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FULL PAPER

Synthesis and structure of novel rhodium complexes of multi-functionalised amine-phosphine ligands

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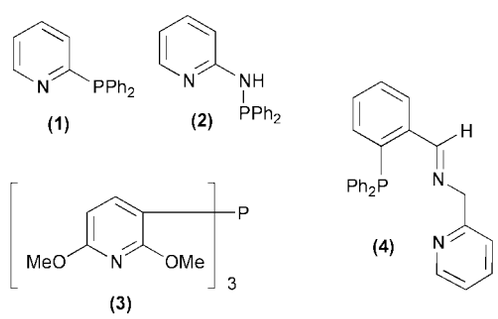
The coordination behaviour of a variety of amine containing phosphine ligands has been studied. Two new multifunctionalised ligands have been prepared and shown along with three known ligands to favour a variety of coordination modes when complexed with rhodium(III) centres. The hemilabile P^N chelate ligands show three different types of behaviour: strong P,N chelation even in the presence of chloride ions, strong P,N chelation after a chloride ligand is removed (Ag salts), and weak coordination after chloride abstraction. Five of the complexes have been characterised by X-ray crystallography. Multinuclear NMR and IR spectroscopies were also highly diagnostic in assigning the coordination chemistry favoured by each ligand.

Introduction

Bidentate ligands containing phosphorus and nitrogen donors are extremely useful in both coordination chemistry and homogenous catalysis.[1] In fact there are a number of processes in which complexes of P^N bidentate ligands make them catalysts of choice. Important examples are carbonylation of alkynes,[2] asymmetric hydrogenation of highly substituted alkenes,[3] asymmetric allylic alkylation,[4] asymmetric hydroboration,[5] Stille coupling,[6] and nickel catalysed cycloaddition reactions.[7] Pyridyl phosphines such as 2-diphenylphosphinopyridine **1** have been applied successfully in several processes.[8] Phosphorus–nitrogen donors are particularly useful in catalytic processes as one half of the ligand is capable of dissociating from an otherwise stable chelate complex, allowing an organic substrate to coordinate to the metal and undergo some transformation. In other cases there is no stable chelate complex formed, but transient coordination of the nitrogen donor allows the formation of stable coordinatively unsaturated species which would not exist if a monodentate ligand were used. Thus, 2-PPh_2Py and Ph_3P share similar electronic and steric properties, yet 16 e^- $(2\text{-}PPh_2Py)_3Pt$ is the only zerovalent platinum species detected even when a large excess of 2-PPh_2Py is present. In contrast, $(Ph_3P)_4Pt$ is the platinum complex formed if an excess of Ph_3P is present. Another useful feature of ligands containing P,N donor sets is the electronic asymmetry that is induced by the ligands. This allows selective reactions to occur *trans* to the stronger phosphorus ligand. This has been exploited with considerable success in asymmetric catalysis.[4] We wished to develop some new P,N donor ligands which might improve existing catalytic processes, and as the initial stage of this project have sought to understand which coordination modes are favoured by which structural motifs. A survey of the literature and a recent study of our own shows that ligands with P,N donor sets favour several different coordination modes depending on their exact structure. 2-Diphenylphosphinopyridine **1** seems to favour a bidentate bridging mode (although some chelate complexes have been isolated).[8,9] 2-(Diphenylphosphino)aminopyridine **2** forms a strong P,N chelate with several transition metals,[10] while other pyridyl phosphine ligands like **3** prefer to bind in monodentate fashion.[9] Some P,N ligands which contain further functionality can bind to metals in tridentate fashion. For example Van Leeuwen and coworkers have prepared the tridentate P^NN ligand **4** and shown it to form allyl complexes in which the amino-phosphine ligand adopts an η^3 coordination mode and the allyl ligand unusually adopts η^1 coordination.[11]



The preferred mode of coordination has a very significant impact on a ligand's applications in catalysis and organometallic chemistry. For example, a ligand that forms a very strong chelate may not be sufficiently capable of partially dissociating and allowing coordination of an organic substrate. In asymmetric catalysis, on the other hand, a strong chelate $(\eta^2\text{-P^N})M$ is necessary to prevent dilution of enantioselectivity by competing unselective monodentate complexes, $(\eta^1\text{-P^N})_2M$.[12] In order to clarify which co-ordination modes are favoured for different ligands containing PN_x (x = 1, 2 or 3) donors, we have studied the coordination behaviour of five P,N ligands with rhodium complexes.

Experimental

General

All manipulations were carried out under an atmosphere of nitrogen, unless stated otherwise. All solvents were either freshly distilled from an appropriate drying agent (THF, Et_2O, DCM) or obtained as anhydrous grade. ^1H and ^{31}P NMR spectra were recorded using a "Varian 2000" 300 MHz spectrometer. IR spectra were recorded as KBr discs (prepared in air) on a Perkin Elmer PE1720 FTIR/RAMAN spectrometer. All significant peaks > 800 cm^{-1} are quoted to serve as a fingerprint. Silver salts, diphenylphosphine, 2-hydrazinopyridine, formaldehyde,

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2-diphenylphosphinopyridine (Aldrich Chemical Co.), and 2-piperidinopyridine (Lancaster Synthesis) were purchased and used as received. Triethylamine and chlorodiphenylphosphine were distilled prior to use. $[Cp^*RhCl_2]_2$ and Ph_2PNHPy **2** were prepared by literature methods.[10,13] Diphenylphosphinomethanol was obtained by heating neat diphenylphosphine (one equiv.) and formaldehyde (one equiv.) in a Schlenk tube at 100 °C for 3 h. This gives on cooling a quantitative yield of pure material. (**CAUTION**: halide abstractions carried out within this paper were carried out on a microscale, often using <0.020 g of silver perchlorate. However, since organometallic perchlorate salts can be explosive, the authors strongly suggest the use of other silver salts that are less inherently dangerous, but often equally effective.)

2-Diphenylphosphinohydrazinopyridine 5

Chlorodiphenylphosphine (2.33 ml, 13 mmol) was added to a solution of 2-hydrazinopyridine (1.42 g, 13 mmol) and triethylamine (2.01 ml, 14.3 mmol) in THF (40 ml) and stirred overnight under nitrogen. The reaction mixture was filtered to remove the triethylamine hydrochloride and solvent was removed *in vacuo* leaving a yellow solid. Crude yield 2.79 g, 73%. 2.16 g of the solid was recrystallised by cooling a concentrated chloroform solution in the fridge overnight (yield: 1.90 g, 6.5 mmol, 50%). $C_{17}H_{16}N_2P$ requires: C, 69.60; H, 5.50; N, 14.33. Found: C, 69.09; H, 5.29; N, 14.01%. ν_{max}/cm^{-1}: 3313, 3200, 1602, 989. ^{31}P NMR (121.4 MHz, $CDCl_3$), δ 49.6. ^1H NMR (300 MHz, $CDCl_3$), δ 7.9 (1H, d, J = 8 Hz, pyC[6]H), 7.1–7.6 (12H, m, aromatic), 6.7 (1H, d, J = 16 Hz, aromatic) 6.5 (1H, t, J = 8 Hz), 6.1 (1H, s, NH[py]), 4.5 (1H, d, J = 12 Hz, NH[P]).

2-(*N*-Diphenylphosphino)piperazinopyridine 6

A solution of diphenylphosphinomethanol (2.386 g, 11.035 mmol) in acetonitrile (40 mL) was added to 2-piperizinopyridine (1.68 mL, 1.80 g, 11.035 mmol). This solution was then heated to reflux overnight. On cooling to room temperature, analytically pure microcrystals of pippyphos **6** formed in the reaction flask. These were filtered off very briefly in air and dried *in vacuo* (yield: 2.04 g, 5.63 mmol, 51%). This compound has also been prepared directly from diphenylphosphine in toluene by other workers.[14] $C_{22}H_{24}N_3P$ requires: C, 73.11; H, 6.69; N, 11.63. Found: C, 73.33; H, 6.32; N, 11.80%.

2-Diphenylphosphinobenzylideneaminopiperidine 7

2-Diphenylphosphinobenzaldehyde (0.3 g, 1.033 mmol) and *N*-aminopiperidine (0.113 mL, 0.105 g, 1.044 mmol) were heated in THF at reflux for 5 h. The reaction mixture was then cooled and solvent removed to give a quantitative yield of **7** as a colourless wax. Compound **7** was further purified by cooling a solution (Et_2O, 1 ml: hexane, 3 ml) in a freezer overnight to give colourless crystals of 2-dppbap **7** (yield: 0.170 g, 0.456 mmol, 44%). $C_{24}H_{25}N_2P\cdot 0.25Et_2O$ requires: C, 76.80; H, 7.09; N, 7.17. Found: C, 76.63; H, 6.46; N, 7.20%. IR (ν_{max}/cm^{-1}): 3051, 1584, 1550, 1570, 1477, 1464, 1448, 1375, 1348, 1259, 1242, 1164, 1119. ^{31}P NMR (121.4 MHz, $CDCl_3$), δ −12.9. ^1H NMR (300 MHz, $CDCl_3$), δ 1.4 (2H, m), 1.58 (4H, m), 2.94 (4H, appt, J = 5.6 Hz), 6.88 (1H, m), 7.0 (1H, t, J = 7.6 Hz), 7.3 (1H, m), 7.86, (1H, m), 8.0 (1H, d, J = 4.7 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$), δ 20.8, 21.6, 48.6, 122.3 (d, J = 4.3 Hz), 124.6, 125.2, 125.4 (d, J = 7.6 Hz), 125.8, 130.2 (d, J = 24 Hz), 130.3, 133.7 (J = 9.8 Hz), 133.9 (d, J = 8.0 Hz), 137.1 (d, J = 9.8 Hz). HRMS (ES^+): found: m/z 373.1834, $(MH)^+$ requires 373.1834.

General procedure for synthesis of compounds of type $Cp^*Rh(L)Cl_2$

A dichloromethane solution of ligand was added dropwise over *ca.* 1 min to a solution of $[Cp^*RhCl_2]_2$ in the same solvent. After stirring for 30 min, the solvent was evaporated to near dryness and the resulting compound was washed twice with either diethyl ether or light petroleum (bp 60–80 °C) to yield the rhodium complexes in essentially quantitative yield. The complexes obtained in this way were generally analytically pure, but further purification was sometimes carried out by size exclusion chromatography (in air, dichloromethane as eluent) or by recrystallisation by slow diffusion of diethyl ether into dichloromethane solutions of the complexes.

[Cp*RhCl(2-dppap-*P*,*N*)]Cl 8. Crude material was pure as judged by spectroscopy, and obtained in 100% yield. Recrystallisation by slow diffusion (CH_2Cl_2–Et_2O) gave crystals of the dichloromethane solvate complex suitable for X-ray diffraction study. $C_{27}H_{30}N_2PCl_2Rh\cdot CH_2Cl_2$ requires: C, 50.90; H, 4.71; N, 4. 09. Found: C, 51.17; H, 4.77; N, 4.17%. IR (ν_{max}/cm^{-1}): 3416, 3051, 2985, 1612, 1572, 1475, 1435, 1377, 1330, 1158, 1102, 1019. ^{31}P NMR (121.4 MHz, $CDCl_3$), δ 89.1($J_{P–Rh}$ = 145 Hz). ^1H NMR (300 MHz, $CDCl_3$), δ 1.5 (15H, d, J = 3.6 Hz), 6.8 (1H, t, J = 7.0 Hz), 7.2–7.6 (10H, m), 7.9–8.1 (3H, m), 11.9 (1H, s, br). FAB MS: m/z 551/553 $(M - Cl)^+$, 515/517 $(M - 2Cl)^+$. HRMS (ES^+): found: m/z 551.0886, $(M - Cl)^+$ requires 551.0890.

Cp^*RhCl_2(2-PPh_2Py) 9. The compound was obtained in analytically pure form by removing solvent and washing with Et_2O, and thus in quantitative yield. $C_{27}H_{29}NPRhCl_2$ requires: C, 56.66; H, 5.11; N, 2.45. Found: C, 56.12; H, 4.91; N, 2.34%. IR (ν_{max}/cm^{-1}): 3150, 1638, 1618, 1571, 1482, 1435, 1421, 1372, 1159, 1094, 1026. ^{31}P NMR (121.4 MHz, $CDCl_3$), δ 28.9 ($J_{P–Rh}$ = 141 Hz). ^1H NMR (300 MHz, $CDCl_3$), δ 1.4 (15H, d, J = 3.6 Hz), 7.1–7.6 (10H, m), 7.9–8.1 (3H, m) 8.7 (1H, s, br). FAB MS: m/z 536/538 $(M - Cl)^+$, 500/502 $(M - 2Cl)^+$. HRMS (ES^+): found: m/z 536.0780, $(M - Cl)^+$ requires 536.0781.

Cp^*RhCl_2(pippyphos-*P*) 11. The compound was obtained in analytically pure form by removing solvent and washing with Et_2O, and thus in quantitative yield. Crystals suitable for X-ray diffraction were grown by slow diffusion (Et_2O–CH_2Cl_2). $C_{32}H_{39}N_3PRhCl_2$ requires: C, 57.33; H, 5.86; N, 6.27. Found: C, 56.90; H, 5.77; N, 6.15%. IR (ν_{max}/cm^{-1}): 3051, 2813, 1592, 1565, 1480, 1436, 1377, 1312, 1242, 1099, 1008. ^{31}P NMR (121.4 MHz, $CDCl_3$), δ 32.5 ($J_{P–Rh}$ = 139 Hz). ^1H NMR (300 MHz, $CDCl_3$), δ 1.35 (15H, d, J = 3.3 Hz), 2.26 (4H, t, J = 4.94 Hz), 3.10 (4H, s, br), 4.0 (2H, app s?), 6.48 (1H, d, J = 8.8 Hz), 6.54 (1H, dd, J = 8.0, 4.9 Hz), 7.4–7.6 (8H, m), 8.0–8.3 (4H, m). ^{13}C NMR (75.5 MHz, $CDCl_3$), δ 5.3, 42.0, 51.5, 53.9 (d, J = 40.0 Hz), 95.3, 104.1, 110.1, 124.7 (d, J = 9.8 Hz), 125.3 (d, J = 42.20 Hz), 127.8, 131.8 (d, J = 8.7 Hz), 134.1, 144.7. FAB MS: m/z 670 $(MH)^+$, 633/5 $(M - Cl)^+$, 597/9 $(M - 2Cl)^+$. HRMS (FAB): found: m/z 670.1407, $C_{32}H_{40}N_3PCl_2Rh$ requires 670.1392.

[RhCp*Cl_2(Ph_2PNHNHPy-*P*)] 10. Analytically pure material was obtained by removing most of the solvent and precipitating out the red solid using hexane (yield 93 mg, 57%) $C_{27}H_{31}N_3PCl_2Rh$ requires: C, 53.84; H, 5.19; N, 6.98; Found: C, 53.57; H, 5.12; N, 7.05%. ^{31}P NMR (121.4 MHz, $CDCl_3$), δ 77.1 ($J_{P–Rh}$ = 148 Hz). ^1H NMR (300 MHz, $CDCl_3$), δ 1.4 (15H, d), 5.75 (1H, d, J = 34.6 Hz, NH), 6.05 (1H, s, br, NH), 6.4 (1H, t, J = 4.1 Hz), 6.75 (1H, d, J = 8.5 Hz), 7.15 (1H, t, J = 5.5 Hz), 7.4 (6H, m), 7.8 (1H, d, J = 3.9 Hz), 7.95 (4H, m). IR (KBr) ν/cm^{-1}: 3318 (N–H stretch), 3056 (N–H stretch), 1598 (C–N [py] stretch), 987 (P–N stretch). FAB MS: m/z 602 (M^+), 566 $(M - Cl)^+$, 531 $(M - 2Cl)^+$.

[RhCp*Cl_2(Ph_2P(*o*-C_6H_4CH=N-*c*-NC_5H_{10})-*P*)] 12. $C_{34}H_{40}N_2PRhCl_2$ requires: C, 59.92; H, 5.92; N, 3.66. Found: C, 59.03; H, 5.74; N, 3.66%. IR (ν_{max}/cm^{-1}): 3053, 1956, 1637, 1567, 1481, 1435, 1373, 1353, 1258, 1163, 1120, 1085. ^{31}P NMR

(121.4 MHz, $CDCl_3$), δ 30.5 (J_{P-Rh} = 145 Hz). ^1H NMR (300 MHz, $CDCl_3$), δ 1.37 (15H, d, J = 3.0 Hz), 1.6 (s, br), 1.7 (app. s), 2.7–2.9 (m, br), 7.2–7.8 (m, br), 8.1 (d, br, J = 8.0 Hz). HRMS (ES^+): found: m/z 645.1666, ($M - Cl^+$ requires 645.1679 (spectrum was broadened and uninformative).

General procedure for reaction of Cp^*RhCl_2L compounds with silver salts

To a dichloromethane solution of the monodentate rhodium complexes, **9**–**12** was added one (or in some cases two) equivalents of silver salts. After stirring in the dark overnight, the solutions were either filtered through Celite™ or centrifuged to remove silver chloride. After removal of solvent and drying *in vacuo*, the compounds were characterised spectroscopically. In some cases, the complexes were isolated in analytically pure form by addition of diethyl ether to concentrated dichloromethane solutions of the relevant compound.

[$Cp^*RhCl(2\text{-}Ph_2PPy\text{-}P,N)$]$ClO_4$ 13. The compound was obtained from **9** in analytically pure form by removing solvent and washing with Et_2O, and thus in quantitative yield. A good quality crystal (suitable for X-ray crystallography) was grown by slow diffusion (CH_2Cl_2–Et_2O). $C_{27}H_{29}NPRhCl_2O_4$ requires: C, 50.96; H, 4.59; N, 2.20. Found: C, 50.60; H, 4.79; N, 2.00%. IR (ν_{max}/cm^{-1}) 3058, 1638, 1615, 1571, 1482, 1436, 1377, 1262, 1095, 1020. ^{31}P NMR (121.4 MHz, $CDCl_3$), δ −11.6 (J_{P-Rh} = 116 Hz). ^1H NMR (300 MHz, $CDCl_3$), δ 1.66 (15H, d, J = 4.67 Hz), 7.0–8.2 (13H, m), 8.6 (1H, d, J = 5.2 Hz). FAB MS: m/z 536/538 $(M - ClO_4)^+$, 500/502 $(M - ClO_4 - Cl)^+$. HRMS (ES^+): found m/z 536.0778, $(M - Cl)^+$ requires 536.0781.

[$RhCp^*Cl(Ph_2PNHNHPy\text{-}P,N)$]$ClO_4$ 14. This compound obtained from **10** was purified by removing most of the solvent, adding hexane and cooling in the fridge overnight. Crystals could be obtained by layering a DCM solution with diethyl ether. (Yield 43 mg, 26%.) There can be no doubt as to the identification and high purity (spectroscopy, XRD evidence) of **14**. However, it repeatedly gave chemical analysis with too much carbon. $C_{27}H_{37}Cl_2N_3O_4PRh$ requires: C, 47.14; H, 4.63; N, 6.20. Found: C, 48.67; N, 4.69; N, 6.31%. IR (ν_{max}/cm^{-1}) 3319, 3058, 1599, 987. ^{31}P NMR (121.4 MHz, $CDCl_3$), δ 88.7 (d, J_{P-Rh} = 143 Hz). ^1H NMR (300 MHz, $CDCl_3$), δ 1.2 (15H, d, 1.3 Hz), 4.6 (1H, d, J = 4.6 Hz), 6.25 (1H, d, J = 3.4 Hz), 7–8 (13H, m, ArH), 8.7 (1H, d, J = 6.0 Hz). FAB MS: m/z 566 $(M - ClO_4)^+$, 530 $(M - Cl - ClO_4)^+$.

X-Ray crystallography

Crystal structures were obtained using a Bruker SMART diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Intensity data were collected using 0.3 or 0.15° width ω 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. Structures were solved by direct methods and refined by full-matrix least squares against F^2 (SHELXTL).[15] In **11** there were serious disorder problems associated with an acetone solvate; the acetone was refined isotropically in two 50% occupancy orientations with a common C=O group, the solvate protons were not included in the refinement. In **13** the hydrogen atoms of the CH_2Cl_2 solvate were not included in the refinement. In **14** the perchlorate anion was disordered and refined in two 50% orientations.

Crystal data for all the compounds are given in Table 1.

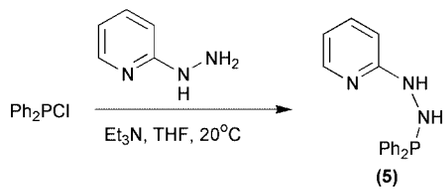
CCDC reference numbers 165059–165063.

See http://www.rsc.org/suppdata/dt/b1/b104523g/ for crystallographic data in CIF or other electronic format.

Results and discussion

(a) Synthesis of ligands

Ligand 2-dpphp **5** contains a P–N bond, and is prepared by the addition of chlorodiphenylphosphine to 2-hydrazinopyridine in the presence of triethylamine (Scheme 1). This ligand can be

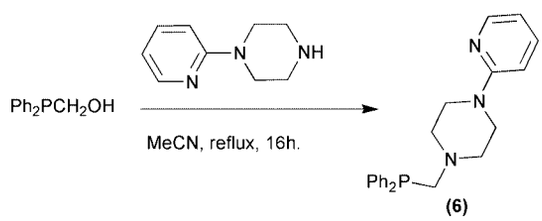


(5)

Scheme 1

obtained in good purity after removal of triethylamine hydrochloride by-product, providing the reactions are carried out under anhydrous, anaerobic conditions. Slow addition of chlorodiphenylphosphine is required, to prevent disubstitution of the amine. This ligand, which is fairly tolerant to moisture and air, can be purified by recrystallisation from cold chloroform to give a moderate yield of analytically pure material. This ligand was of considerable interest to us as it can provide a comparison to 2-Ph_2PNHPy, which we have studied in some detail.[10] Furthermore, the presence of the extra NH functionality opens up the possibility for tridentate coordination and supramolecular structures resulting from hydrogen bonding between pyridine and NH moieties.

The synthesis of pippyphos **6** is even more straightforward (Scheme 2). After heating a solution of 2-piperidinopyridine

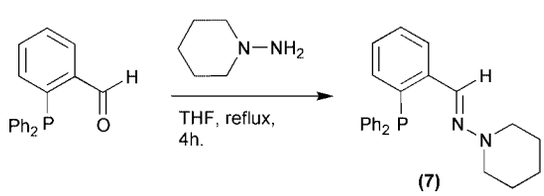


(6)

Scheme 2

with diphenylphosphinomethanol overnight, analytically pure pippyphos crystallises out of the reaction mixture on cooling. Unbeknown to us, this ligand had already been prepared directly from diphenylphosphine.[14] However, its coordination chemistry has not been studied to any extent.

Given the huge number of amines that are readily available and the mild reaction conditions employed, the condensation reaction between Ph_2PCH_2OH and amines is undoubtedly a useful and under used method for phosphine synthesis. It is complimentary to P–N bond formation, and allows the effect of increasing ring size to be evaluated. It has recently been applied by Smith and coworkers in the preparation of pyridine functionalised diphosphines.[16] Another interesting method to prepare phosphines with P,N donor sets is the condensation of phosphine-substituted aldehydes with amines/hydrazines. The phosphino-hydrazone ligand **7** was synthesised by reaction of commercially available 2-diphenylphosphinobenzaldehyde with *N*-aminopiperidine (Scheme 3). The reaction proceeds very



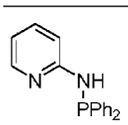
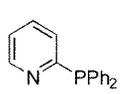
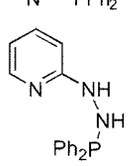
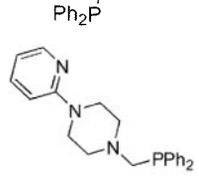
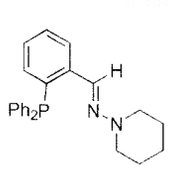
(7)

Scheme 3

Table 1 Crystal data for compounds **8**, **10**, **11**, **13** and **14**

	8	**10**	**11**	**13**	**14**
Empirical formula	$C_{28}H_{32}Cl_4N_2PRh$	$C_{27}H_{31}Cl_2N_3PRh$	$C_{35}H_{46}Cl_2N_3O_{1.5}PRh$	$C_{27.50}H_{30}Cl_3NO_4PRh$	$C_{31}H_{41}Cl_2N_3O_5PRh$
M	672.4	602.33	737.53	678.76	740.45
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$C2/c$	$P2_1/n$
a/Å	8.5863(4)	20.1794(3)	13.0569(3)	32.668(2)	16.6792(11)
b/Å	10.3041(5)	14.2417(4)	19.4344(5)	8.1102(5)	9.7256(6)
c/Å	18.7795(9)	20.7001(2)	13.9166(3)	24.401(2)	21.2011(13)
α/°	97.6060(10)	90	90	90	90
β/°	94.2100(10)	110.993(2)	91.1350	102.928(2)	97.3360(10)
γ/°	112.4040(10)	90	90	90	90
U/Å	1508.60(12)	5554.1(2)	3530.69(14)	6300.9(7)	3411(4)
Z	2	8	4	8	4
μ/mm^{-1}	0.993	0.885	0.713	0.878	0.746
Reflections measured	9484	23956	14889	13306	14412
Independent reflections	4353	7976	5036	4515	4891
Final R 1,	0.0447	0.0639	0.0589	0.0574	0.0411
$wR2[I > 2\sigma(I)]$	0.1102	0.1019	0.1414	0.1460	0.0820

Table 2 ^{31}P NMR data and coordination modes of the six ligands studied

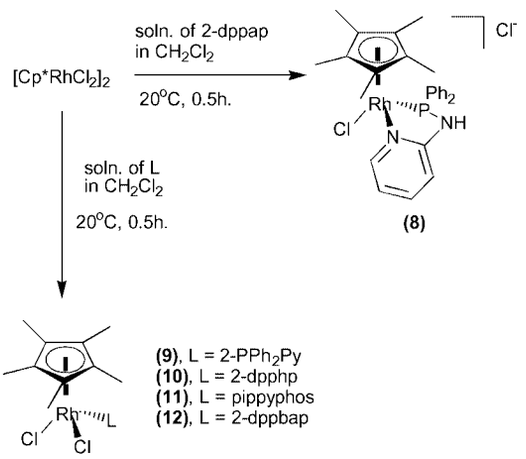
Ligand	δ_P	Coordination + $[Cp^*RhCl_2]_2$	$\delta_P(^1J_{P-Rh})$[a]	Coordination + $AgClO_4$	$\delta_P(^1J_{P-Rh})$[a]
	26.2	Bidentate (**8**)	89.1 (145)	N/A	—
	−4.6	Monodentate (**9**)	28.9 (141)	Bidentate (**13**)	−11.6 (116)
	49.6	Monodentate (**10**)	77.1 (148)	Bidentate (**14**)	88.7 (143)
	−27.1	Monodentate (**11**)	32.5 (139)	Mixture (2 compounds)	27.1 (148)[40%] −13.3 (128) [60%]
	−12.9	Monodentate (**12**)	30.5 (145)	Mixture (2 compounds)	35.5 (138) [70%] 33.1 (140) [30%]

[a] Chemical shifts in ppm relative to external H_3PO_4, coupling constants in Hz.

cleanly to give a quantitative yield of essentially pure material. The ligand can be purified further by recrystallisation. This ligand was of additional interest as a related phosphino-imine ligand, in which the c-NC_5H_{10} group of **7** was replaced with a c-C_6H_{12} group, has very recently been found to be the best ligand for palladium catalysed carbostannylation of alkynes.[6] Other nitrogen substituents were found to be significantly less selective or efficient. Phosphino-hydrazone ligands have also been used in Pd catalysed allylic alkylation.[17] The remaining two ligands, 2-Ph_2PPy and 2-dppap have been prepared previously, with 2-diphenylphosphinopyridine, being commercially available. The ^{31}P NMR chemical shift of each of the ligands is shown in Table 2.

(b) Reaction with $[Cp^*RhCl_2]_2$

Four of the ligands react with $[Cp^*RhCl_2]_2$ to give monodentate complexes **9**–**12** of type $Cp^*RhCl_2(L)$ (Scheme 4). All ligands show a downfield shift (between 35 and 50 ppm) in their phosphorus NMR spectra on coordination to the rhodium centres (Table 2). In the case of 2-dpphp and **2**-PPh_2Py, the complexes display a broadened doublet in their ^{31}P NMR spectra, which may suggest either transient coordination to form a cationic chelate complex or perhaps the presence of two interconverting structures which differ only in the conformation of the ligand. The other complexes all show sharp doublets with coupling constants of 139–148 Hz. The ^{1}H NMR spectra of the monodentate complexes **9**–**12** broadly resemble those of the corresponding ligands. In particular, there is no large downfield shift associated with protons adjacent or near to the nitrogen substituents, which could be indicative of N coordination. There is also no great change in the position of C=N stretching vibrations in the IR spectrum in going from free ligand to monodentate complex (although in the case of **12** an extra band is observed in the IR spectrum at 1637 cm^{-1}). All the complexes were additionally characterised by elemental analysis which gave good agreement with the proposed formulae in each case. The FAB mass spectra of the complexes generally gave



Scheme 4

ions due to $(M - Cl)^+$ and $(M - 2Cl)^+$ [and in several cases $(M + Na)^+$and $(MH)^+$] and therefore also fully supports the structures **9**–**12**.

In the case of the ligand 2-dppap **2** a bidentate complex is formed in which one of the chloride ions is found outside the coordination sphere. The particularly large downfield shift from the free ligand (δ 26.2 to 89.1) is consistent and diagnostic of the formation of a five-membered chelate ring.[10,18,19] The IR spectrum of this complex also shows ν(C=N) moving from 1587 (free ligand) to 1612 cm^{-1}. In a study which focused on the coordination behaviour of this ligand with a wide selection of other metals, a large downfield shift in the phosphorus NMR spectra and an increase in the value of ν(C=N) were always indicative of P,N chelation. Another useful diagnostic tool to assign N coordination is a considerable downfield shift for the proton *ortho* to the aromatic nitrogen. This is observed in complex **8** (*ortho* H shifted from δ 7.97 in **2** to 11.87 in **8**). The structure of this complex demonstrates the strong preference for chelation shown by this ligand. It has been found previously that even non-symmetrical diphosphine ligands can exhibit monodentate coordination to Cp^*RhCl_2 fragments, so **2** can be considered to form quite a strong chelate. It is likely that the formation of a five membered ring enhances the strength of a phosphine/pyridine chelate ring.[10,18,19] In actual fact, it has recently been found that the related ligand Ph_2POPy shows identical chemistry with this metal fragment. An X-ray crystal structure determination of $[Cp^*Rh(Cl)(\eta^2\text{-}Ph_2POPy)]Cl$ revealed similar molecular parameters and the presence of the strong five-membered P,N chelate.[20]

(c) X-Ray crystal structures of $Cp^*RhCl_2(L)$ complexes

Recrystallisation of complex **8** from CH_2Cl_2–Et_2O (slow diffusion) yielded crystals suitable for a crystal structure determination. The crystal structure of compound **8** (Fig. 1) shows the rhodium centre to be approximately octahedral with the Cp* ligand occupying three facial positions of this octahedron. The structure confirms the η^2 chelation mode for ligand **2** and the expected η^5-coordination of the Cp* ligand. The crystallographic bite angle of this angle, P(1)–Rh(1)–N(14) is 80.65(12)°, which is significantly smaller than the idealised 90° for octahedral geometry. It is therefore clear that the formation of a somewhat constrained metallocyclic ring is actually beneficial to chelate strength, as ligand **2** is clearly the strongest chelating ligand of those we have studied (none of the other ligands can displace chloride from the coordination sphere). The angle N(14)–Rh(1)–Cl(1), which is 84.43(12)° is also significantly smaller than in idealised octahedral geometry. The structure clearly shows the location of the chloride counter-ion, which is found outside the coordination sphere, and hydrogen bonded to the NH functionality present within the phosphine ligand [length of hydrogen bond: N(1)H1–Cl(2) 2.126(8), N(1)–Cl(2) 3.101(4) Å]. This type of hydrogen bond has been observed previously in complexes of 2-dppap.[10] The nitrogen that is bound to phosphorus shows planar geometry and the P–N bond length is somewhat shorter in **8** than that found in the free ligand [1.679(4) *vs.* 1.705(3) Å]. Rh–Cl and Rh–P bond lengths are very similar to those found in $Cp^*Rh(P(OEt)_3)Cl_2$.[21] The Rh–C bond distances vary from 2.160(6) to 2.238(6) Å, which reflects whether the carbon atom is located directly opposite the phosphorus donor (strong *trans* influence) or the chloride ligand. Selected bond lengths and angles are found in Table 3.

Table 3 Selected bond lengths (Å) and angles (°) for **8**

Rh(1)–N(14)	2.104(4)	N(14)–Rh(1)–P(1)	80.65(1)
P(1)–N(1)	1.679(4)	P(1)–Rh(1)–Cl(1)	93.37(5)
Rh(1)–P(1)	2.286(1)	C(13)–N(1)–P(1)	120.1(4)
Rh(1)–C(21)	2.217(6)	N(14)–C(13)–N(1)	117.3(4)
Rh(1)–C(22)	2.169(5)	N(1)–P(1)–Rh(1)	100.8(2)
Rh(1)–C(23)	2.186(6)		
Rh(1)–C(24)	2.160(6)		
Rh(1)–Cl(1)	2.389(1)		
C(13)–N(14)	1.339(7)		

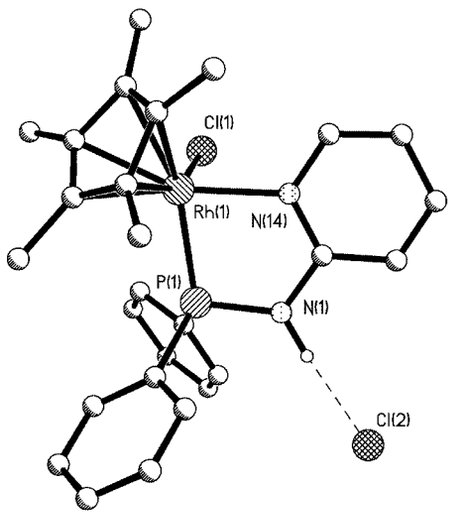


Fig. 1 Crystal structure of **8**.

Complex **10** was also characterised by X-ray diffraction. The molecular structure of **10** is particularly interesting, as the complex forms hydrogen bonded dimers *via* the acidic NH functionalities on the ligand (a good H-bond donor) and both the pyridine and chloride ligands (H-bond acceptors). This arrangement is shown in Fig. 2. The structure shows how the 2-aminopyridine units are complementary to each other. It is the presence of these hydrogen bonds that enables the two complexes to associate together. The aromatic NH groups [N(2)H and N(32)H in Fig. 2(b)] form an intermolecular bond to the pyridine nitrogen belonging to the other complex in the dimer [N(2)H ··· N(44) 2.37(6), N(32)H ··· N(14) 2.13(2) Å; N(32)–N(32)H ··· N(14) 172(6), N(2)–N(2)H ··· N(44) 130(6)°]. There is a slight difference between the two members of the dimer regarding the H-bonding between the P bound NH and the chloride ligands. In molecule 1 [contains labels Rh(1), P(1) *etc.*], the hydrogen bond is a simple bond, between one Cl and one H. In molecule 2 [denoted with labels Rh(2), P(2) *etc.*], the hydrogen bonding is less strong, and bifurcated between two Cl and one H. The relevant parameters for the intramolecular bonds are N(1)H ··· Cl(1) 2.53(7), N(31)H ··· Cl(3) 2.88(9), N(31)H–Cl(4) 2.92(1) Å; N(1)–N(1)H···Cl(1) 119(6), N(31)–N(31)H ··· Cl(3) 106(6), N(31)–N(31)H ··· Cl(4) 92(6)°. The structures of each of the two rhodium complexes shown in Fig. 2 are both approximately octahedral in geometry and do not show any particularly unusual bond lengths or angles (Table 4).

Table 4 Selected bond lengths (Å) and angles (°) for **10**

Rh(1)–P(1)	2.314(3)	P(1)–Rh(1)–Cl(2)	89.14(9)
Rh(1)–Cl(2)	2.415(3)	P(1)–Rh(1)–Cl(1)	86.69(9)
P(1)–C(7)	1.800(10)	Cl(1)–Rh(1)–Cl(2)	91.23(10)
N(1)–N(2)	1.396(10)	N(1)–P(1)–Rh(1)	108.2(3)
Rh(2)–P(2)	2.324(3)	N(2)–N(1)–P(1)	119.5(6)
Rh(2)–Cl(4)	2.395(3)	C(13)–N(2)–N(1)	119.1(8)
P(2)–C(31)	1.807(9)	N(14)–C(13)–N(2)	115.2(9)
N(31)–N(32)	1.393(10)	P(2)–Rh(2)–Cl(4)	86.27(9)
Rh(1)–Cl(1)	2.403(3)	Cl(3)–Rh(2)–Cl(4)	91.61(10)
P(1)–N(1)	1.679(8)	P(2)–Rh(2)–Cl(3)	88.52(9)
P(1)–C(1)	1.839(9)	N(31)–P(2)–Rh(2)	106.8(3)
N(2)–C(13)	1.39(1)	N(32)–N(31)–P(2)	123.1(7)
Rh(2)–Cl(3)	2.417(3)	C(43)–N(32)–N(31)	119.5(8)
P(2)–N(31)	1.663(9)	N(44)–C(43)–N(32)	114.8(9)
P(2)–C(37)	1.811(9)		
C(43)–N(44)	1.32(1)		

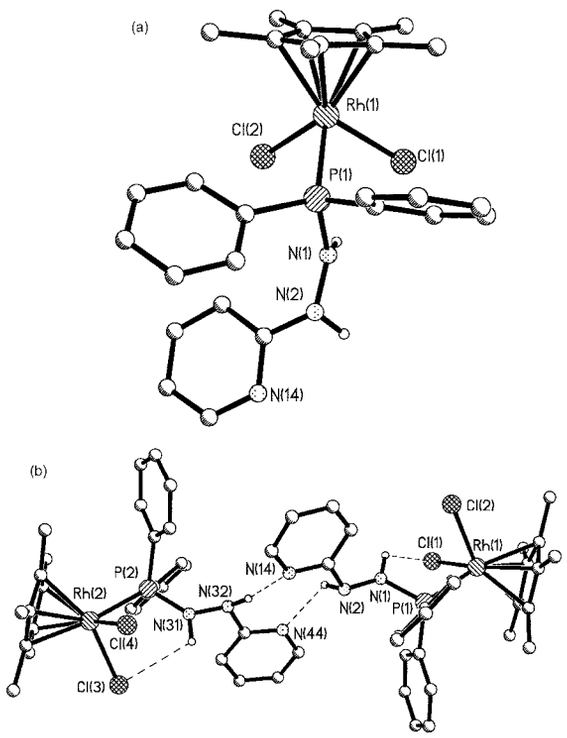


Fig. 2 (a) Crystal structure of **10** and (b) of hydrogen-bonded dimers formed in **10**.

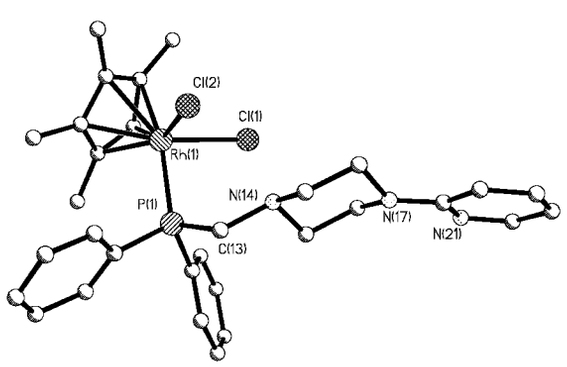


Fig. 3 Crystal structure of **11**.

All the nitrogen atoms found in the structure are planar, as a result of the sp^2 character of P–N, C=N and N=C–N–N–P bonding environments.

The crystal structure of **11** is shown in Fig. 3. This confirms the mononuclear, monodentate structure of this compound in which the piperazine ring adopts a chair conformation. The rhodium centre is octahedral and the angles between phosphorus and chlorine ligand are fairly close to the ideal 90° [P(1)–Rh(1)–Cl(1) 89.86(5), P(1)–Rh(1)–Cl(2) 87.53(5), Cl(2)–Rh(1)–Cl(1) 88.53(5)°]. Selected bond lengths and angles are shown in Table 5.

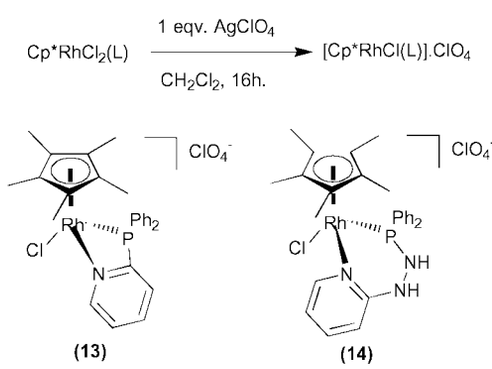
Table 5 Selected bond lengths (Å) and angles (°) for **11**

Rh(1)–P(1)	2.339(1)	P(1)–Rh(1)–Cl(1)	89.86(5)
Rh(1)–Cl(1)	2.428(1)	C(13)–N(14)–C(15)	108.2(4)
Rh(1)–Cl(2)	2.411(1)	Cl(1)–Rh(1)–Cl(2)	88.53(5)
Rh(1)–C(26)	2.166(5)	P(1)–Rh(1)–Cl(2)	87.53(5)
Rh(1)–C(27)	2.156(5)		
Rh(1)–C(28)	2.229(5)		
Rh(1)–C(29)	2.193(5)		
Rh(1)–C(30)	2.174(5)		
C(13)–N(13)	1.519(6)		
C(20)–N(21)	1.339(7)		

The average Rh–P bond length from the monodentate structures [2.326(3) Å] is clearly considerably longer than that found in bidentate **8** [2.286(1)]. This is presumably a reflection of the increased bond strength that is found in chelate complexes. The cationic nature of **8** may also enhance the P ⟶ Rh donor interaction. This trend is also present, but somewhat less pronounced, in the Rh–Cl bond lengths [average for **10** and **11** is 2.411(3) *vs.* 2.389(1) Å]. Our results clearly show that the majority of P,N ligands will form a monodentate complex on reaction with $[Cp^*RhCl_2]_2$, but that a bidentate cationic complex can be formed if the ligand is quite strongly chelating. It was now of interest to determine the affinity of the nitrogen donors for the Cp^*RhCl_2 fragment by removal of the competing chloride ligands.

(d) Addition of silver salts to monodentate $Cp^*RhCl_2(L)$ complexes

L = 2-PPh$_2$Py. When silver perchlorate was added to a dichloromethane solution of monodentate **9** complete conversion to a new species was observed by ^{31}P NMR spectroscopy (Scheme 5). The formation of a chelate complex was deduced



Scheme 5

from the following spectroscopic data. The ^{31}P NMR spectrum was especially informative as it shows a doublet that is shifted significantly upfield from the starting complex **9** (δ −11.6 *vs.* +28.9). An upfield shift in the ^{31}P NMR spectrum (relative to a monodentate complex) is known to be diagnostic for a four-membered chelate complex.[19,22] In addition, the coupling constant J_{P-Rh} was reduced in magnitude from that found in **9** (116 *vs.* 141 Hz). Although there are no comparable rhodium systems known, it seems likely that a reduction in coupling constant may also be a diagnostic feature of a four-membered rhodium–phosphorus containing ring (see remaining discussion). Unusually small coupling constants have been found in the four-membered ring system (dppm)Pt(CH_3)$_2$ [dppm = bis-(diphenylphosphino)methane] when compared to other diphosphine dimethylplatinum complexes.[22] The ^{1}H NMR spectra of both monodentate and chelate complex are fairly similar in appearance (although the aromatic protons show more signals in the chelate complex). This is somewhat surprising as it has

Table 6 Selected bond lengths (Å) and angles (°) for one of the independent molecules of **13**

Rh(1)–P(1)	2.338(2)	P(1)–Rh(1)–N(14)	67.3(2)
Rh(1)–Cl(1)	2.394(2)	N(14)–C(13)–P(1)	102.0(5)
Rh(1)–N(14)	2.132(6)	P(1)–Rh(1)–Cl(1)	90.94(8)
Rh(1)–C(21)	2.171(8)	N(14)–Rh(1)–Cl(1)	84.4(2)
Rh(1)–C(22)	2.195(8)	C(13)–P(1)–Rh(1)	84.4(3)
Rh(1)–C(23)	2.195(8)	C(13)–N(14)–Rh(1)	105.8(5)
Rh(1)–C(24)	2.142(8)		
Rh(1)–C(25)	2.171(8)		
C(13)–N(14)	1.33(10)		
C(13)–P(1)	1.819(7)		

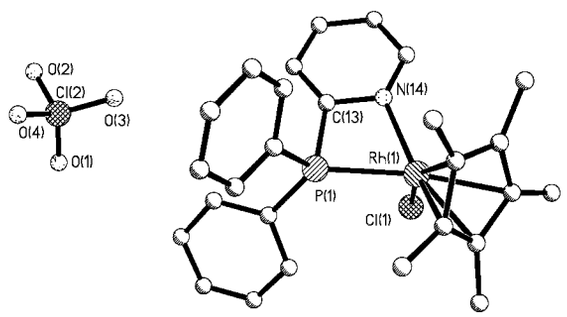


Fig. 4 Crystal structure of **13**.

been noted that N-coordinated pyridylphosphines sometimes show a shift of the *ortho*-N proton to higher frequency. The IR spectra of pyridyl phosphines is not especially informative in assigning coordination behaviour as ν(C=N) does not normally shift to higher frequency as is found with 2-dppap. The IR spectrum of **13** shows bands at 1638, 1615 and 1571 cm^{-1}, which are presumably due to C=N and C=C vibrations. This is fairly similar to the monodentate complex, (1636, 1615 and 1587 cm^{-1}) although there is clearly a shift for the band found at the lowest wavenumber. There is also a very intense band (1095 cm^{-1}) attributed to the ClO_4^- counter-ion. The formulation of **13** was also supported by microanalytical and mass spectral data.

X-Ray crystal structure of [Cp*RhCl(2-PPh$_2$Py-P,N)]ClO$_4$. As the spectroscopic data was not quite as conclusive as we may have hoped, crystals of **13** were grown by slow diffusion (CH_2Cl_2–Et_2O). The crystal structure of **13**, which is shown in Fig. 4, clearly confirms the bidentate, mononuclear structure that was suggested from the spectroscopic data. The P,N chelate shows, as might be expected for a four-membered ring, a severe distortion from idealised octahedral geometry [N(14)–Rh(1)–P(1) 67.3(2)°]. The Rh–Cl bond length is significantly shorter than that found in the neutral monodentate complex **10**. However, the Rh–P bond length, which was much shorter in **8**, is of similar length to that found in monodentate **10** and **11** [Rh(1)–P(1) 2.338(2) *vs.* average bond length of 2.326(3) Å]. These values support the idea that the shortened bond length found in **8** is predominantly due to its particularly strong chelate ring. The strained chelate ring obtained here also has a longer Rh–N bond length than that of **8** [Rh(1)–N(14) 2.104(4) Å in **8** *vs.* 2.132(6) Å in **13**]. Selected bond lengths and angles are shown in Table 6.

L = 2-dpphp. On treatment of the monodentate complex **10** with one equivalent of silver perchlorate, a single new species is formed as judged by ^{31}P NMR spectroscopy. This spectrum shows a doublet (δ 88.7, J = 143 Hz) that is shifted slightly down field from the monodentate complex. The position of the aromatic proton *ortho* to the pyridine nitrogen has moved downfield from δ 7.8 (complex **10**) to δ 8.7 in the cationic complex which we assign structure **14**. It is reasonable to assume that this downfield shift could only be due to nitrogen coordination

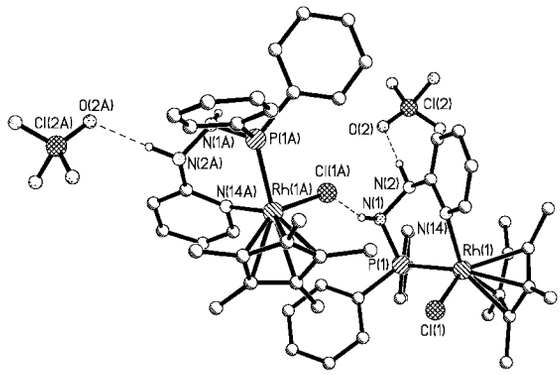


Fig. 5 Crystal structure of **14**.

to the rhodium centre. The IR spectrum of this new species is also informative and confirms the chelate structure **14**. In particular, the position of ν(C=N) which is found at 1599 cm^{-1} in **10** and the free ligand, has shifted in frequency to 1611 cm^{-1}. This type of shift is diagnostic of aromatic N coordination for 2-dppap, and it likely that this is also the case for 2-dpphp. The identity of this complex was further confirmed by the FAB mass spectrum which shows peaks due to $(M - ClO_4)^+$ and $(M - Cl - ClO_4)^+$.

X-Ray crystal structure of [Cp*RhCl(2-dpphp-*P*, *N*)]ClO$_4$ 14. Since the crystal structure of the monodentate complex **10** displayed an interesting hydrogen bonded dimer structure, it was of considerable interest to determine the crystal structure of complex **14**. This structure also allowed us to make a comparison with structural data obtained in the other chelate complexes studied and to fully corroborate the proposed structure. The crystal structure of **14** clearly confirms the bidentate P,N coordination of 2-dpphp and is shown in Fig. 5. The are two independent molecules within the structure, but the molecular parameters for each are very similar. The structure also shows that this ligand is still capable of forming a mono-dimensional hydrogen bonding network even when the pyridine nitrogen, which is a key hydrogen bond acceptor in the solid state structure of [Cp*RhCl$_2$(2-dpphp-*P*)]), is bound to the metal. The complexes form infinite chains in which an intermolecular hydrogen bond [N(1)–Cl(1) 3.415(4), N(1)H–Cl(1) 2.47(2) Å] between the P bound N(1)H and the chloride ligands on a separate rhodium complex link the chains together. The N-functionality which is bound to the pyridine ring, N(2)H, additionally forms a hydrogen bond to the perchlorate counter-ion [N(2)–O(2) 2.944(7), N(2)H–O(2) 1.99(1) Å]. These complexes represent an interesting example of a supramolecular architecture that can be modified from strong H-bonded dimers to infinite chains by altering the coordination mode of the ligand. The coordination chemistry of 2-dpphp and its derivatives will therefore be studied further in due course. Complex **14** has a shorter Rh–P bond length than in the monodentate structure **10** [Rh(1)–P(1) 2.305(1) *vs.* 2.314(3), 2.324(3) Å]. The Rh–Cl bond distance on the other hand is slightly elongated [Rh(1)–Cl(1) 2.417(1) Å in **14** *vs.* average bond length of 2.408(3) Å in **10**]. This is in contrast with the other two chelate structures and is presumably a reflection of the hydrogen bonding that is taking place between the chloride ligands and NH from an adjacent molecule. Other relevant bond lengths and angles are shown in Table 7.

L = pippyphos. On addition of either one or two equivalents of $AgBF_4$, the starting complex **11** is converted into two new species as monitored by ^{31}P NMR spectroscopy. One of these species appears as a broadened doublet that can be found significantly upfield from the ^{31}P NMR resonance of the starting material (δ −13.3 *vs.* 32.5). This doublet has a smaller $^1J_{P-Rh}$

Table 7 Selected bond lengths (Å) and angles (°) for **14**

Rh(1)–P(1)	2.305(1)	P(1)–Rh(1)–N(14)	88.0(1)
Rh(1)–Cl(1)	2.417(1)	P(1)–N(1)–N(2)	112.4(3)
Rh(1)–N(14)	2.15(4)	P(1)–Rh(1)–Cl(1)	95.90(5)
Rh(1)–C(21)	2.183(5)	N(14)–Rh(1)–Cl(1)	87.5(1)
Rh(1)–C(22)	2.167(5)	N(1)–N(2)–C(13)	117.9(4)
Rh(1)–C(23)	2.235(5)	N(1)–P(1)–Rh(1)	107.7(2)
Rh(1)–C(24)	2.221(5)		
Rh(1)–C(25)	2.161(5)		
C(13)–N(14)	1.348(6)		
N(2)–N(1)	1.424(6)		
P(1)–N(1)	1.697(4)		

coupling constant than **11** (128 *vs.* 139 Hz). We have already discussed how this NMR data is highly diagnostic of a four-membered chelate complex in a variety of other systems. We therefore can suggest, on this evidence alone, that a P,N chelate complex is likely to account for this signal in the ^{31}P NMR spectrum. Unfortunately, we have not been able to separate the two products formed in this reaction, and both the ^{1}H NMR spectrum, which is broad and messy, and IR spectrum are not informative in fully corroborating the proposed structure. The other compound detected from this reaction displays a sharp doublet in its ^{31}P NMR spectrum. Its chemical shift (δ +27.1) and $^{1}J_{\mathrm{P-Rh}}$ (148 Hz) are more reminiscent of the starting complex **11**. There are several possible structures which could be formed in this case: a simple P-monodentate complex in which BF_4 binds weakly to the Rh centre, a cationic aqua complex (formed from adventitious water), or P,N-coordinated Rh complexes in which either the pyridine or the other piperazine nitrogen coordinate. In addition, compounds in which the nitrogen donors bridge two rhodium centres are also eminently feasible. Despite several attempts, we have been unable to make this halide abstraction go cleanly or purify the two products formed. Thus we can only speculate as to the structures formed. We suggest that pippyphos is a weaker chelating ligand than those discussed thus far, and that this prevents us from isolating a chelate complex.

L = 2-dppbap. On addition of one equivalent of silver tetrafluoroborate to complex **12**, there are two new doublet peaks observed at fairly similar shift in the ^{31}P NMR spectra of the resulting solution. Removal of the solvent gives an orange solid, which displays several bands in the region typical for ν(C=N) stretching vibrations. This is tentative evidence that the two complexes formed may differ in the coordination of the nitrogen atoms. The mass spectrum of this solid supports a cationic complex of formulation [Cp*Rh(Cl)(2-dppbap)]-BF_4. Unfortunately, attempts to separate these two complexes by size exclusion chromatography or recrystallisation failed. Although it is tempting to assign this mixture as the two complexes that would form if both sp^2 C=N and sp^3 C–N coordination could occur, the evidence we have obtained is not sufficient to characterise these products.

(e) Conclusions and summary

The complexes prepared in this study have allowed a greater understanding of the varying affinity of P,N ligands to chelate rhodium centres.

We have synthesised two new multifunctional ligands which consist of PN_x (x = 1,2 or 3) donor atoms. These ligands, along with the three known ligands, smoothly react with $[Cp^*RhCl_2]_2$ to give complexes of type $Cp^*RhCl_2(L)$. In one instance, a bidentate complex is formed indicating that the ligand 2-dppap, strongly favours a chelate coordination mode. The other ligands all form monodentate complexes. On addition of one equivalent of $AgClO_4$ (or $AgBF_4$), a variety of coordination behaviours were observed: a relatively strong chelate (well defined NMR spectra), and weak fluxional chelates (probably) (broadened NMR spectra with poor signal to noise ratio). For a given transition metal, a hemilabile ligand should perhaps be further defined according to whether it shows: (a) unassisted stable chelate coordination, (b) assisted stable chelate coordination (assisted by removal of competing ligands), or (c) assisted fluxional weak chelate coordination. These three classes are not, by any means, peculiar to Cp^*RhCl_2 centres. For example, various researchers, including ourselves, have observed that some P,N ligands sometimes react with platinum precursors such as $(cod)PtCl_2$ (cod = cycloacta-1,5-diene) or $(PhCN)_2PtCl_2$ to give chelate complexes $(\eta^2\text{-L})PtCl_2$ and $[(\eta^2\text{-L})_2Pt]2Cl$ (class a).[10,12b,18] Other ligands form monodentate complexes $(\eta^1\text{-L})_2PtCl_2$, which on treatment with silver salts give chelates, $[(\eta^2\text{-L})_2Pt]^{2+}$ and $[(\eta^2\text{-L})(\eta^1\text{-L})PtCl]^{+}$ (class b). Some P,N ligands do not yield isolable chelate complexes that are stable in the presence of competing ligands (*e.g.* water) even when halide ligands are removed (class c). These distinctions are useful when considering the design of phosphorus ligands in catalysis: a strong chelate is required in asymmetric catalysis or as replacement as a diphosphine. A conventional hemilabile ligand can often increase the reactivity of catalyst in comparison to a kinetically inert diphosphine system. In some instances a very weak chelate is required to generate a very reactive transition metal complex. We now hope that we will be able to apply a specific type of hemilabile ligand to its ideal task in organometallic chemistry and catalysis. Indeed, since the completion of this work, we have prepared weakly chelating (class c) ligands that contain a bulky and electron rich phosphine moiety and shown palladium complexes derived from them to catalyse cross-coupling reactions of aryl chlorides: a reaction that does not occur if normal monodentate or bidentate phosphine ligands are used.[23] Further studies on the application of functionalised phosphino-amines in catalysis and coordination chemistry are now underway.

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