/cm^{-1}: 3203, 1678, 1446, 1388, 997. ^{31}P NMR ($CDCl_3$) δ 64.3 ppm. ^1H NMR ($CDCl_3$) 11.3 (1H, d, $J = 18$ Hz, N–H), 8.7 (1H, d, $J = 5$ Hz, pyC[6]H), 8.2 (4H, m, aromatic), 8.0 (1H, d, aromatic), 7.8 (1H, d, aromatic), 7.6 (1H, d, aromatic), 7.5–7.4 (10H, m, aromatic), 6.7 (1H, m, aromatic), 6.5 (1H, m, aromatic), 3.5 (6H, d, $J = 3$ Hz, NMe–H).

3.1.11. [RuCl2(p-Cymene)(dpppa-P)] (11)

Prepared as for **5**. Dpppa (200 mg, 0.66 mmol) and $[\{RuCl(\mu\text{-}Cl)(p\text{-Cymene})\}_2]$ (200 mg, 0.33 mmol) gave a red solid, (yield: 324 mg, 84%). *Anal.* Calc. for $C_{28}H_{29}N_2OPCl_2Ru$: C, 54.9; H, 4.77; N, 4.57. Found: C, 55.8; H, 4.82; N, 4.07%. ν_{max}/cm^{-1}: 3261, 1684, 1449, 1406, 997, 292. ^{31}P NMR ($CDCl_3$) δ 59.3 ppm.. ^1H NMR ($CDCl_3$) δ 9.6 (1H, d, $J = 18$ Hz, N–H), 8.6 (1H, d, $J = 7$ Hz, pyC[6]H), 8.0 (6H, m, aromatic), 7.8 (1H, m, aromatic), 7.6 (1H, m, aromatic) 7.4 (4H, m, aromatic), 7.2 (1H, m, aromatic), 5.3 (2H, m, aromatic [*p*-Cymene]), 5.2 (2H, m, aromatic [*p*-Cymene]), 2.6 (1H, m, Pr^i-H), 1.8 (3H, m, Me–H), 0.8 (6H, d, $J = 7$ Hz, Pr^i–Me).

3.1.12. [RhCl2(η5-C5Me5)(dpppa-P)] (12)

Prepared as for **5**. Dpppa (198 mg, 0.65 mmol) and $[\{RhCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)\}_2]$ (200 mg, 0.32 mmol) gave a orange solid, (yield: 363 mg, 91%). *Anal.* Calc. for $C_{28}H_{30}N_2OPCl_2$ Rh: C, 54.6; H, 4.91; N, 4.55. Found: C, 54.0; H, 4.65; N, 4.40%. ν_{max}/cm^{-1}: 3298, 1678, 1449, 1410, 997, 282. ^{31}P NMR ($CDCl_3$) δ 62.8 ppm, J_{RhP} 150 Hz. ^1H NMR ($CDCl_3$) δ 9.9 (1H, d, $J = 18$ Hz, N–H), 8.6 (1H, d, $J = 5$ Hz, pyC[6]H), 8.1 (4H, m, aromatic), 7.9 (1H, d, aromatic), 7.7 (1H, m, aromatic), 7.5 (7H, m, aromatic), 7.3 (1H, m, aromatic), 1.4 (15H, d, $J = 12$ Hz, Cp*–H).

3.1.13. [IrCl2(η5-C5Me5)(dpppa-P)] (13)

Prepared as for **5**. Dpppa (77 mg, 0.25 mmol) and $[\{IrCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)\}_2]$ (100 mg, 0.13 mmol) gave a yellow/orange solid, (yield: 162 mg, 91%). *Anal.* Calc. for $C_{28}H_{30}N_2OPCl_2Ir$: C, 47.6; H, 4.29; N, 3.98. Found: C, 47.1; H, 4.27; N, 3.83%. ν_{max}/cm^{-1}: 3288, 1678, 1450, 1412, 997. ^{31}P NMR ($CDCl_3$) δ 32.7 ppm. ^1H NMR ($CDCl_3$) δ 10.2 (1H, d, $J = 17$ Hz, N–H), 8.6 (1H, d, $J = 4$ Hz, pyC[6]H), 8.1–7.7 (6H, m, aromatic), 7.4 (6H, m, aromatic), 1.4 (15H, d, $J = 2$ Hz, Cp*–H).

3.1.14. [PtCl2(Me2PhP)(dpppa-P)] (14)

Prepared as for **5**. Dpppa (76 mg, 0.25 mmol) and $[\{PtCl(\mu\text{-}Cl)(PMe_2Ph)\}_2]$ (100 mg, 0.12 mmol) gave a white solid, (yield: 114 mg, 65%). *Anal.* Calc. for $C_{26}H_{26}N_2OP_2Cl_2Pt$: C, 44.0; H, 3.69; N, 3.95. Found: C, 43.77; H, 3.61; N, 3.82%. ν_{max}/cm^{-1}: 1686, 1447, 1384, 1107. ^{31}P NMR ($CDCl_3$) δ 30.9 ($^1J_{Pt-P} = 3930$), −14.5 ($^1J_{Pt-P} = 3500$), $^2J_{P-P} = 19$ Hz. ^1H NMR ($CDCl_3$) δ 11.1 (1H, d, $J = 15$ Hz, N–H), 8.6 (1H, d, $J = 4$ Hz, pyC[6]H), 8.0–7.7 (6H, m, aromatic), 7.5–7.0 (12H, m, aromatic), 1.6–1.5 (6H, d, $J = 11$ Hz, Me–H).

3.1.15. [PtCl2(Et3P)(dpppa-P)] (15)

A solution of $[\{PtCl(\mu\text{-}Cl)(PEt_3)\}_2]$ (50 mg, 0.07 mmol), in CH_2Cl_2 (10 cm^3) was added dropwise to a solution of dpppa (40 mg, 0.13 mmol) in CH_2Cl_2 (10 cm^3). The solution was stirred for 10 min and the majority of the solvent removed in vacuo. A white solid was precipitated after addition of Et_2O then isolated by filtration and washed with further ether (10 cm^3) (yield: 55 mg, 66%). *Anal.* Calc. for $C_{24}H_{30}N_2OP_2Cl_2Pt$: C, 41.9; H, 4.38; N, 4.06. Found: C, 42.8; H, 3.60; N, 4.15%. ν_{max}/cm^{-1}: 3162, 1687, 1446, 1385, 998, 310. ^{31}P NMR ($CDCl_3$) δ 30.0 ($^1J_{Pt-P} = 4010$), 7.6 ($^1J_{Pt-P} = 3360$), $^2J_{P-P} = 19$ Hz. ^1H NMR ($CDCl_3$) δ 11.4 (1H, d, $J = 16$ Hz, N–H), 8.7 (1H, d, $J = 1$ Hz, pyC[6]H), 8.2 (2H, m, aromatic), 7.9–7.7 (5H, m, aromatic), 7.5–7.3 (3H, m, aromatic), 7.1 (1H, m, aromatic), 1.5 (6H, m, $-CH_2-$), 0.9 (9H, m, Me–H).

3.1.16. [RhCl(cod)(dpppa-P)] (16)

Dpppa (125 mg, 0.41 mmol), and $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$ (100 mg, 0.20 mmol) were weighed into a schlenk type flask and toluene (5 cm^3) added. The solution was stirred for 10 min and the majority of the solvent removed in vacuo. A yellow solid was precipitated after addition of *n*-hexane (20 cm^3) then isolated by filtration and washed with further hexane (10 cm^3) (yield: 142 mg, 63%). *Anal.* Calc. for $C_{26}H_{27}N_2OPClRh$: C, 56.5; H, 4.92; N, 5.07. Found: C, 56.05; H, 4.76; N, 4.90%. ν_{max}/cm^{-1} : 3194, 1698, 1448, 1407, 997. ^{31}P NMR

($CDCl_3$) δ 58.3 ($^1J_{Rh-P}$ = 162 Hz). ^1H NMR (270 MHz, $CDCl_3$) δ 10.4 (1H, d, J = 21Hz, N–H), 8.6 (1H, d, J = 2Hz, pyC[6]H), 8.0–7.8 (6H, m, aromatic), 7.6–7.2 (6H, m, aromatic), 2.3 (4H, br.s, cod), 2.0 (8H, br.s, cod).

3.1.17. [AuCl(dpppa-P)] (17)

Prepared as for **5**, Dpppa (67 mg, 0.021 mmol) and [AuCl(tht)] (70 mg, 0.021 mmol) reacted in CH_2Cl_2 gave a white solid, (yield: 78 mg, 70%). *Anal.* Calc. for $C_{15}H_{15}N_2OPClAu$: C, 40.0; H, 2.80; N, 5.20. Found: C, 39.5; H, 2.75; N, 5.09%. ν_{max}/cm^{-1} : 3288, 1698, 1391, 998. ^{31}P NMR ($CDCl_3$) 53.5 ppm. ^1H NMR ($CDCl_3$) 9.1 (1H, d, J = 13 Hz, N–H), 8.6 (1H, d, J = 1 Hz, pyC[6]H), 8.2–7.5 (13H, m, aromatic).

3.1.18. [RuCl(p-Cymene)(dpppa-P,O)] (18)

A solution of BuLi (65 μ l,. 0.16 mmol) in THF (2 cm^3) was added dropwise to a solution of [$RuCl_2$-(*p*-Cymene)(dpppa-*P*)] (100 mg, 0.16 mmol) in THF (5 cm^3) at 0 °C. The solution was stirred for 10 min and allowed to reach room temperature, and filtered through a bed of celite. The majority of the solvent removed in vacuo. A dull beige solid was precipitated after addition of Et_2O then isolated by filtration and washed with further ether (10 cm^3) (yield: 47 mg, 52%). Recryst from CH_2Cl_2/hexane. *Anal.* Calc. for $C_{28}H_{28}N_2OPCl$-$Ru(CH_2Cl_2)$: C, 52.7; H, 4.57; N, 4.24. Found: C, 51.9; H, 4.00; N, 4.38%. ν_{max}/cm^{-1}: 3312, 1351, 249. ^{31}P NMR ($CDCl_3$) δ 101.5. ^1H NMR (270 MHz, $CDCl_3$) δ 8.4 (1H, d, J = 8 Hz, pyC[6]H), 7.9–7.7 (3H, m, aromatic), 7.6–7.2 (10H, m, aromatic), 6.0 (1H, d, J = 6 Hz, *p*-Cy-H), 5.7 (1H, d, J = 4 Hz, *p*-Cy-H), 5.4 (1H, d, J = 6 Hz, *p*-Cy-H), 5.0 (1H, d, J = 4 Hz, *p*-Cy-H), 2.5 (1H, m, C–H), 2.0 (3H, s, Me–H), 1.1 (6H, d, J = 10 Hz, Pr^i-H).

3.1.19. [RuCl(p-Cymene)(dpppa-P,N)][ClO_4] (19)

$AgClO_4$ (33 mg, 0.16 mmol) was added under dark conditions to a solution of [$RuCl_2$(*p*-Cy)(dpppa-*P*)] (100 mg, 0.16 mmol) in CH_2Cl_2 (5 cm^3). The solution was stirred overnight and filtered through a celite bed. The majority of the solvent was removed in vacuo. An orange solid was precipitated after addition of Et_2O then isolated by filtration and washed with further ether (10 cm^3) (yield: 87 mg, 0.15 mmol, 93%). *Anal.* Calc. for $C_{28}H_{28}N_2O_5PCl_2Ru(CH_2Cl_2)_{0.5}$: C, 47.6; H, 4.21; N, 3.90. Found: C, 47.2; H, 4.00; N, 3.89%. ν_{max}/cm^{-1}: 1482, 1084. ^{31}P NMR ($CDCl_3$) δ 98.1 ppm. ^1H NMR ($CDCl_3$) δ 8.6 (1H, d, J = 5 Hz, N–H), 8.2 (1H, d, J = 8 Hz, pyCH), 8.0 (1H, t, J = 8 Hz, pyCH), 7.8 (2H, m, aromatic), 7.7–7.5 (10H, m, aromatic), 5.8 (2H, m, *p*-Cymene-H), 5.6 (2H, m, *p*-Cymene-H), 2.8 (1H, m, C–H), 2.1 (3H, s, Me–H), 1.3 (6H, t, J = 6 Hz, Pr^i-H).

Table 5
Crystallographic data for complexes **1**, **2**, **3**, **7**, **13**, **15**, **17** and **18**

	1	**2**	**3**	**7**	**13**	**15**	**17**	**18**
	Mercury/293K/Cu	Smart/125K/Mo	Smart/125K/Mo	Smart/125K/Mo	Smart/125K/Mo	Smart/125K/Mo	Smart/298K/Mo	Smart/125K/Mo
Formula	$C_{18}H_{15}N_2OP$	$C_{18}H_{15}N_2O_2P$	$C_{18}H_{15}N_2OPS$	$C_{21}H_{20}N_2OClPPd$	$C_{28}H_{30}N_2OPCl_2Ir$	$C_{24}H_{30}N_2OP_2Cl_2Pt$	$C_{18}H_{15}N_2OPClAu$	$C_{29}H_{30}N_2OPCl_3Ru$
M	306.29	322.29	338.35	489.21	704.61	690.43	538.71	660.94
Crystal system	triclinic	monoclinic	triclinic	triclinic	orthorhombic	monoclinic	monoclinic	orthorhombic
Space group	$P\bar{1}$	$P2(1)/c$	$P\bar{1}$	$P\bar{1}$	$P(2)1(2)1(2)1$	$P2(1)/c$	$P2(1)/c$	$Pca2(1)$
a (Å)	8.4419(17)	8.4497(1)	8.7701(17)	9.9452(12)	8.2751(16)	15.771(2)	13.271(4)	17.576(3)
b (Å)	10.271(2)	17.369(3)	9.0319(17)	15.3618(19)	17.750(3)	10.4905(16)	12.119(4)	9.0772(15)
c (Å)	10.416(2)	11.264(2)	11.043(2)	15.7040(19)	17.892(4)	17.092(3)	11.111(4)	17.593(3)
α (°)	110.94(3)		77.738(3)	118.018(2)				
β (°)	103.74(3)	108.389(3)	85.554(3)	101.038(2)		113.589(2)	102.124(6)	
γ (°)	90.27(3)		72.540(3)	95.688(2)				
U (Å) [8–10]	815.3(3)	1568.8(5)	815.3(3)	2028.7(4)	2628.1(9)	2591.6(7)	1747.1(10)	2806.8(8)
Z	2	4	2	4	4	4	4	4
ρ_{calcd} (g/cm^3)	1.248	1.365	1.378	1.602	1.781	1.770	2.048	1.564
μ (mm^{-1})	1.511	0.186	0.302	1.138	5.369	5.764	8.672	0.927
Reflections measured	6683	6672	4092	10246	11,347	10858	7308	13398
Independent reflections	2850	2230	2273	5783	3757	3699	2484	3965
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0881, 0.2260	0.0461, 0.1141	0.0393, 0.1018	0.0273, 0.0731	0.0297, 0.0674	0.0277, 0.641	0.0301, 0.0695	0.0447, 0.1002

*3.1.20. [RhCl(η⁵-C₅Me₅)(dpppa-P,N)][BF₄] (**20**)*

$AgBF_4$ (31 mg, 0.16 mmol) was added under dark conditions to a solution of $[RhCl_2(\eta^5\text{-}C_5Me_5)$(dpppa-*P*)] (100 mg, 0.16 mmol) in CH_2Cl_2 (5 cm^3). The solution was stirred overnight and filtered through a celite bed. The majority of the solvent was removed in vacuo. An orange solid was precipitated after addition of Et_2O then isolated by filtration and washed with further ether (10 cm^3) (yield: 70 mg, 0.12 mmol, 74%). *Anal.* Calc. for $C_{28}H_{30}N_2OPClRhBF_4$: C, 50.4; H, 4.54; N, 4.20. Found: C, 49.8; H, 4.25; N, 4.04%. ν_{max}/cm^{-1}: 1684, 1477, 1421. ^{31}P NMR ($CDCl_3$) δ 85.2 ppm. ^1H NMR ($CDCl_3$) δ 8.6 (1H, d, $J = 4$ Hz, pyC[6]H), 8.3 (1H, d, $J = 8$ Hz, pyC[3]H), 8.0 (1H, t, $J = 8$ Hz, pyC[5]H), 7.8 (2H, m, aromatic), 7.6 (8H, m, aromatic), 1.6 (15H, d, $J = 4$ Hz, Cp*-H).

4. X-ray crystallography

Details of the structure determination are given in Table 5. X-ray diffraction measurements were made with graphite-monochromated Mo Kα X-radiation using a Bruker SMART diffractometer or with Cu Kα radiation and a Rigaku Mercury diffractometer. In both cases, intensity data were collected using ω/ϕ steps accumulating area detector frames spanning a hemisphere of reciprocal space for all structures. All data were corrected for Lorentz, polarisation and long-term intensity fluctuations. Absorption effects were corrected on the basis of multiple equivalent reflections or by semi-empirical methods. Structures were solved by direct methods and refined by full-matrix least-squares against F^2 (SHELXTL). Hydrogen atoms were assigned isotropic displacement parameters and were constrained to idealised geometries. Complex **7** contains some disorder; in both **7** and **18** not all of the protons could be included in the final refinement. Refinements converged to residuals given in Table 5. All calculations were made with SHELXTL [28].

5. Supplementary material

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic data centre (CCDC) Nos 238211–238218. Any request to CCDC for this material should quote the full literature citation and the reference number. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or at www: http://www.ccdc.cam.ac.uk).

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