DALTON
FULL PAPER

Complexes of ruthenium with tridentate [P,N,O] ligands

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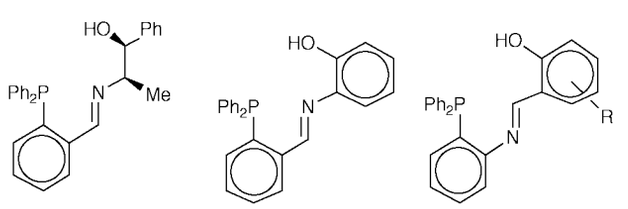
Tridentate ligands with [P,N,O] donor sets, prepared either by the condensation of 2-(diphenylphosphino)-benzaldehyde with 1*S*,2*R*-norephedrine (HL^1) or 2-aminophenol (HL^2) or by the condensation of 2-(diphenylphosphino)aniline with salicylaldehyde (sal) (HL^3), 5-(NO_2)sal (HL^4), 5-(Cl)sal (HL^5), 5-(Br)sal (HL^6), 5-(MeO)sal (HL^7) or 3-(MeO)sal (HL^8), reacted with $[Ru^{II}Cl_2(dmso)_4]$ in refluxing thf solution to yield complexes of the general formula *cis*-$[Ru^{II}Cl(\eta^3\text{-}L^{1\text{–}8})(dmso)_2]$. Use of two equivalents of ligand HL^1 resulted in the formation of *mer*-$[Ru^{II}(\eta^3\text{-}L^1)_2]$, a reaction not seen for $HL^{2\text{–}8}$. Aerial oxidation of *cis*,*mer*-$[Ru^{II}Cl(\eta^3\text{-}L^3)(dmso)_2]$ in a chloroform solution yielded *cis*,*fac*-$[Ru^{III}Cl_2(\eta^3\text{-}L^3)(dmso)]$, which has undergone an unexpected rearrangement of co-ordination geometry.

There has been an increasing interest during recent years in complexes of transition metals with bidentate ligands comprising both hard and soft donor groups. The majority of such ligands are functionalised phosphines, where the phosphorus is the soft donor and either oxygen or nitrogen is a harder donor.[1] Examples have been reported which incorporate chirality, and complexes prepared from these ligands have been shown to have utility in stereoselective transformations.[2]

Tridentate ligands which comprise three different donor groups [P,N,E], where E = N′ or O, are still comparatively rare. The examples known for E = O are either neutral ligands, where the oxygen is part of an ether group[3–6] or monobasic, where either the oxygen or nitrogen has an ionisable proton.[7–12] Since some of these [P,N,O] ligands have been shown to form complexes with ruthenium(II) which are active catalysts for transfer hydrogenation reactions[5,6] we have extended our study of the ligands $HL^{1\text{–}3}$ and prepared the new ligands $HL^{4\text{–}8}$ to investigate their co-ordination behaviour with ruthenium(II). Complexes of HL^1 and $[L^{2,3}]^-$ with nickel, palladium and platinum[11] and complexes of $[L^2]^-$ with iron, cobalt and rhenium[12] have previously been reported. The ligands reported here depend upon a Schiff base condensation in their preparation, and may be considered as examples of this class of ligand. Although Schiff base complexes of ruthenium(II)[13] and ruthenium(III)[14] are known, as with all the platinum group metals they are very much less well studied than their first-row counterparts.



HL^1 HL^2 $HL^{3\text{-}8}$

R = H, HL^3; 5-NO_2, HL^4; 5-Cl, HL^5; 5-Br, HL^6; 5-MeO, HL^7; 3-MeO, HL^8

Results and discussion

Ligand synthesis

The ligands $HL^{1\text{–}3}$ were prepared according to previously published methods and $HL^{4\text{–}8}$ by analogous routes. As previously noted in the synthesis of HL^3, the ligands derived from 2-(diphenylphosphino)aniline require recrystallisation from chloroform–diethyl ether or thf–diethyl ether before use to free them from the traces of unreacted substituted salicylaldehydes which usually persist. The ligands are soluble in a range of organic solvents and are stable to hydrolysis and to aerial oxidation both in the solid state and in solution over several weeks.

Complexation reactions of $[Ru^{II}Cl_2(dmso)_4]$ with $HL^{1\text{–}8}$

The reaction of a stoichiometric quantity of $HL^{1\text{–}8}$ with $[Ru^{II}Cl_2(dmso)_4]$ in refluxing thf solution leads to the formation of the neutral octahedral complexes *cis*-$[Ru^{II}Cl(\eta^3\text{-}L^{1\text{–}8})(dmso)_2]$ **1**–**8** respectively, in moderate to high yields. This is supported by elemental analysis, IR spectroscopy and both ^1H and $^{31}P\text{-}\{^1H\}$ NMR data, Table 1, and in the case of **3** a single crystal structure determination (Fig. 1).

Unlike the previously reported complexation of HL^1 with M^{II} (Ni, Pd or Pt),[11] here the ligand readily deprotonates on complexation to co-ordinate as an alkoxide ligand. This is based on the disappearance both of the resonance due to the alcohol proton in the ^1H NMR and of the large ν(OH) peak in the IR spectrum, as well as on the microanalysis. This difference in complexation behaviour of HL^1 is not unexpected, as ruthenium is well known to deprotonate and co-ordinate alcohols in this way, for example in hydrogen transfer reactions, whereas alkoxides of Group 10 metals are largely unknown.

From the marked similarity of the spectroscopic data for complexes **1**–**8**, it seems reasonable to infer that they are all the same isomer, and from the crystal structure of **3** the most probable is *cis*,*mer*-$[Ru^{II}Cl(\eta^3\text{-}L)(dmso)_2]$, although this assignment is tentative and has not been definitively established.

In order to explore the lability of the remaining solvent and chloride ligands, the preparation of $[Ru^{II}(L)_2]$ complexes was attempted. If the reaction is performed using two equivalents of ligand HL^1 the major product obtained is *mer*-$[Ru^{II}(\eta^3\text{-}L^1)_2]$ **9** (Fig. 2). Attempts to prepare analogous complexes of $HL^{2\text{–}8}$ were unsuccessful, resulting largely in the isolation of the previously prepared complexes **2**–**8**. Since $[L^1]^-$ is no less sterically demanding than $[L^{2\text{–}8}]^-$, the explanation of the difference in behaviour may lie in the greater affinity of the ruthenium(II) centre for an alkoxide ligand than for an aryloxide ligand.

In the reaction of $[Ru^{II}Cl_2(dmso)_4]$ with two equivalents of HL^3 a small amount of a new product was detected by $^{31}P\text{-}\{^1H\}$ NMR which has been identified as *mer*-$[Ru^{II}Cl(\eta^3\text{-}L^3)\{Ph_2P(C_6H_4NH_2\text{-}2)\text{-}\kappa P,N\}]$ **10** (Fig. 3). This compound contains an

Table 1 Selected spectroscopic (^{31}P-{^{1}H} and ^{1}H NMR, IR) and microanalytical data for complexes **1**–**11** and HL$^{1-8}$

Compound	^{31}P-{^{1}H} (ligand)[a]	^{1}H HC=N (ligand)[b]	IR ν(C=N) (ligand)[c]	IR ν(S=O)[c]	Analysis (%) C (calc.)	H (calc.)	N (calc.)
1	66.3 (−10.5)	8.92 (8.62)	1623 (1638)	1093	53.0 (53.7)	5.1 (5.2)	2.1 (2.0)
2	48.2 (−9.0)	8.98 (8.92)	1612 (1624)	1096	53.3 (51.7)	4.8 (4.6)	2.2 (2.1)
3	55.5 (−14.6)	8.86 (8.40)	1605 (1614)	1095	53.0 (51.7)	4.5 (4.6)	2.2 (2.1)
4	55.6 (−14.6)	8.20 (8.19)	1598 (1602)	1098	48.2 (48.5)	4.5 (4.2)	3.6 (3.9)
5	55.4 (−14.6)	8.75 (8.27)	1603 (1613)	1096	49.0 (49.2)	4.2 (4.3)	2.2 (2.0)
6	54.8 (−14.5)	8.76 (8.27)	1596 (1619)	1095	46.7 (46.3)	3.8 (4.0)	1.9 (1.9)
7	55.3 (−14.9)	8.78 (8.33)	1594 (1615)	1097	50.4 (51.3)	4.5 (4.7)	1.8 (2.0)
8	55.8 (−15.4)	8.85 (8.36)	1602 (1611)	1096	48.2 (51.3)	4.8 (4.7)	2.1 (2.0)
9	61.2 (−10.5)	8.94 (8.62)	1619 (1638)	—	68.8 (71.1)	5.4 (5.3)	2.8 (3.0)
10	68.8, 62.6[d] (−10.5)	8.88 (8.40)	1606 (1614)	—	63.3 (65.0)	4.5 (4.4)	3.3 (3.5)
11	—	—	1589 (1614)	1108	48.2 (49.0)	4.5 (4.4)	2.1 (2.0)

[a] In ppm referenced to external 85% phosphoric acid. [b] In ppm referenced to external TMS. [c] In cm^{-1}. [d] ^{2}J(^{31}P-^{31}P) 30 Hz.

intact [L^{3}]$^{-}$ ligand in addition to a P,N co-ordinated 2-(diphenylphosphino)aniline fragment which appears to have been generated *in situ* by the hydrolysis of HL^{3}. This hydrolysis of imines is a reaction which is often accelerated by the presence of metal ions and is sometimes observed as an unwanted side reaction in the complexation of metal ions by Schiff base ligands.[15] A species which is spectroscopically identical with the complex **10** can be prepared independently by direct reaction of **3** and 2-(diphenylphosphino)aniline.

Chloroform solutions of complexes **1–8** which are exposed to aerial oxidation change from a deep red-purple to a deep green typical of complexes of ruthenium(III) over a period of a few days, indicating that the complexes formed are somewhat unstable to oxidation. Diffusion of hexane into such an oxidised solution of **3** produced a quantity of green-black crystals which proved on analysis to be *cis*,*fac*-[Ru^{III}Cl$_2$(η^3-L^{3})(dmso)] **11** (Fig. 4). The ligand has rearranged about the ruthenium(III) centre to a facial configuration, a result entirely unexpected for this type of ligand which have otherwise only exhibited meridional co-ordination to ruthenium. Why the complex undergoes this rearrangement is not clear, although from the bond length and angle data it can be seen that the degree to which the structure of the ligand is perturbed to allow this co-ordination is limited. It has previously been shown that on deprotonation HL^{2} can form the octahedral complex ion [Co^{III}(L^{2})$_2$]$^{+}$ in which both [L^{2}]$^{-}$ ligands bind η^3 in a facial configuration. The original report of this ligand suggested that it would be incapable of co-ordinating in a meridional configuration, on the basis of the short distance between the phosphorus and the oxygen found in its crystal structure.[12] The complexes of Group 10 metals previously reported,[11] together with the results given here, show that such meridional co-ordination is not only possible, but in many cases preferred, a result which indicates a greater degree of flexibility in the backbone of the ligands than might have been expected.

IR Spectroscopy

Selected IR data for the ligands HL$^{1-8}$ and complexes **1**–**11** are shown in Table 1. The peaks which convey most information are those due to ν(C=N) which occur as strong peaks at around 1600 cm^{-1}. On complexation, there is a distinct bathochromic shift of between 4 and 25 cm^{-1}, which is typical for co-ordinated imines of this type.[16] The greatest shift is seen for **11**, where the ligand is facially co-ordinated to ruthenium(III). The peaks due to ν(S=O) in the co-ordinated dmso moieties at around 1090 cm^{-1} are remarkably convergent, with little variation (15 cm^{-1}) seen across the complexes **1**–**8,** with **11** again exhibiting the greatest change.

NMR Spectroscopy

Selected NMR data for the complexes **1**–**10** are collected in Table 1. In the ^{31}P-{^{1}H} data there is a consistent and noticeable shift to lower field on complexation of between 57 and 70 ppm, which is comparable to the behaviour seen previously.[11] The great similarity in chemical shift seen both amongst the free ligands HL$^{3-8}$ and amongst the complexes prepared from these ligands indicates that the substitution on the salicylaldehyde moiety has little influence on this value. In the ^{1}H NMR the spectra are similarly consistent, with a typical low field displacement of the imine proton resonance with respect to the free ligand upon complexation. The dmso methyl resonances appear as four singlets between δ 3.4 and 2.3, a pattern typical for dmso co-ordinated to ruthenium(II).[17]

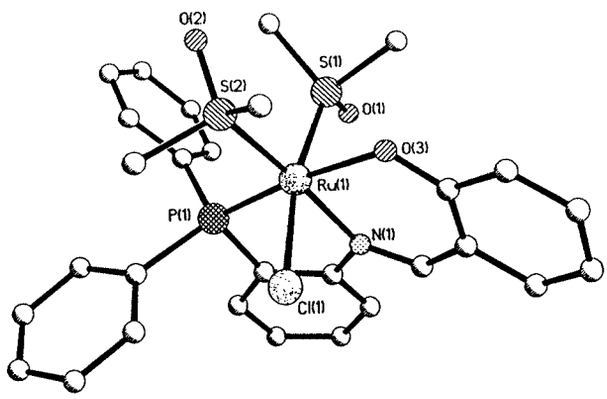


Fig. 1 The molecular structure of complex **3**; hydrogen atoms omitted for clarity, as in all cases.

Single crystal X-ray diffraction studies

The crystal structures of the ruthenium complexes **3**, **9**–**11** are presented in Figs. 1–4. Selected bond length and angle data are collected in Table 2.[18] These structures reveal in each case distorted octahedral geometries at the metal with tridentate co-ordination of monobasic [P,N,O] ligands. Complexes **3**, **10** and **11** all incorporate the ligand [L^{3}]$^{-}$, which forms on co-ordination a five membered ring by P,N chelation and a six membered ring by N,O chelation. For **3** and **10**,† the complexes with meridional [L^{3}]$^{-}$ co-ordination, the angles P–Ru–N within the ligand are 83.1(3) and 84.0(4)° respectively, whereas N–Ru–O are 90.1(7) and 92.4(4)° respectively, indicating the dependence of bond angle on ring size. The angle P–Ru–N within the co-ordinated 2-(diphenylphosphino)aniline in **10** is 83.5(3)° which suggests that these angles are not greatly influenced by the incorporation of the salicylaldehyde fragment into the ligand. In the case of **11**, the facial co-ordination of [L^{3}]$^{-}$ leads to

† The lattice of complex **10** contains two half-weight dichloromethane molecules which leads to a poor solution (R = 10.3%) with high thermal anisotropy. As a consequence little detailed discussion of the structural parameters is included.

Table 2 Seleceted bond lengths (Å) and angles (°) data for complexes **3**, **9**–**11**

	3	**9**	**10**	**11**
Ru–P	2.309(7)	2.258(2)	2.245(4) P(1) 2.253(4) P(2)	2.318(2)
Ru–N	2.108(2)	2.059(5)	2.050(11) N(1) 2.140(10) N(31)	2.066(2)
Ru–O	2.092(2)	2.164(4)	2.090(9)	1.964(6)
Ru–S	2.2960(7) S(1) 2.2976(7) S(2)			2.366(2)
Ru–Cl	2.4232(7)		2.478(4)	2.443(2) Cl(1) 2.366(3) Cl(2)
C=N	1.305(3)	1.303(8)	1.303(8)	1.304(11)
S=O	1.479(2) S(1) 1.477(2) S(2)			1.478(6)
P–Ru–N	83.12(6)	89.7(2) 94.7(2) N(A)	84.0(4) P(1)N(1) 101.0(3) P(1)N(31) 100.0(3) P(2)N(1) 85.5(3) P(2)N(31)	79.0(2)
P–Ru–O	173.18(6)	162.8(2) 98.7(2) O(A)	174.4(3) P(1) 88.9(3) P(2)	98.5(2)
N–Ru–O	90.16(8)	79.8(2)	92.4(4) N(1) 82.3(4) N(31)	87.9(3)
P–Ru–Cl	95.07(2)		90.95(13) P(1) 169.15(13) P(2)	171.42(9) Cl(1) 86.65(9) Cl(2)
N–Ru–Cl	85.20(6)		89.0(3) N(1) 86.9(3) N(31)	95.1(2) Cl(1) 91.0(2) Cl(2)
P–Ru–S	93.84(2) S(1) 99.41(2) S(2)			95.57(8)
Cl–Ru–S	168.62(3) S(1) 88.32(2) S(2)			90.99(8) Cl(1) 95.61(9) Cl(2) 95.16(9) Cl(2)
Cl–Ru–O	83.11(6)		84.7(3)	87.4(2) Cl(1) 174.4(2) Cl(2)
N–Ru–N(A)		173.4(3)	173.6(5)	
P–Ru–P(A)		95.65(8)	95.96(13)	
O–Ru–O(A)		69.0(3)		
Cl–Ru–Cl				87.22(9)

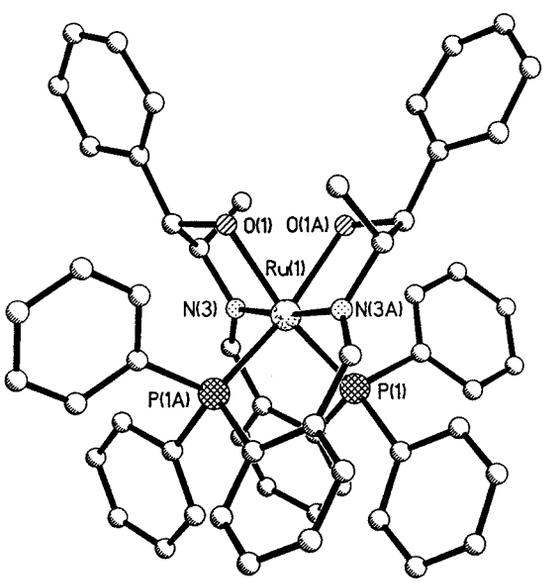


Fig. 2 The molecular structure of complex **9**.

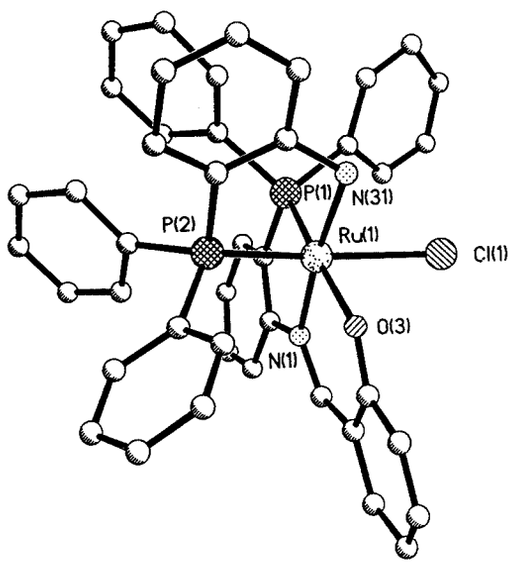


Fig. 3 The molecular structure of complex **10**.

an angle P–Ru–N of 79.0(2)° and an angle N–Ru–O of 87.9(3)°, both of which are compressed with respect to the values for meridional co-ordination of the same ligand. The bond lengths Ru–O and Ru–N are both less for **11** than **3**, the Ru–P bond length slightly longer, changes which may be associated with either the change in formal oxidation state or the change in geometry.

The structure of complex **9** has a twofold axis of symmetry running through the ruthenium centre, and as a consequence of the bis meridional configuration the two phosphorus donors and the two oxygen donors are *cis*, the two nitrogen donors *trans*. The angle P–Ru–N within a ligand unit is 89.7(2)° and N–Ru–O 79.8(2)° as the former is now a six membered ring and the latter a five membered ring. The angle P–Ru–O within a ligand is 162.8(2)°, smaller than the value for the analogous angle in **3**, 173.18(6)°. The angle between the two oxygen donors in **9** is very much compressed at 69.0(3)° which suggests that there is very little steric congestion in this part of the complex despite the oxygens being secondary alkoxides.

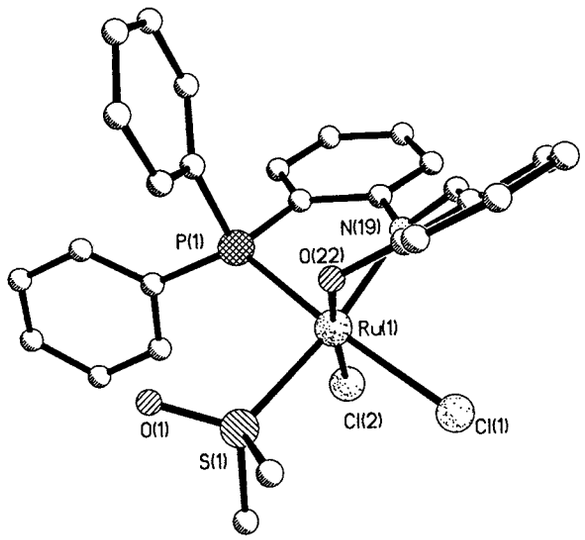


Fig. 4 The molecular structure of complex **11**.

Conclusion

The tridentate ligands $HL^{1–8}$ react with $[Ru^{II}Cl_2(dmso)_4]$ to form a series of complexes of general formula *cis*-$[Ru^{II}Cl(\eta^3\text{-}L^{1–8})(dmso)_2]$. These complexes are liable to further substitution, as shown by the exchange of the two solvent ligands for a chelating ligand in **10**, and their applications in homogeneous catalysis are currently under investigation.

Experimental

Ligand syntheses and complexation reactions were performed under an atmosphere of oxygen-free nitrogen; thf and dichloromethane were distilled under nitrogen from sodium–benzophenone and calcium hydride respectively, and all other solvents were analytical grade and used without further purification. The compounds $[Ru^{II}Cl_2(dmso)_4]$[17] and 2-(diphenylphosphino)aniline[18] were prepared by literature methods, 2-(diphenylphosphino)benzaldehyde, 1*S*,2*R*-norephedrine (HL^1), 2-aminophenol and substituted salicylaldehydes were commercial (Aldrich) and used as received. The ^1H (250.13 MHz) and $^{31}P\text{-}\{^1H\}$ (36.21 MHz) NMR spectra were recorded on Bruker AM250 and JEOL FX-90Q NMR spectrometers as $CDCl_3$ solutions, and are referenced to external tetramethylsilane (δ 0) and 85% phosphoric acid (δ 0) respectively using the high-frequency positive convention. Infrared spectra (pressed KBr discs) were recorded on a Perkin-Elmer System 2000 NIR FT-Raman spectrometer. Elemental analyses (Perkin-Elmer 2400 CHN elemental analyser) were performed by the Loughborough University Analytical Service. Some of the microanalytical results for complexes fall outside the range which is normally acceptable, and repeated analyses of single samples did not give consistent results. It is our contention that the presence of the solvent dmso molecules, along with other fugitive lattice solvents (as seen in the structures of **9**–**11**), leads to somewhat variable and non-stoichiometric samples. The values reported are from freshly prepared samples.

Ligand syntheses

Ligands $HL^{1–3}$ were prepared according to published procedures.[11,12] The preparation of $HL^{4–8}$ was by a general method, given here for HL^4.

2-(2-$Ph_2PC_6H_4$N=CH)-5-$NO_2C_6H_3$OH HL^4. A thf solution (30 cm^3) of 2-(diphenylphosphino)aniline (0.7 g, 2.5 mmol) and 5-nitrosalicylaldehyde (0.45 g, 2.7 mmol) was heated at reflux for 12 h, during which time the solution became orange. The solvent was removed *in vacuo* and the solid product obtained recrystallised from chloroform–diethyl ether as 0.61 g of pale yellow crystals. Yield 53%. Found (Calc. for $C_{25}H_{19}N_2O_3P$): C, 70.2 (70.4); H, 4.6 (4.5); N, 6.4 (6.6)%. $\delta(^1H)$ 12.47 (1 H, br, OH), 8.19 (1 H, s, CH=N) and 7.50–6.80 (17 H, m, aryl). The following ligands were all prepared under the same conditions and on the same scale. 2-(2-$Ph_2PC_6H_4$N=CH)-5-ClC_6H_3OH HL^5: yield 62%. Found (Calc. for $C_{25}H_{19}ClNOP$): C, 72.1 (72.3); H, 4.6 (4.6); N, 3.3 (3.4)%. $\delta(^1H)$ 12.44 (1 H, br, OH), 8.27 (1 H, s, CH=N) and 7.49–6.75 (17 H, m, aryl). 2-(2-$Ph_2PC_6H_4$N=CH)-5-BrC_6H_3OH HL^6: yield 74%. Found (Calc. for $C_{25}H_{19}BrNOP$): C, 64.9 (65.2); H, 4.3 (4.2); N, 3.1 (3.0)%. $\delta(^1H)$ 12.47 (1 H, br, OH), 8.27 (1 H, s, CH=N) and 7.70–6.47 (17 H, m, aryl). 2-(2-$Ph_2PC_6H_4$N=CH)-5-$(CH_3O)C_6H_3$OH HL^7: yield 42%. Found (Calc. for $C_{26}H_{22}NO_2P$): C, 76.2 (75.9); H, 5.4 (5.4); N, 3.3 (3.4)%. $\delta(^1H)$ 11.99 (1 H, br, OH), 8.33 (1 H, s, CH=N), 7.70–6.60 (17 H, m, aryl) and 3.89 (3 H, s, OCH_3). 2-(2-$Ph_2PC_6H_4$N=CH)-3-$(CH_3O)C_6H_3$OH HL^8: yield 52%. Found (Calc. for $C_{26}H_{22}NO_2P$): C, 76.1 (75.9); H, 5.5 (5.4); N, 3.3 (3.4)%. $\delta(^1H)$ 12.81 (1 H, br, OH), 8.36 (1 H, s, CH=N), 7.44–6.39 (17 H, m, aryl) and 3.72 (3 H, s, OCH_3).

Metal complexes 1–9

The preparation of complexes **1**–**8** was by a general method, given here for **1**.

***cis*-$[Ru^{II}Cl(\eta^3\text{-}L^1)(dmso)_2]$ 1.** To a suspension of $[Ru^{II}Cl_2(dmso)_4]$ (0.20 g, 0.40 mmol) in 20 cm^3 of thf was added HL^1 (0.175 g, 0.41 mmol) as a solid. The mixture became deep red almost immediately and was heated under reflux for four hours. The solution was cooled to room temperature before removal of the solvent on a rotary evaporator. The deep red-orange residue was dissolved in the minimum volume of chloroform (1 cm^3) and filtered through a Celite pad before addition of 10 cm^3 of diethyl ether. The solid produced was collected by filtration, washed with 5 cm^3 of diethyl ether and dried *in vacuo*. Yield 0.21 g, 77%. $\delta(^1H)$ 8.92 (1 H, s, HC=N), 7.90–7.05 (19 H, m, aromatic), 5.78 (1 H, d, *J* 4, HCO), 4.45 (1 H, m, $HCCH_3$), 3.46 (3 H, s, dmso), 3.21 (3 H, s, dmso), 2.73 (3 H, s, dmso), 2.52 (3 H, s, dmso) and 1.32 (3 H, d, *J* 13 Hz, CH_3CH). Complex **2**: yield 0.22 g, 82%. $\delta(^1H)$ 8.98 (1 H, s, HC=N), 8.09–6.29 (18 H, m, aromatic), 3.38 (3 H, s, dmso), 3.10 (3 H, s, dmso), 2.58 (3 H, s, dmso) and 2.49 (3 H, s, dmso). Complex **3**: yield 0.20 g, 75%. $\delta(^1H)$ 8.86 (1 H, s, HC=N), 7.96–6.51 (18 H, m, aromatic), 3.32 (3 H, s, dmso), 3.09 (3 H, s, dmso), 2.56 (3 H, s, dmso) and 2.36 (3 H, s, dmso). Complex **4**: yield 0.17 g, 58%. $\delta(^1H)$ 8.20 (1 H, s, HC=N), 7.70–6.46 (17 H, m, aromatic), 3.26 (3 H, s, dmso), 3.09 (3 H, s, dmso), 2.56 (3 H, s, dmso) and 2.36 (3 H, s, dmso). Complex **5**: yield 0.16 g, 56%. $\delta(^1H)$ 8.75 (1 H, s, HC=N), 8.00–6.49 (17 H, m, aromatic), 3.25 (3 H, s, dmso), 3.07 (3 H, s, dmso), 2.54 (3 H, s, dmso) and 2.44 (3 H, s, dmso). Complex **6**: yield 0.26 g, 86%. $\delta(^1H)$ 8.76 (1 H, s, HC=N), 8.10–6.44 (17 H, m, aromatic), 3.30 (3 H, s, dmso), 3.07 (3 H, s, dmso), 2.69 (3 H, s, dmso) and 2.48 (3 H, s, dmso). Complex **7**: yield 0.19 g, 67%. $\delta(^1H)$ 8.78 (1 H, s, HC=N), 8.10–6.48 (17 H, m, aromatic), 3.74 (3 H, s, OCH_3), 3.28 (3 H, s, dmso), 3.07 (3 H, s, dmso), 2.58 (3 H, s, dmso) and 2.48 (3 H, s, dmso). Complex **8**: yield 0.18 g, 63%. $\delta(^1H)$ 8.85 (1 H, s, HC=N), 8.20–6.80 (17 H, m, aromatic), 3.76 (3 H, s, OCH_3), 3.31 (3 H, s, dmso), 3.07 (3 H, s, dmso), 2.58 (3 H, s, dmso) and 2.50 (3 H, s, dmso).

***mer*-$[Ru^{II}(\eta^3\text{-}L^1)_2]$ 9.** To a suspension of $[Ru^{II}Cl_2(dmso)_4]$ (0.20 g, 0.4 mmol) in 20 cm^3 of thf was added HL^1 (0.347 g, 0.82 mmol) as a solid. The mixture became deep red-brown almost immediately and was heated under reflux for four hours. The solution was cooled to room temperature before removal of the solvent on a rotary evaporator. The deep brown residue was dissolved in the minimum volume of chloroform (1 cm^3) and filtered through a Celite pad before addition of 10 cm^3 of diethyl ether. The solid produced was collected by filtration,

Table 3 Details of the X-ray data collections and refinements for compounds **3**, **9**–**11**

	3	**9**	**10**	**11**
Formula	$C_{29}H_{31}ClNO_3PRuS_2$	$C_{56}H_{50}N_2O_2P_2Ru\cdot 2H_2O\cdot 0.2CH_2Cl_2$	$C_{43}H_{33}ClN_2OP_2Ru\cdot CH_2Cl_2$	$C_{27}H_{25}Cl_2NO_2PRuS\cdot CHCl_3$
M	673.16	999.01	877.10	749.85
System	Triclinic	Trigonal	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P3_121$	$P2_1/n$	$P\bar{1}$
a/Å	9.5381(2)	19.9054(1)	13.4070(6)	9.7225(2)
b/Å	12.0818(2)	19.9054(1)	15.4418(5)	10.499(2)
c/Å	13.0204(2)	12.0417(1)	20.7336(9)	16.2582(4)
α/°	76.46(1)			107.859(1)
β/°	82.001(1)		97.480(1)	90.136(1)
γ/°	80.014(1)			98.515(1)
V/Å^3	1429.02(4)	4132.00(5)	4255.9(3)	1555.86(6)
Z	2	3	4	2
μ/mm^{-1}	0.876	0.405	0.667	1.079
Data	88.02	18400	25719	7899
Unique data	6386	3970	9965	4406
R_{int}	0.0292	0.0483	0.2295	0.0408
$R1[I > 2\sigma(I)]$	0.0308	0.0493	0.1032	0.0685
$wR2$	0.0765	0.1281	0.2259	0.1522
Absolute structure parameter	—	0.01(6)	—	—

washed with 5 cm^3 of diethyl ether and dried *in vacuo*. Yield 0.21 g, 77%. δ(^{1}H) 8.94 (2 H, s, HC=N), 7.90–6.95 (38 H, m, aromatic), 5.85 (2 H, d, *J* 4, HCO), 4.46 (2 H, m, *H*CCH$_3$) and 1.25 (6 H, d, *J* 12 Hz, C*H*$_3$CH).

***mer*-[Ru^{II}Cl(η^3-L^2){Ph$_2$P(C$_6$H$_4$NH$_2$-2)-*P*,*N*}] 10.** To a suspension of [Ru^{II}Cl$_2$(dmso)$_4$] (0.20 g, 0.4 mmol) in 20 cm^3 of thf was added HL^2 (0.308 g, 0.81 mmol) as a solid. The mixture became deep brown almost immediately and was heated under reflux for four hours. The solution was cooled to room temperature before removal of the solvent on a rotary evaporator. The deep brown-purple residue was dissolved in the minimum volume of chloroform (1 cm^3) and filtered through a Celite pad before addition of 10 cm^3 of diethyl ether. The solid produced was collected by filtration, washed with 5 cm^3 of diethyl ether and dried *in vacuo*. The ^{31}P-{^{1}H} NMR spectrum indicated that the major product from this reaction was identical with **3**, but a small amount (*ca*. 5% by integration) of a second species was detected. Attempts to separate this product by fractional crystallisation gave several crystals of **10** suitable for X-ray analysis. δ(^{1}H) 8.88 (1 H, s, HC=N) and 8.09–6.25 (32 H, m, aromatic).

Crystal structure determination

The crystal structures of were determined at 298 K using a Siemens SMART diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The crystal data, a summary of the data collections and the structure refinements are given in Table 3. All structures were solved by direct methods and all of the non-hydrogen atoms refined with anisotropic displacement parameters; the hydrogen atoms bound to carbon were included in calculated positions (C–H 0.95 Å) with a fixed isotropic displacement parameter. Structural refinements were by full-matrix least-squares methods on F^2; calculations were performed using the program SHELXTL PC.[19]

CCDC reference number 186/1580.

See http:///www.rsc.org/suppdata/dt/1999/2917/ for crystallographic files in .cif format.

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