Complexes of $Rh(C_5Me_5)$ with Picolinic Acid, Pyrones and Pyridinones†

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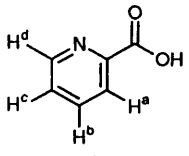
Picolinic acid (pyridine-2-carboxylic acid), pyrones and pyridinones (HL) reacted with $[\{Rh(C_5Me_5)Cl_2\}_2]$ and sodium methoxide to give complexes $[Rh(C_5Me_5)Cl(L)]$ which are all soluble in water. The structures where HL = picolinic acid or 2-methylpyran-4-one have been determined by X-ray diffraction. The aquation of the complexes when dissolved in water has been examined by NMR spectroscopy and conductivity measurements and the results indicate an equilibrium between chloro and aqua species which is fast on the NMR time-scale.

Bioorganometallic chemistry is an area which has attracted increasing attention in the last few years. Metal carbonyl complexes with biomolecules have applications in biochemical analysis and in probing the structure of hormone receptors.[1] In many cases biological ligands can confer water solubility on organometallic species and the resulting complexes may find applications in catalysis in aqueous media. In addition many naturally occurring ligands are readily available in an enantiomerically pure form *e.g.* amino acids, and complexes of them may have applications in asymmetric synthesis. There has been a lot of interest recently in the reactions of the chloro-bridged dimers $[\{M(C_5Me_5)Cl_2\}_2]$ (M = Rh or Ir) with biologically important molecules such as amino acids,[2,3] peptides,[4,5] and nucleosides or their analogues.[6,7] Similar reactions are possible with the isoelectronic $[\{Ru(arene)Cl_2\}_2]$ dimers.[2,5,8–12] Picolinic acid (pyridine-2-carboxylic acid, HL^1) is an analogue of amino acids and pyrones and pyridinones have found applications in medicinal chemistry.[13,14] We have recently reported the reactions of such compounds with $[\{Ru(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)Cl_2\}_2]$.[15] In this paper we report the reactions of $[\{Rh(C_5Me_5)Cl_2\}_2]$ with picolinic acid and some pyrones and pyridinones, and the crystal structures of some of the products.

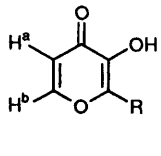
Results and Discussion

Refluxing the ligands HL^{1-5} and 1 equivalent of sodium methoxide with $[\{Rh(C_5Me_5)Cl_2\}_2]$ in methanol gives good yields of complexes $[Rh(C_5Me_5)Cl(L)]$ **1–5** (L = L^1–L^5) in which the ligands are bidentate. Complex **1** contains an N,O chelate whilst **2–5** have O,O chelating ligands. Analogous amino acidate (aa) complexes $[Rh(C_5Me_5)Cl(aa)]$ have been made previously.[2,3] Complex **1** can be separated from the sodium chloride by-product by recrystallization from methanol–water solution, whilst **2–5** can be dissolved in dichloromethane. Complexes **2–5** are also soluble in water.

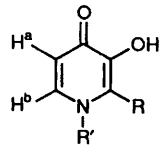
The complexes have all been characterized by microanalysis, ^1H NMR and mass spectroscopy (Table 1). All the ^1H NMR spectra show signals due to the C_5Me_5 as well as the ligand L. For **2–5** the alkene protons (H^a and H^b) are observed as two doublets between δ 6.1 and 8.0 with mutual couplings of *ca.* 5–7 Hz. Since the ligands are all unsymmetrical the rhodium atom in each complex is a chiral centre and the complexes exist as a racemic mixture of two enantiomers. This is confirmed in the crystal structures of **1** and **2** (see below). The chirality at rhodium is particularly noticeable in the NMR spectra of complexes **3** and **5** which contain an ethyl group. In these cases the two protons of the CH_2 are necessarily inequivalent and the ethyl group is observed as an ABX_3 spin system, the AB portion of which is slightly second order.



HL^1



HL^2 R = Me
HL^3 R = Et



HL^4 R = Me, R' = Me
HL^5 R = Et, R' = H

The aquation of the complexes has been studied by ^1H NMR spectroscopy in D_2O. Replacement of chloride by water has been observed for the corresponding ruthenium complexes $[Ru(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)Cl(L)]$,[15] and the related species $[Ru(arene)Cl(aa)]$[3,10] and $[Rh(C_5Me_5)Cl(aa)]$.[3] The ^1H NMR spectrum of complex **1** in D_2O shows a sharp signal for the C_5Me_5 at δ 1.69 but the signals for the picolinate are rather broad, particularly that at δ 8.86. Addition of LiCl leads to these latter signals becoming much sharper, that at δ 8.86 being a well resolved doublet as expected. Addition of 1 equivalent of $AgNO_3$ to **1** in D_2O leads to complete conversion into the aqua species. The ^1H NMR spectrum shows the same pattern as that of the chloride complex but with all the signals shifted downfield slightly. In particular, the low-field doublet is observed at δ 9.01, a downfield shift of 0.15 ppm. Thus, the initial broad spectrum of **1** in D_2O can be explained in terms of the equilibrium between co-ordinated water and chloride for which the rate of interconversion is comparable with the NMR time-scale. This rate is much faster than for the corresponding $[Ru(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)Cl(L^1)]$ complex for which both the chloro and aqua species can be observed simultaneously with sharp resonances for each species.[15] The rates of anation and water exchange for comparable $(C_5Me_5)Rh$ and (arene)Ru systems have recently been investigated and the rhodium complexes have been shown to have rate constants which are 10^4 times larger.[16]

The ^1H NMR spectra of complexes **2–5** in D_2O show one set of sharp signals. Addition of LiCl has no noticeable effect on the spectra. Addition of $AgBF_4$ leads to precipitation of AgCl but there is very little change in the peak positions in the ^1H NMR spectrum though the solubility of the complex decreases.

† Bioorganometallic Chemistry. Part 1.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Analytical and spectroscopic data for the new compounds

Compound	^{1}H NMR[a] (δ, *J*/Hz)	Analysis[b] (%) C	H	N	Mass[c]
1	1.69 (15 H, s, C_5Me_5), 7.89 (1 H, t, 6, H^c), 8.03 (1 H, d, 7, H^a), 8.19 (1 H, t, 7, H^b), 8.86 (1 H, d, 5, H^d)[e]	45.90 (45.55)	4.70 (4.85)	3.35 (3.55)	396,[d] 360
	1.72 (15 H, s, C_5Me_5), 7.93 (1 H, t, 7, H^c), 8.08 (1 H, d, 8, H^a), 8.25 (1 H, t, 8, H^b), 9.01 (1 H, d, 5, H^d)[f]				
2	1.72 (15 H, s, C_5Me_5), 2.41 (3 H, s, Me), 6.46 (1 H, d, 5, H^a), 7.55 (1 H, d, 5, H^b)	48.10 (48.20)	5.10 (5.05)		399,[d] 363
3[g]	1.21 (3 H, t, 7.5, CH_2CH_3), 1.72 (15 H, s, C_5Me_5), 2.76 (1 H, m, CHH^1), 2.95 (1 H, m, CHH^1), 6.46 (1 H, d, 5, H^a), 7.58 (1 H, d, 5, H^a)	48.25 (48.40)	5.65 (5.50)		412, 377
4[g]	1.72 (15 H, s, C_5Me_5), 2.39 (3 H, s, Me), 3.58 (3 H, s, NMe), 6.33 (1 H, d, 7, H^a), 6.91 (1 H, d, 7, H^b)	48.30 (48.55)	6.10 (5.75)	3.05 (3.35)	411, 376
5[h]	1.10 (3 H, t, 7.5, CH_2CH_3), 1.67 (15 H, s, C_5Me_5), 2.53 (2 H, m, CH_2), 6.20 (1 H, d, 6, H^a), 7.00 (1 H, d, 6, H^b), 10.65 (1 H, br, NH)	44.85 (45.60)	6.05 (6.05)	3.15 (3.15)	411, 376

[a] In $CDCl_3$. [b] Calculated values are given in parentheses. [c] *m/z* values for $[M]^+$ and $[M - Cl]^+$. [d] $[M + H]^+$ observed rather than $[M]^+$. [e] In D_2O with added LiCl. [f] In D_2O with added $AgNO_3$. [g] Includes half a molecule of H_2O. [h] Includes two molecules of H_2O.

Addition of LiCl to this sample caused a return to the original chemical shifts, however the resolution and signal-to-noise ratio in this spectrum were not very good. A possible explanation of these observations is that once the complexes are dissolved in water the chloride is displaced from the co-ordination sphere. Indeed we put forward this explanation for similar observations on an areneruthenium complex of L^3.[15] An alternative explanation is that both species, chloro or aqua, are present but that they interconvert quickly on the NMR time-scale and hence only an averaged set of signals is observed. We have investigated this possibility by carrying out conductivity measurements on complex **3** in aqueous solution. The complex is conducting ($\Lambda°_m$ 101.4 S cm^2 mol^{-1}) which corresponds to a degree of dissociation of 0.80 for a 10 mmol solution. In the light of this result the conductivity was measured of the corresponding areneruthenium complex [Ru(η-$C_6H_3Me_3$-1,3,5)Cl(L^3)], which we had previously thought was completely dissociated,[15] and found that it too is only partly dissociated (α = 0.49). Thus, the observation of only one species in the NMR spectrum implies a fast rate of exchange between co-ordinated chloride and water even in the areneruthenium case which is expected to be much slower than with the corresponding (C_5Me_5)Rh complex.[16] As a further check we have measured the conductivity of [Ru(η-$C_6H_3Me_3$-1,3,5)Cl(L^1)],[15] for which both the aqua and chloro species give sharp signals in the NMR spectrum, and this has a degree of dissociation of 0.68 for a 10 mmol solution which agrees well with the ratio from the NMR spectrum.

A further feature of the spectra of complexes **3** and **5** in D_2O, or CD_3OD, is that in each case the CH_2 group is observed as a simple quartet, whilst in $CDCl_3$ the two protons form the AB part of an ABX_3 spin system (see above). This suggests that either the two protons are accidentally equivalent or that a fluxional process is occurring which makes them equivalent on the NMR time-scale. A study of the NMR spectrum of **3** in CD_3OD at low temperature shows that the latter is indeed the case (Fig. 1). On cooling to −45 °C the quartet has split into two overlapping multiplets which can be analysed as the AB part of an ABX_3 system. This fluxional process involves exchange of a ligand (water, methanol or chloride) at the rhodium occurring with net inversion of configuration at the rhodium. This may in principle occur *via* an associative or dissociative mechanism though water exchange of related complexes has been shown to be dissociative in nature.[16] Either way a symmetrical transition state is possible in which the two CH_2 protons are equivalent (Scheme 1). This is an example

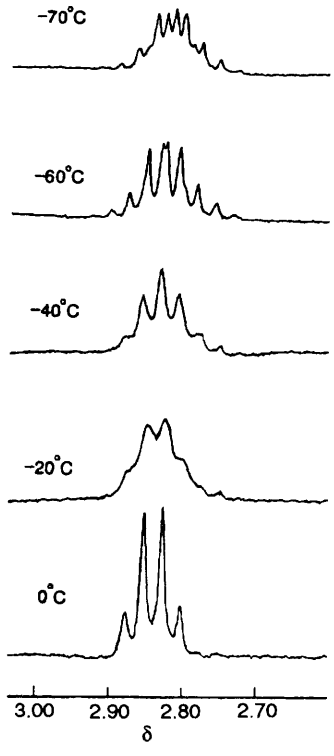
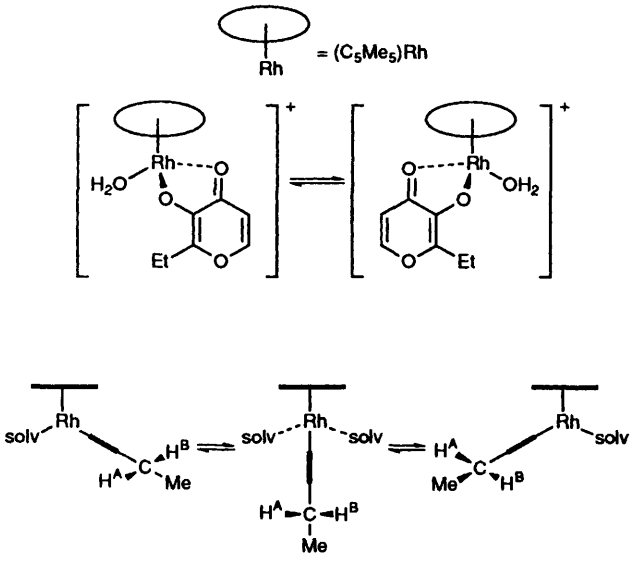


Fig. 1 Variable-temperature NMR spectra in the CH_2 region of complex **3**

where a prochiral ligand can be used to investigate racemization at an adjacent metal centre. Details of the rate of exchange and the application of this strategy to other systems will be reported elsewhere.

We have determined the structures of complexes **1** and **2** (Figs. 2 and 3), and selected bond lengths and angles are listed in Table 2 with the fractional atomic coordinates in Tables 3 and 4. In both complexes the geometry around the rhodium atom can be described as pseudo-octahedral with a η-C_5Me_5 group occupying three *fac* co-ordination sites. The metal co-ordination sphere is completed by a chlorine atom and a bidentate ligand. In each case the complex is chiral at rhodium and both enantiomers are present in the unit cell. For complex **1** the Rh–Cl, Rh–N and Rh–O bond lengths 2.404(1), 2.117(3)



Scheme 1 Proposed mechanism of fluxionality for complex **3**. solv = Solvent, D_2O or possibly CD_3OD

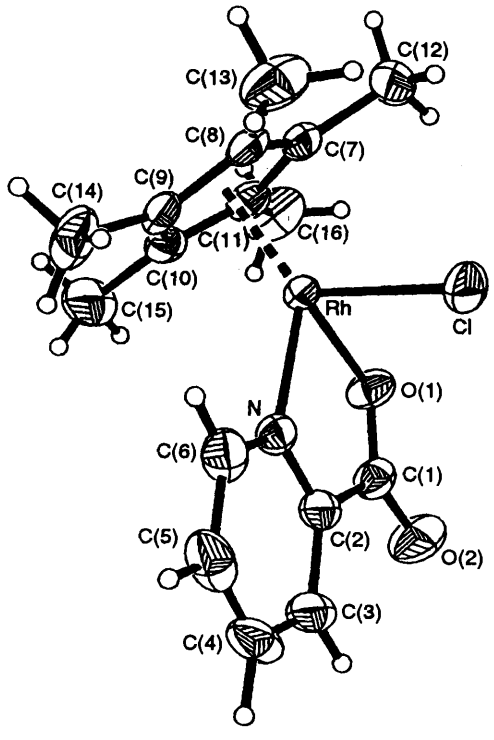


Fig. 2 Molecular structure of $[Rh(C_5Me_5)Cl(L^1)]$ **1** showing 50% probability displacement ellipsoids for non-H atoms

and 2.108(2) Å respectively are very similar to those of a related amino acidate complex $[Rh(C_5Me_5)Cl(L)]$ (L = azetidine-2-carboxylate) 2.403(2), 2.103(5) and 2.105(5) Å (average for two diastereomers).[2] The chelate bite angle is 77.7(1)° which is the same as that, 77.9(2)°, in the corresponding complex $[Ru(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)Cl(L^1)]$.[15] In complex **2** two independent molecules are found in the unit cell. They have slightly different Rh–Cl bond distances, 2.409(2) and 2.388(1) Å respectively. The Rh–O(1) and Rh–O(2) distances in molecule 1 are the same [2.116(3) and 2.118(5) Å], whilst in molecule 2 they are significantly different from each other, 2.111(4) and 2.133(5) Å respectively. The O–Rh–O angles are 78.3(2) and 78.8(2)° which are similar to the N–Rh–O angle in the picolinate complex **1** described above.

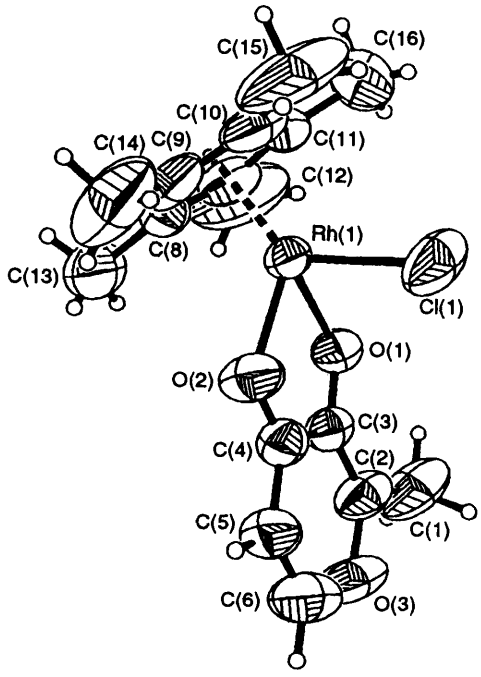


Fig. 3 Molecular structure of $[Rh(C_5Me_5)Cl(L^2)]$ **2** showing 50% probability displacement ellipsoids for non-H atoms

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

Complex **1**			
Rh–Cl	2.404(1)	Rh–C(7)	2.141(3)
Rh–O(1)	2.108(2)	Rh–C(8)	2.145(3)
Rh–N	2.117(3)	Rh–C(9)	2.154(3)
C(1)–O(1)	1.283(4)	Rh–C(10)	2.152(3)
O(2)–C(1)	1.231(4)	Rh–C(11)	2.162(3)
Cl–Rh–N	85.9(1)	Cl–Rh–O(1)	87.8(1)
N–Rh–O(1)	77.7(1)	O(1)–C(1)–O(2)	124.5(3)
O(1)–C(1)–C(2)	115.8(3)	C(1)–C(2)–N	116.1(3)
Complex **2**			
Molecule 1		Molecule 2	
Rh(1)–Cl(1)	2.409(2)	Rh(1A)–Cl(1A)	2.388(1)
Rh(1)–O(1)	2.116(3)	Rh(1A)–O(1A)	2.111(4)
Rh(1)–O(2)	2.118(5)	Rh(1A)–O(2A)	2.133(5)
O(1)–C(3)	1.326(7)	O(1A)–C(3A)	1.363(8)
O(2)–C(4)	1.250(6)	O(2A)–C(4A)	1.254(7)
Rh(1)–C(7)	2.114(7)	Rh(1A)–C(7A)	2.114(7)
Rh(1)–C(8)	2.093(6)	Rh(1A)–C(8A)	2.104(9)
Rh(1)–C(9)	2.114(8)	Rh(1A)–C(9A)	2.095(5)
Rh(1)–C(10)	2.109(6)	Rh(1A)–C(10A)	2.110(6)
Rh(1)–C(11)	2.108(7)	Rh(1A)–C(11A)	2.148(6)
O(1)–Rh(1)–O(2)	78.3(2)	O(1A)–Rh(1A)–O(2A)	78.8(2)
Cl(1)–Rh(1)–O(1)	87.7(1)	Cl(1A)–Rh(1A)–O(1A)	86.7(1)
Cl(1)–Rh(1)–O(2)	88.2(1)	Cl(1A)–Rh(1A)–O(2A)	87.4(1)
O(1)–C(3)–C(4)	117.5(4)	O(1A)–C(3A)–C(4A)	121.3(5)
O(2)–C(4)–C(3)	120.1(6)	O(2A)–C(4A)–C(3A)	118.7(6)

Experimental

Light petroleum (b.p. 40–60 °C) and diethyl ether were dried by refluxing over purple sodium–benzophenone under nitrogen, whilst dichloromethane was purified by refluxing over calcium hydride. The compounds HL^4 and HL^5 were prepared using literature procedures[17] or analogous methods as was $[\{Rh(C_5Me_5)Cl_2\}_2]$.[18] The reactions described were carried out in deoxygenated solvents under nitrogen; however, once isolated as pure solids, the compounds are relatively air-stable and no precautions for their storage are necessary.

Proton NMR spectra were recorded on a Bruker AM300 or a Varian EM390 spectrometer. Microanalyses were performed by Butterworth Laboratories Ltd., Middlesex. The FAB mass spectra were recorded on a Kratos Concept mass spectrometer using a 3-nitrobenzyl alcohol matrix. Conductivity measurements were obtained using a Solex model 4070 conductivity meter, over a range of concentration from 10 to 0.2 mmol dm^{-3}. From these data the dissociation constant, limiting molar conductivities and degree of ionization were obtained using the method developed by Fuoss and Krauss.[19]

Preparations.—$[Rh(C_5Me_5)Cl(L^1)]$ **1**. A mixture of $[\{Rh(C_5Me_5)Cl_2\}_2]$ (50 mg, 0.08 mmol), sodium methoxide (9 mg, 0.16 mmol) and HL^1 (20 mg, 0.16 mmol) in methanol (30 cm^3) was refluxed for 3 h to provide a red solution. The solution was filtered and the solvent removed *in vacuo*. The solid was recrystallized from methanol–water to provide red crystals of complex **1** (52 mg, 81%).

$[Rh(C_5Me_5)Cl(L^2)]$ **2**. A mixture of $[\{Rh(C_5Me_5)Cl_2\}_2]$ (50 mg, 0.08 mmol), sodium methoxide (9 mg, 0.17 mmol) and HL^2 (21 mg, 0.17 mmol) in methanol (20 cm^3) was refluxed for 3 h to provide a red solution. The solvent was removed and the resultant solid extracted with dichloromethane; this solution was then filtered through Celite and evaporated to dryness. The solid was recrystallized from dichloromethane–light petroleum to provide complex **2** as a red microcrystalline solid (61 mg, 90%).

The complexes $[Rh(C_5Me_5)Cl(L)]$ (L = L^3 **3**, L^4 **4** or L^5 **5**) were prepared in the same way as **2** using $[\{Rh(C_5Me_5)Cl_2\}_2]$ (50 mg, 0.08 mmol) as a red solid (63 mg, 96%), a red microcrystalline solid (59 mg, 90%) and a red solid (46 mg, 70%) after recrystallization from dichloromethane–light petroleum, dichloromethane–diethyl ether and dichloromethane–diethyl ether respectively.

Crystallography.—Crystals of complex **1** were grown from the NMR sample in D_2O, whilst slow evaporation of a dichloromethane–light petroleum mixture gave suitable crystals of **2** as the hemihydrate.

Complex **1**. *Crystal data.* $C_{16}H_{19}ClNO_2Rh$, M = 395.7, orthorhombic, space group *Pbca*, a = 14.356(1), b = 14.504(1), c = 14.908(1) Å, U = 3104.2(3) $Å^3$ (by least-squares refinement of diffractometer angles for 31 central reflections with $5.2 < \theta < 12.5°$), λ(Mo-Kα) = 0.7107 Å, Z = 8, D_c = 1.693 g cm^{-3}, $F(000)$ = 1600, red prisms, crystal size 0.4 × 0.17 × 0.17 mm, μ(Mo-Kα) = 1.275 mm^{-1}.

Data collection and processing. Siemens P4 diffractometer, ω mode with ω scan width = 1.0 + $\delta\lambda$ splitting, ω scan speed 3.0–30.0° min^{-1}; 4237 reflections measured ($4.0 \leqslant 2\theta \leqslant 54°$, $-1 \leqslant h \leqslant 18$, $-1 \leqslant k \leqslant 18$, $-1 \leqslant l \leqslant 18$), 3393 independent reflections [merging R_{int} = 0.019 (after semiempirical absorption correction, maximum, minimum transmission factors = 0.795, 0.685)], giving 2732 with $F > 4\sigma(F)$.

Structure analysis and refinement. Direct methods. Full-matrix least-squares refinement using the program package SHELXTL PC[20] with all non-hydrogen atoms anisotropic and hydrogens in calculated positions with one overall fixed U_{iso} (= 0.08 $Å^2$). The weighting scheme $w = 1/[\sigma^2(F) + 0.0008F^2]$ gave final values of R = 0.0309 and R' = 0.0426.

Complex **2**. *Crystal data.* $C_{16}H_{20}ClO_3Rh \cdot 0.5H_2O$, M = 407.7, triclinic, space group $P\bar{1}$, a = 7.695(1), b = 15.791(2), c = 16.205(2) Å, α = 62.36(1), β = 83.47(1), γ = 82.14(1)°, U = 1725.4(4) $Å^3$ (by least-squares refinement of diffractometer angles for 37 central reflections with $5.4 < \theta < 12.5°$), λ(Mo-Kα) = 0.7107 Å, Z = 4 (Z = 2 for each unique molecule),

Table 3 Fractional atomic coordinates (× 10^4) for complex **1**

Atom	x	y	z
Rh	960(1)	3227(1)	3201(1)
Cl	874(1)	4813(1)	3661(1)
N	1633(2)	3729(2)	2036(2)
O(1)	−171(2)	3490(2)	2337(2)
O(2)	−561(2)	4134(2)	1035(2)
C(1)	23(2)	3868(2)	1581(2)
C(2)	1039(2)	3982(2)	1379(2)
C(3)	1358(3)	4328(2)	568(2)
C(4)	2316(3)	4421(2)	443(3)
C(5)	2914(3)	4197(2)	1132(3)
C(6)	2550(3)	3857(3)	1927(3)
C(7)	626(2)	2640(2)	4479(2)
C(8)	1622(2)	2752(2)	4406(2)
C(9)	1930(2)	2202(2)	3671(2)
C(10)	1147(3)	1758(2)	3285(2)
C(11)	347(2)	2007(2)	3789(2)
C(12)	14(3)	3081(3)	5163(3)
C(13)	2199(4)	3295(3)	5038(3)
C(14)	2919(3)	2078(3)	3381(3)
C(15)	1189(4)	1057(3)	2542(3)
C(16)	−623(3)	1679(3)	3613(3)

Table 4 Fractional atomic coordinates (× 10^4) for complex **2**

Atom	x	y	z
Rh(1)	4 363(1)	7 211(1)	4 944(1)
Cl(1)	7 238(2)	6 669(2)	5 555(1)
O(1)	5 338(4)	8 543(2)	4 025(2)
O(2)	5 368(5)	6 974(3)	3 788(3)
O(3)	7 903(6)	9 168(4)	1 847(3)
C(1)	7 393(10)	10 104(5)	2 682(5)
C(2)	7 087(7)	9 238(4)	2 632(4)
C(3)	6 186(6)	8 511(4)	3 278(3)
C(4)	6 130(7)	7 665(4)	3 171(4)
C(5)	6 978(8)	7 661(6)	2 346(4)
C(6)	7 795(10)	8 403(7)	1 731(5)
C(7)	1 937(8)	7 787(5)	5 317(5)
C(8)	1 650(7)	7 320(5)	4 829(4)
C(9)	2 266(9)	6 338(5)	5 335(5)
C(10)	3 022(8)	6 233(5)	6 150(5)
C(11)	2 796(8)	7 143(6)	6 124(4)
C(12)	1 423(12)	8 826(6)	5 046(7)
C(13)	756(10)	7 729(9)	3 950(5)
C(14)	2 243(13)	5 553(7)	5 070(8)
C(15)	3 835(11)	5 341(7)	6 882(7)
C(16)	3 364(13)	7 309(10)	6 886(6)
Rh(1A)	10 638(1)	6 829(1)	300(1)
Cl(1A)	7 713(2)	6 457(1)	908(1)
O(1A)	9 654(5)	8 288(3)	−211(3)
O(2A)	9 806(5)	7 131(3)	−1 029(3)
O(3A)	7 230(7)	9 722(4)	−2 289(4)
C(1A)	7 620(12)	10 119(6)	−1 122(7)
C(2A)	7 950(9)	9 434(5)	−1 446(5)
C(3A)	8 875(7)	8 554(4)	−1 021(4)
C(4A)	9 034(7)	7 957(5)	−1 442(4)
C(5A)	8 260(8)	8 294(5)	−2 338(4)
C(6A)	7 414(12)	9 148(8)	−2 700(6)
C(7A)	12 019(9)	6 140(7)	1 535(5)
C(8A)	12 986(9)	6 912(5)	798(7)
C(9A)	13 367(7)	6 669(4)	53(4)
C(10A)	12 710(7)	5 794(4)	326(4)
C(11A)	11 939(9)	5 469(5)	1 218(5)
C(12A)	11 379(14)	6 017(10)	2 489(5)
C(13A)	13 385(14)	7 777(8)	801(11)
C(14A)	14 332(10)	7 242(7)	−821(6)
C(15A)	12 710(10)	5 283(6)	−248(7)
C(16A)	11 142(12)	4 568(6)	1 800(8)
O(4A)	6 580(12)	9 002(7)	5 306(6)

D_c = 1.569 g cm^{-3}, $F(000)$ = 828, red block, crystal size 0.45 × 0.38 × 0.34 mm, μ(Mo-Kα) = 1.154 mm^{-1}.

Data collection and processing. Siemens P4 diffractometer, ω mode with ω scan width = 1.2 + δλ splitting, ω scan speed 4.0–30.0° min^{-1}; 7786 reflections measured ($4.0 \leqslant 2\theta \leqslant 55.0°$, $-1 \leqslant h \leqslant 9$, $-18 \leqslant k \leqslant 18$, $-20 \leqslant l \leqslant 21$), 7232 independent reflections (R_{int} = 0.012), giving 5351 with $F > 4\sigma(F)$.

Structure analysis and refinement. As for complex **1** except as follows. The oxygen atom of the water molecule was refined with isotropic thermal parameters; the hydrogen atoms of the water molecule were located and refined. All other hydrogen atoms were included in calculated positions with one overall fixed U_{iso} (= 0.1 Å^2). The weighting scheme $w = 1/[\sigma^2(F) + 0.0004F^2]$ gave final values of R = 0.0444 and R' = 0.0568.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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