

Synthesis, Characterization and Crystal Structures of some Half-sandwich Ruthenium(II) Complexes of 1,4,7-Trimethyl-1,4,7-triazacyclononane containing π -Acidic Ancillary Ligands†

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The synthesis of a series of ruthenium(II) complexes of 1,4,7-trimethyl-1,4,7-triazacyclononane L of type $[\text{RuL}(\text{X})\text{Y}(\text{Z})]^+$ containing H, O_2CCF_3 , CO, PPh_3 , dppe [1,2-bis(diphenylphosphino)ethane] or 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{N}\equiv\text{C}$ as auxiliary ligands are described where X = Y = CO, Z = Cl **1**; X, Y = dppe, Z = Cl **2**; X, Y = dppe, Z = H **3**; X = CO, Y = PPh_3 , Z = H **4**; X = Y = 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{N}\equiv\text{C}$, Z = O_2CCF_3 **5**. All complexes were characterized by spectroscopic methods. The crystal structures of **1** and **4** as PF_6^- salts have been determined. The two CO groups in complex **1** are in *cis*-fashion with a OC–Ru–CO angle of $90.1(3)^\circ$ and the Ru–C distances are 1.850(6) and 1.893(6) Å. Complex **4** features one of the few ruthenium complexes containing three different piano-stool ligands, namely, CO, PPh_3 and H. The measured Ru–CO and Ru–H distances in **4** are 1.785(9) and 1.54(9) Å respectively.

The co-ordination chemistry of the facially co-ordinating ligand 1,4,7-trimethyl-1,4,7-triazacyclononane L has continued to be an area of immense interest.¹ However, research in the chemistry of ruthenium complexes of L is still in its infancy. Apart from structural interests,^{2–4} some of the metal–L complexes show intriguing reactivities. For example, $[\text{Ru}^{\text{VI}}\text{L}(\text{O})_2(\text{O}_2\text{CCF}_3)]\text{ClO}_4$ ³ and $[\text{Ru}^{\text{IV}}\text{L}(\text{O})(\text{bipy})][\text{ClO}_4]_2$ ⁴ (bipy = 2,2'-bipyridine) are active oxidants for organic oxidation, and $[\text{RhLMe}_3]$ is a catalyst for olefin metathesis.⁵

Recent studies by Che and Yam⁶ have witnessed the rich oxidation chemistry of high-valent ruthenium–oxo complexes of macrocyclic amines. However, studies on the catalytic activities and redox properties of macrocyclic ruthenium amine complexes in low valent states are sparse. This is in contrast to the intensive studies reported on ruthenium(0) and -(II) phosphine and carbonyl complexes, which are commonly employed as homogeneous catalysts for hydrogenation reactions and olefin metathesis reactions. Previously, we reported two air-stable organoruthenium complexes of L, which were prepared from $[\{\text{Ru}(\text{cod})\text{Cl}_2\}_n]$ (cod = cycloocta-1,5-diene).⁷ As part of the continuing program in the quest for organometallic chemistry of ruthenium macrocyclic amine complexes, we herein describe the synthesis and characterization of some Ru–L complexes containing π -acid ligands, *e.g.* CO, isocyanide and phosphine. A novel complex containing different piano-stool ancillary ligands has also been identified by a X-ray crystal analysis.

Experimental

All reactions were performed under a nitrogen atmosphere by using standard Schlenk techniques. All solvents were distilled and degassed before use. Macrocyclic L,⁸ $[\text{RuLCl}_3]$,^{2a} $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ ⁹ and $[\text{RuL}(\text{H}_2\text{O})_2(\text{O}_2\text{CCF}_3)][\text{O}_3\text{SCF}_3]_2$ ³ were synthesized according to literature methods. 1,2-Bis(diphenylphosphino)ethane (dppe), silver trifluorometh-

anesulfonate and SiClMe_3 were used as received. Elemental analyses were conducted in Butterworth Laboratories Ltd. 270 MHz ¹H and ¹³C NMR spectra were run on a JEOL 270 FT-NMR spectrometer with SiMe_4 as internal reference at 298 K. Infrared spectra were taken as Nujol mulls on a Shimadzu IR-408 spectrophotometer. FAB mass spectra were recorded on a Finnigan MAT 95 mass spectrometer using 3-nitrobenzyl alcohol as matrix.

Syntheses.— $[\text{RuL}(\text{CO})_2\text{Cl}]\text{PF}_6$ **1**. The complex $[\text{RuLCl}_3]$ (0.1 g, 0.26 mmol) was dissolved in HCO_2H (10 cm³). The solution was heated to 110 °C for 24 h and then evaporated to give a yellow-orange residue. This was dissolved in water (5 cm³). Upon addition of NH_4PF_6 (1 g), a yellow solid was obtained. Recrystallization by the diffusion of diethyl ether into an acetone solution gave yellow plate crystals. Yield 0.05 g (36%) (Found: C, 24.45; H, 3.90; N, 7.75. Calc. for $\text{C}_{11}\text{H}_{21}\text{ClF}_6\text{N}_3\text{O}_2\text{PRu}$: C, 25.35; H, 4.20; N, 8.30%).

NMR $[(\text{CD}_3)_2\text{CO}]$: ¹H, δ 3.32 (6 H, s, 2 NCH₃) and 3.47 (3 H, s, NCH₃); ¹³C, δ 194 (CO). FAB mass spectrum: *m/z* 364 {Calc. for $[\text{RuL}(\text{CO})_2\text{Cl}]^+$ 364}, 336 {Calc. for $[\text{RuL}(\text{CO})\text{Cl}]^+$ 336} and 307 {Calc. for $[\text{RuLCl}]^+$ 308}. IR (cm⁻¹): 2006s and 2067s [$\nu(\text{C}\equiv\text{O})$].

$[\text{RuL}(\text{dppe})\text{Cl}]\text{O}_3\text{SCF}_3$ **2**. A mixture of $[\text{RuLCl}_3]$ (0.1 g, 0.26 mmol) and $\text{Ag}(\text{O}_3\text{SCF}_3)$ (0.23 g, 0.78 mmol) in tetrahydrofuran (20 cm³) was refluxed for 2 h. This was filtered and zinc powder (1 g) and dppe (0.12 g, 30 mmol) were added to the pale yellow filtrate. The mixture was then refluxed for 18 h. After removal of zinc powder, SiClMe_3 was added to the yellow filtrate which was evaporated to dryness. The yellow residue was chromatographed on an alumina column (Activity I, 90–230 mesh). The yellow band was eluted with acetone. Recrystallization by diffusion of diethyl ether to dichloromethane solution gave a yellow–orange crystalline product. Yield 0.1 g (44%) (Found: C, 50.50; H, 5.15; N, 4.80; Calc. for $\text{C}_{36}\text{H}_{45}\text{ClF}_3\text{N}_3\text{O}_3\text{P}_2\text{RuS}$: C, 50.55; H, 5.30; N, 4.90%). ¹H NMR (CDCl_3); δ 1.97 (3 H, s, NCH₃), 2.22–3.18 (16 H, m, CH₂) and 3.28 (6 H, s, NCH₃). FAB mass spectrum: *m/z* 706 {Calc. for $[\text{RuL}(\text{dppe})\text{Cl}]^+$ 706}, 672 {Calc. for $[\text{RuL}(\text{dppe})]^+$ 672}.

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

Table 1 Experimental data for single-crystal X-ray structure determinations of **1** and **4·H₂O***

| Complex | 1 | 4·H₂O |
|------------------------------------------------------------------------------|------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------|
| Formula | C ₁₁ H ₂₁ ClF ₆ N ₃ O ₂ PRu | C ₂₈ H ₃₇ F ₆ N ₃ OP ₂ Ru·H ₂ O |
| <i>M_r</i> | 508.79 | 726.64 |
| Crystal dimensions/mm | 0.15 × 0.30 × 0.35 | 0.20 × 0.25 × 0.50 |
| <i>a</i> /Å | 7.452(6) | 9.010(2) |
| <i>b</i> /Å | 15.283(9) | 20.610(9) |
| <i>c</i> /Å | 16.336(11) | 19.884(3) |
| β/° | 96.91(7) | 99.53(2) |
| <i>U</i> /Å ³ | 1847.0(22) | 3641(4) |
| <i>D_c</i> /g cm ⁻³ | 1.830 | 1.325 |
| μ/cm ⁻¹ | 11.697 | 5.75 |
| <i>F</i> (000) | 1016 | 1488 |
| <i>T</i> /K | 298 | 298 |
| <i>hkl</i> Ranges | -8 to 7, 0-16, 0-17 | 0-9, 0-22, -21 to 21 |
| Data measured | 2407 | 5326 |
| Data used | 1818 [<i>I</i> ≥ 2 σ(<i>I</i>)] | 3658 [<i>I</i> ≥ 3 σ(<i>I</i>)] |
| Weighting scheme <i>w</i> | 1/σ ² (<i>I</i>) | 4 <i>F_o</i> ² /[σ ² (<i>I</i>) + (0.021 <i>F_o</i>) ²] |
| <i>R</i> , <i>R'</i> | 0.035, 0.027 | 0.060, 0.086 |
| Goodness-of-fit | 1.92 | 3.36 |
| Maximum and minimum residues in final Δ <i>F</i> synthesis/e Å ⁻³ | -0.38, 0.55 | 1.04, -1.01 |
| (Δ/σ) _{max} | 0.0382 | 0.02 |

* Details in common: monoclinic, space group *P*2₁/*n*, *Z* = 4, 2θ_{max} = 45 °C, λ 0.7107 Å.

[RuL(dppe)H]O₃SCF₃ **3**. A mixture of [RuLCl₃] (0.1 g, 0.26 mmol) and AgO₃SCF₃ (0.23 g, 0.78 mmol) in ethanol (30 cm³) was refluxed for 2 h. This was filtered to remove insoluble AgCl. Zinc powder (1 g) and dppe (0.12 g, 30 mmol) were added to the green filtrate and the mixture refluxed for 12 h, after which the zinc powder was filtered off to give a yellow solution. The solvent was removed to give a yellow solid which was then chromatographed on an alumina column (Activity I, 90–230 mesh) with CHCl₃ as eluent. The yellow band was collected and evaporated to give a yellow crystalline product. Yield 0.14 g (65%) (Found: C, 52.35; H, 5.40; N, 5.85. Calc. for C₃₆H₄₆F₃N₃O₃P₂RuS; C, 52.70; H, 5.65; N, 5.10%). IR (cm⁻¹): 2022s [ν(Ru–H)]. ¹H NMR (CDCl₃): δ -16.0 to -16.5 (1 H, br s, Ru–H), 2.44 (3 H, s, NCH₃), 3.07 (6 H, s, NCH₃), 7.33 (6 H, s, phenyl), 7.46 (10 H, s, phenyl) and 8.04 (4 H, s, phenyl). FAB spectrum: *m/z* 672 {Calc. for [¹⁰²RuL(dppe)H]⁺ 672}.

[RuL(CO)(PPh₃)H]PF₆ **4**. A mixture of L (0.1 g, 0.58 mmol) and [RuHCl(CO)(PPh₃)₃] (0.56 g, 0.58 mmol) in 2-methoxyethanol (50 cm³) was refluxed for 18 h. The solution was filtered and concentrated to ca. 10 cm³. Upon addition of NH₄PF₆ (1 g), a white solid was obtained. This was collected on a frit, washed with ethanol, diethyl ether and air-dried. Recrystallization from CHCl₃–diethyl ether gave the product as white needle crystals. Yield 0.25 g (60%) (Found: C, 46.20; H, 5.30; N, 6.65. Calc. for C₂₈H₃₇F₆N₃OP₂Ru; C, 47.45; H, 5.25; N, 5.95%). IR (cm⁻¹): 1927s [ν(C≡O)] and 1967m [ν(Ru–H)]. ¹H NMR (CDCl₃): δ -13.75 (1 H, d, Ru–H, *J*_{RH} = 31 Hz), 2.2, 2.5, 3.3 (each 3 H, s, NCH₃), 7.4–7.6 (9 H, m, phenyl) and 7.61–7.67 (6 H, m, phenyl). FAB spectrum: *m/z* 564 {Calc. for [¹⁰²RuL(CO)(PPh₃)H]⁺ 564}.

[RuL(CNC₆H₃Me₂-2,6)₂(O₂CCF₃)]PF₆ **5**. A mixture of [RuL(H₂O)₂(O₂CCF₃)]₂[O₃SCF₃]₂ (0.1 g, 0.18 mmol), 2,6-dimethylphenyl isocyanide (0.05 g, 0.38 mmol) and zinc amalgam (1 g) in acetone (15 cm³) was stirred under an argon atmosphere for 18 h. The solution was filtered and concentrated to ca. 5 cm³ and a saturated aqueous solution (2 cm³) of NH₄PF₆ was added to give a pale yellow solid which was filtered on a frit, washed with diethyl ether and air-dried. Recrystallization by diffusion of diethyl ether into an acetone solution gave a yellow crystalline solid. Yield 0.02 g (14%) (Found: C, 43.40; H, 4.70; N, 8.55. Calc. for C₂₉H₃₉F₉N₅O₂PRu; C, 43.95; H, 4.90; N, 8.85%). ¹H NMR [(CD₃)₂CO]: δ 2.49 (12 H, s, CH₃), 3.22 (3 H, s, NCH₃) and 7.21 (6 H,

s, phenyl). FAB mass spectrum: *m/z* 648 {Calc. for [¹⁰²RuL(CNC₆H₃Me₂-2,6)₂(O₂CCF₃)⁺ 648}. IR (cm⁻¹): 2125s, 2145s [ν(C≡N)] and 1695s [ν(C=O)].

Single-crystal Structure Determinations.—Single crystals of **1** and **4·H₂O** were obtained by diffusion of diethyl ether vapour into acetone solutions of the complexes. Intensities and lattice parameters were measured on a Rigaku AFC7R or Enraf-Nonius CAD-4 diffractometer using the ω–2θ scan mode. Crystal parameters and details of data collection and refinement are given in Table 1. Intensity data were corrected for Lorentz and polarization effects. Empirical absorptions were based on the ψ-scan of five strong reflections. Both structures were solved by the heavy-atom Patterson method and refined by full-matrix least squares and Fourier-difference syntheses.^{10,11} All non-H atoms were refined anisotropically. The H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. For complex **4·H₂O**, the H atom bonded to the Ru atom was located in the Fourier-difference synthesis and its positional parameters were refined but its thermal parameter was not refined. The two hydrogen atoms of the water molecule were not included in the calculation.

Atomic coordinates of non-hydrogen atoms of **1** and **4·H₂O** are listed in Tables 2 and 3 respectively. Selected bond distances and angles are listed in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles for **1** and **4·H₂O** and a full listing of atomic coordinates, bond lengths and angles and thermal parameters for **5**.

Results and Discussion

Synthesis and Characterization.—The complex [RuLCl₃] has been found to be a good starting material for the synthesis of organoruthenium complexes. In this work, it reacts with formic acid to give [RuL(CO)₂Cl]PF₆ **1** in low yield. Presumably, the two CO ligands are derived from decarbonylation of formic acid in a manner similar to the preparation of [{RuCl₂(CO)₃]₂} from hydrated RuCl₃.¹² The ν(CO) stretching frequencies (2067, 2006 cm⁻¹) in **1** are at lower values than found in [RuL'(CO)₂Cl]PF₆.¹³ [L' = 1,1,1-tris(diphenylphosphino-

methyl)ethane; $\nu(\text{CO})$ 2076, 2040 cm^{-1}) but are comparable to those in $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cl}]$; $\nu(\text{CO})$ 2059, 2008 cm^{-1}). This shows that the RuL^{2+} moiety has a comparable π basicity towards CO as $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)^+$. From the ^1H and ^{13}C NMR spectra, a C_s symmetry of **1** in solution is suggested. Preliminary studies showed that, similarly to $[\text{Ru}(\text{bipy})_2(\text{CO})_2]^{2+}$,¹⁵ **1** is a catalyst for the electrochemical reduction of carbon dioxide and further investigation is in progress.

The complex $[\text{RuLCl}_3]$ was found to react with 3 equivalents of $\text{Ag}(\text{O}_3\text{SCF}_3)$ in ethanol to give a green solution. Gravimetric analysis revealed the formation of 3 equivalents of AgCl . The green solution rapidly reacts with dppe to give $[\text{RuL}(\text{dppe})\text{H}]\text{O}_3\text{SCF}_3$ **3** in moderate yield. The ^1H NMR spectrum of **3** shows a broad high field signal at *ca.* δ -16. Presumably this is due to the ruthenium-hydride moiety, which is derived from a β -hydride shift from ethanol. Similar findings have previously

been noted in $[\text{RuL}(\text{cod})\text{H}]\text{ClO}_4$.⁷ In the synthesis of $[\text{RuL}(\text{dppe})\text{Cl}]\text{O}_3\text{SCF}_3$ **2**, 3 equivalents of AgCl were also formed as suggested from gravimetric analysis, but hydride formation was not observed in tetrahydrofuran. Complexes **2** and **3** are moderately stable in air. Attempts to prepare $[\text{RuL}(\text{dcpe})\text{X}]^+$ [$\text{X} = \text{H}$ or Cl^- , $\text{dcpe} = 1,2$ -bis(dicyclohexylphosphino)ethane] by similar methods led only to some green unidentified products.

The reaction between $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ and **L** in refluxing 2-methoxyethanol gave $[\text{RuL}(\text{CO})(\text{PPh}_3)_3]\text{PF}_6$ **4** in good yield. The same complex was obtained even with $[\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2]$ as starting material. Its $\nu(\text{CO})$ at 1927 cm^{-1} is lower than that in $[\text{RuH}(\text{CO})(\text{depe})_2]^+$ [$\text{depe} = 1,2$ -bis(diethylphosphino)ethane, $\nu(\text{CO})$ 1958 cm^{-1}]¹⁶ and *cis*- $[\text{RuH}(\text{CO})(\text{bipy})_2]^+$ [$\nu(\text{CO})$ 1930 cm^{-1}]¹⁷ but higher than that in $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)\text{H}(\text{CO})(\text{PPh}_3)]$ [$\nu(\text{CO})$ 1901 cm^{-1}].¹⁸ The hydride ligand appears as a high field doublet (δ -13.75, $^1J_{\text{PH}} = 31$ Hz) in the ^1H NMR spectrum. The three NCH_3 protons of **L** appear as three distinct singlets indicating that the piano-stool ligands are static in solution on the NMR time-scale at room temperature. Complex **4** is the first example of chiral ruthenium-L complexes containing three different ligands as piano-stools. Chirality at the metal centre has attracted a great deal of interest in asymmetric catalysis.¹⁹ Further study will be undertaken to explore the catalytic activities and to prepare **4** in enantiomerically pure form.

Previous studies on the substitutional reactions²⁰ of ruthenium(II)-ammine complexes revealed that $\text{Ru}^{\text{II}}\text{-OH}_2$ is more substitutional labile than $\text{Ru}^{\text{III}}\text{-OH}_2$. In this work, reduction of $[\text{RuL}(\text{H}_2\text{O})_2(\text{O}_2\text{CCF}_3)_2]^{2+}$ by zinc amalgam generates a ruthenium(II)-aqua complex which undergoes rapid ligand exchange with 2,6-dimethylphenyl isocyanide to give **5**, isolated as a PF_6 salt. Its ^1H NMR spectrum revealed C_s symmetry and this coincides with preliminary X-ray diffraction studies. Interestingly, the $\nu(\text{CN})$ stretches (at 2125 and 2145 cm^{-1}) are at higher wavenumbers than that of 2120 cm^{-1} in the free isocyanide, despite the fact that Ru^{II} is a good π donor.

A perspective drawing of the complex cation of **1** is shown in Fig. 1. The $\text{Ru-N}(1)$ and $\text{Ru-N}(3)$ distances [2.125(5) and 2.152(5) Å respectively] are longer than that of $\text{Ru-N}(2)$ [2.119(4) Å]. This is in line with the strong *trans* influence of the CO ligand. The measured Ru-C distances are 1.850(6) and 1.893(6) Å, which are comparatively shorter than those in $[\text{Ru}(\text{CO})(\text{COPh})\text{Ph}(\text{CNBu}^t)(\text{PMe}_2\text{Ph})_2]$ [Ru-C 2.004(15) Å].²¹ The shortening of Ru-C distances in **1** could be attributed to good π -basicity of the RuL^{2+} moiety, which enhances the

Table 2 Non-hydrogen atomic coordinates with estimated standard deviations (e.s.d.s) in parentheses for $[\text{RuL}(\text{CO})_2\text{Cl}]\text{PF}_6$ **1**

| Atom | x | y | z |
|-------|---------------|--------------|--------------|
| Ru | 0.058 69(6) | 0.235 74(3) | 0.051 21(3) |
| Cl | -0.170 01(21) | 0.130 05(11) | 0.003 14(11) |
| N(1) | 0.206 4(6) | 0.208 9(3) | -0.049 4(3) |
| N(2) | 0.278 7(6) | 0.321 3(3) | 0.085 8(3) |
| N(3) | 0.239 9(6) | 0.139 1(3) | 0.110 6(3) |
| C(1) | 0.368 1(7) | 0.269 8(4) | -0.045 8(4) |
| C(2) | 0.342 0(8) | 0.347 7(4) | 0.006 7(4) |
| C(3) | 0.422 7(7) | 0.271 9(4) | 0.139 8(4) |
| C(4) | 0.353 5(8) | 0.190 7(4) | 0.174 9(4) |
| C(5) | 0.350 8(8) | 0.100 9(4) | 0.049 7(4) |
| C(6) | 0.267 1(8) | 0.116 8(4) | -0.037 2(4) |
| C(7) | 0.101 8(9) | 0.216 2(4) | -0.131 8(4) |
| C(8) | 0.229 8(8) | 0.401 8(4) | 0.129 6(4) |
| C(9) | 0.152 7(9) | 0.067 5(4) | 0.152 6(4) |
| C(10) | -0.055 1(7) | 0.250 6(4) | 0.144 9(3) |
| O(10) | -0.126 2(6) | 0.254 9(3) | 0.202 3(3) |
| C(11) | -0.091 6(8) | 0.322 7(4) | -0.003 8(4) |
| O(11) | -0.183 7(6) | 0.371 8(3) | -0.036 6(3) |
| P | 0.764 83(24) | 0.503 81(11) | 0.210 15(11) |
| F(1) | 0.617 5(5) | 0.451 6(3) | 0.252 10(22) |
| F(2) | 0.910 2(5) | 0.557 2(3) | 0.168 1(3) |
| F(3) | 0.608 7(6) | 0.558 6(3) | 0.163 5(3) |
| F(4) | 0.921 8(5) | 0.449 3(3) | 0.258 0(3) |
| F(5) | 0.752 1(6) | 0.436 3(3) | 0.138 6(3) |
| F(6) | 0.778 6(6) | 0.570 0(3) | 0.283 4(3) |

Table 3 Non-hydrogen atomic coordinates with e.s.d.s in parentheses for $[\text{RuL}(\text{CO})(\text{PPh}_3)_3\text{H}]\cdot\text{H}_2\text{O}\cdot 4\text{H}_2\text{O}$

| Atom | x | y | z | Atom | x | y | z |
|------|-------------|-------------|-------------|-------|--------------|------------|------------|
| Ru | 0.117 96(7) | 0.227 00(3) | 0.467 67(3) | C(8) | 0.393(1) | 0.266 4(7) | 0.396 7(5) |
| P(1) | -0.001 4(2) | 0.204 8(1) | 0.357 5(1) | C(9) | 0.123(1) | 0.297 2(7) | 0.604 7(6) |
| P(2) | 0.754 7(3) | 0.080 2(1) | 0.643 1(2) | C(10) | 0.114(1) | 0.071 6(5) | 0.489 7(6) |
| F(1) | 0.613 5(8) | 0.122 7(5) | 0.648 2(4) | C(11) | 0.113 7(9) | 0.186 7(4) | 0.291 0(4) |
| F(2) | 0.742(1) | 0.092 3(7) | 0.566 1(5) | C(12) | 0.140 9(10) | 0.229 5(5) | 0.241 0(5) |
| F(3) | 0.897 8(9) | 0.038 4(5) | 0.640 4(6) | C(13) | 0.234(1) | 0.214 6(6) | 0.194 9(5) |
| F(4) | 0.769(2) | 0.071 6(10) | 0.719 8(6) | C(14) | 0.299(1) | 0.156 9(7) | 0.198 4(7) |
| F(5) | 0.861(1) | 0.136 8(5) | 0.657 5(8) | C(15) | 0.272(1) | 0.110 5(6) | 0.246 5(6) |
| F(6) | 0.655(1) | 0.022 2(5) | 0.623 4(8) | C(16) | 0.180 1(10) | 0.126 7(5) | 0.292 9(5) |
| O(1) | -0.190 6(8) | 0.247 2(4) | 0.497 0(4) | C(17) | -0.137 4(8) | 0.137 3(4) | 0.343 1(4) |
| O(2) | 0.483(3) | 0.490(2) | 0.642(2) | C(18) | -0.209 6(9) | 0.114 3(4) | 0.395 2(5) |
| N(1) | 0.357 7(7) | 0.234 2(4) | 0.456 2(4) | C(19) | -0.317 5(9) | 0.064 9(5) | 0.381 9(6) |
| N(2) | 0.220 3(8) | 0.256 7(4) | 0.571 1(4) | C(20) | -0.356(1) | 0.039 1(5) | 0.317 2(6) |
| N(3) | 0.204 2(7) | 0.129 5(3) | 0.510 4(4) | C(21) | -0.285(1) | 0.061 7(5) | 0.265 8(5) |
| C(1) | -0.069(1) | 0.235 7(4) | 0.485 7(4) | C(22) | -0.178 6(10) | 0.110 7(5) | 0.278 0(5) |
| C(2) | 0.445(1) | 0.268 0(7) | 0.517 6(6) | C(23) | -0.122 0(9) | 0.273 5(4) | 0.321 4(4) |
| C(3) | 0.357(1) | 0.292 8(6) | 0.564 4(6) | C(24) | -0.059(1) | 0.333 1(5) | 0.316 4(5) |
| C(4) | 0.263(2) | 0.198 0(7) | 0.614 8(6) | C(25) | -0.144(1) | 0.385 1(5) | 0.288 5(6) |
| C(5) | 0.211(1) | 0.136 4(6) | 0.586 1(5) | C(26) | -0.301(1) | 0.377 4(6) | 0.269 7(6) |
| C(6) | 0.359(1) | 0.118 9(6) | 0.493 7(7) | C(27) | -0.362 1(10) | 0.319 2(6) | 0.277 6(5) |
| C(7) | 0.414(1) | 0.168 5(7) | 0.452 9(8) | C(28) | -0.277 6(9) | 0.267 0(5) | 0.302 1(5) |

Table 4 Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses for complexes **1** and **4**·H₂O[RuL(CO)₂Cl]PF₆ **1**

| | | | |
|---------------|------------|----------------|------------|
| Ru-Cl | 2.410(2) | Ru-C(10) | 1.850(6) |
| Ru-N(1) | 2.125(5) | Ru-C(11) | 1.893(6) |
| Ru-N(2) | 2.119(4) | C(10)-O(10) | 1.133(7) |
| Ru-N(3) | 2.152(5) | C(11)-O(11) | 1.111(7) |
| Cl-Ru-N(1) | 91.75(13) | N(1)-Ru-C(11) | 95.78(22) |
| Cl-Ru-N(2) | 173.78(13) | N(2)-Ru-C(10) | 96.95(22) |
| Cl-Ru-N(3) | 93.90(14) | N(2)-Ru-C(11) | 95.05(22) |
| Cl-Ru-C(10) | 88.58(19) | N(3)-Ru-C(10) | 92.08(22) |
| Cl-Ru-C(11) | 87.77(19) | N(3)-Ru-C(11) | 177.25(21) |
| N(1)-Ru-C(10) | 174.07(22) | C(10)-Ru-C(11) | 90.1(3) |

[RuL(CO)(PPh₃)H]PF₆·H₂O **4**·H₂O

| | | | |
|---------|----------|-----------|-----------|
| Ru-N(1) | 2.215(7) | Ru-C(1) | 1.785(9) |
| Ru-N(2) | 2.197(7) | Ru-H(1) | 1.54(9) |
| Ru-N(3) | 2.268(7) | C(1)-O(1) | 1.182(10) |
| Ru-P(1) | 2.320(2) | | |

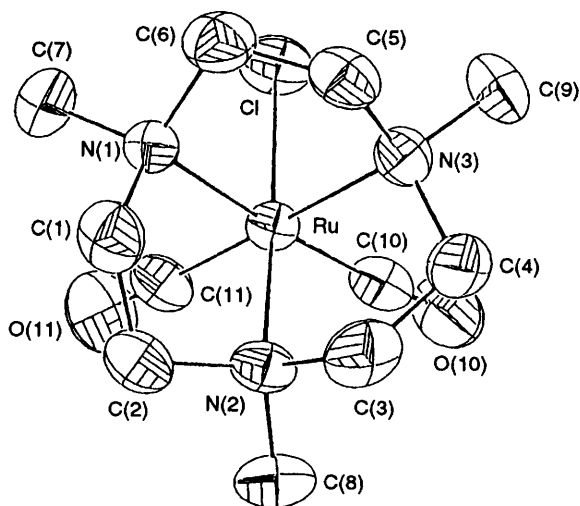
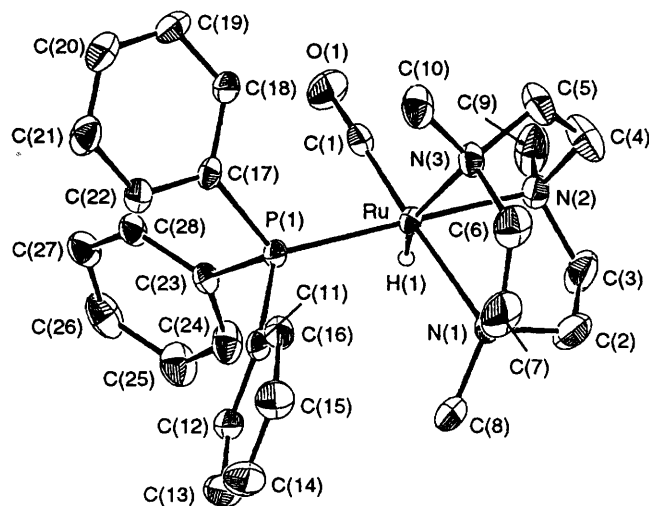
| | | | |
|--------------|----------|---------------|----------|
| P(1)-Ru-N(1) | 102.9(2) | N(3)-Ru-C(1) | 106.8(3) |
| P(1)-Ru-N(2) | 174.7(2) | Ru-P(1)-C(11) | 119.2(3) |
| P(1)-Ru-N(3) | 104.8(2) | Ru-P(1)-C(17) | 119.2(3) |
| P(1)-Ru-C(1) | 84.5(3) | Ru-P(1)-C(23) | 111.4(3) |
| N(1)-Ru-N(2) | 79.2(3) | Ru-C(1)-O(1) | 174.3(8) |
| N(1)-Ru-N(3) | 79.6(3) | P(1)-Ru-H(1) | 88(3) |
| N(1)-Ru-C(1) | 168.8(3) | N(1)-Ru-H(1) | 93(2) |
| N(2)-Ru-N(3) | 80.3(3) | N(2)-Ru-H(1) | 86(3) |
| N(2)-Ru-C(1) | 92.7(3) | N(3)-Ru-H(1) | 166(3) |
| N(3)-Ru-C(1) | 106.8(3) | C(1)-Ru-H(1) | 78(2) |
| N(2)-Ru-C(1) | 92.7(3) | | |

Ru^{II} → CO π back bonding. The C-Ru-C angle is 90.1(3)° which is typical for an octahedral complex.

Fig. 2 depicts a perspective drawing of the complex cation of **4**. The Ru-N(3) [2.268(7) Å] distance is comparatively longer than the Ru-N(1) and Ru-N(2) distances [2.215(7) and 2.197(7) Å respectively]. Presumably this is due to the strong *trans* influence of the hydride ligand. The Ru-C-O [174.3(8)°] group is linear. The measured Ru-P distance of 2.320(2) Å is normal whereas the Ru-C distance [1.785(9) Å] is comparatively shorter than that in e.g. [Ru(η⁵-C₉H₇)(CO){P(CH₂Ph)₃}] [Ru-P 2.266(3), Ru-C 1.97(2) Å]²² and [RuHCl(CO)(SN₂C₆H₄)(PPh₃)₂] [Ru-P 2.339(2), 2.359(2), Ru-C 1.818(7) Å].²³ The P-Ru-C and H-Ru-C angles [84.5(3)° and 78(2)° respectively] are usual for an octahedral complex but the H-Ru-P angle of 88(3)° reflects that the Ru-P bond is bent towards to the small Ru-H moiety.

The structure of complex **5** has also been determined.* Due to the crystal quality, a poor goodness-of-fit of 3.63 was obtained in the final least-square refinement. For this reason, the structure data are included as supplementary material. Nevertheless, the complex contains facially co-ordinating L with two 2,6-dimethylphenyl isocyanide ligands *cis* to each other and a trifluoroacetate anion co-ordinated in a monodentate fashion. The two isocyanides are in a *cis* geometry with a C-Ru-C angle of 89.2°. The Ru-C distances are 1.921(4) and 1.912(4) Å which are similar to those in [Ru(η⁵-C₅H₅)(CN-Bu)₂I] [Ru-C 1.90(3), 1.88(3) Å].²⁴

* Crystal data for C₂₉H₃₉F₉N₂O₂PRu **5**. *M*_r = 792.70, triclinic, space group P $\bar{1}$, *a* = 9.257(1), *b* = 11.336(1), *c* = 17.530(2) Å, α = 90.04(1), β = 92.91(1), γ = 108.36(1)°, *U* = 1743.4(9) Å³, *Z* = 2, *D*_c = 1.510 g cm⁻³, λ = 0.710 73 Å, μ(Mo-Kα) = 5.65 cm⁻¹, *F*(000) = 808, *T* = 297 K, 2θ_{max} = 48°, maximum and minimum residues in final Δ*F* synthesis = 1.10, -0.83 e Å⁻³, (Δ/σ)_{max} = 0.04, *R*, *R*' = 0.053, 0.079, goodness-of-fit = 3.63. The three F atoms in the trifluoroacetate group were disordered, occupying six positions and these were refined isotropically.

**Fig. 1** A perspective view of the cation [RuL(CO)₂Cl]⁺ of complex **1****Fig. 2** A perspective view of the cation [RuL(CO)(PPh₃)H]⁺ of complex **4**·H₂O**Acknowledgements**

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