

Synthesis of novel ruthenium complexes containing bidentate imidazole-based ligands

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Ruthenium(II) complexes containing the bidentate imidazole-based ligands $(\text{MeN}_2\text{H}_2\text{C}_3)_2\text{CO}$ L^1 , $(\text{MeN}_2\text{H}_2\text{C}_3)_2\text{CHOH}$ L^2 and $(\text{MeN}_2\text{H}_2\text{C}_3)_2\text{CH}_2$ L^3 (where 1-MeN₂H₂C₃ = 1-methylimidazol-2-yl), $[\text{Ru}(\text{PPh}_3)_2\text{H}(\text{CO})\text{L}^1]\text{Cl}$ **1**, $[\text{Ru}(\text{PPh}_3)_2\text{H}(\text{CO})\text{L}^2]\text{Cl}$ **2** and $[\text{Ru}(\text{PPh}_3)_2\text{H}(\text{CO})\text{L}^3]\text{Cl}$ **3**, were synthesized by the reaction of L^1 – L^3 with $[\text{Ru}(\text{PPh}_3)_3\text{H}(\text{Cl})(\text{CO})]$ in toluene. The complexes were characterised by NMR spectroscopy and the crystal structures of $[\text{Ru}(\text{PPh}_3)_2\text{H}(\text{CO})\text{L}^1]\text{BF}_4$ **4** and $[\text{Ru}(\text{PPh}_3)_2\text{H}(\text{CO})\text{L}^2]\text{OH}$ **5** determined.

Transition-metal complexes with ligand systems containing nitrogen-donor atoms have been used successfully to promote the transformation of organic compounds,¹ and also to act as structural mimics of metal centres in enzymes.^{2–5} Ruthenium complexes containing bidentate N-donor ligands with sp^2 -hybridised nitrogen atoms such as 2,2'-bipyridyl,⁶ 1,10-phenanthroline⁶ and bis(pyrazol-1-yl)methane⁷ have recently found use in catalytic hydrogenation reactions.

Research into transition-metal complexes containing poly-imidazole ligands has been concerned primarily with metallo-enzyme mimicry, using metal complexes of zinc,^{2,8} iron,^{9,10} cobalt^{2,8} and copper.¹¹ A number of palladium,^{12,13} platinum¹⁴ and ruthenium¹⁵ complexes of polyimidazole ligands have also been reported. In particular, platinum complexes of the bidentate imidazoles $(\text{MeN}_2\text{H}_2\text{C}_3)_2\text{CO}$ L^1 and $(\text{MeN}_2\text{H}_2\text{C}_3)_2\text{CHOH}$ L^2 where $\text{MeN}_2\text{H}_2\text{C}_3$ = 1-methylimidazol-2-yl have been reported and show considerable cytostatic activity.¹⁶ Palladium(II) complexes of the bidentate ligand $(\text{MeN}_2\text{H}_2\text{C}_3)_2\text{CH}_2$ L^3 and closely related symmetrical and unsymmetrical bidentate N-donor ligands with pyridine, pyrazole and imidazole subunits have been investigated in detail.¹³

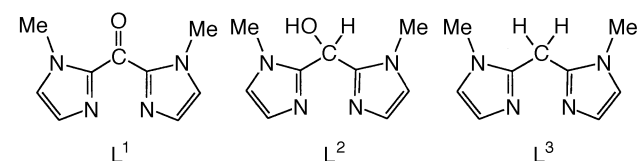
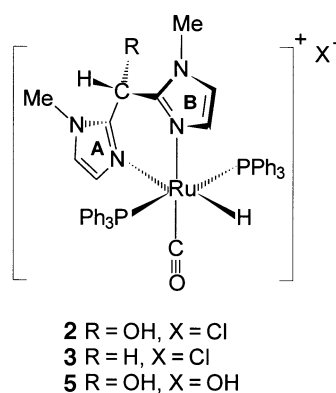
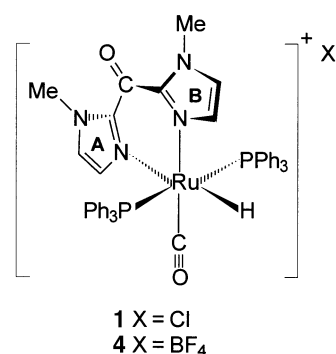
In this paper, we report the syntheses and structures of novel ruthenium(II) complexes of L^1 ,^{9,13,17} L^2 ,⁴ and L^3 .¹³ The complexes $[\text{Ru}(\text{PPh}_3)_2\text{H}(\text{CO})\text{L}^1]\text{Cl}$ **1**, $[\text{Ru}(\text{PPh}_3)_2\text{H}(\text{CO})\text{L}^2]\text{Cl}$ **2** and $[\text{Ru}(\text{PPh}_3)_2\text{H}(\text{CO})\text{L}^3]\text{Cl}$ **3** are readily formed by reaction of the appropriate L with $[\text{Ru}(\text{PPh}_3)_3\text{HCl}(\text{CO})]$ in toluene solvent. The complexes are charged and are of the general form $[\text{RuL}(\text{PPh}_3)_2\text{H}(\text{CO})]\text{Cl}$ in which a single bidentate imidazole ligand L is bound to the metal centre with displacement of triphenylphosphine and Cl^- ligands from the precursor. The complexes were characterised by NMR spectroscopy and $[\text{Ru}(\text{PPh}_3)_2\text{H}(\text{CO})\text{L}^1]\text{BF}_4$ **4** and $[\text{Ru}(\text{PPh}_3)_2\text{H}(\text{CO})\text{L}^2]\text{OH}$ **5** were characterised by X-ray diffraction.

Results and Discussion

Ligand synthesis

The bidentate ketone L^1 was synthesized by deprotonation of *N*-methylimidazole and reaction with diethyl carbonate at low temperature using a modification of the procedure described by Lippard and co-workers.¹⁷ Although L^1 has been synthesized using other methods,^{9,13,17} this route gave yields which were con-

sistently above 60%. Bidentate ketones analogous to L^1 have also been reported previously as intermediates in the synthesis of tridentate imidazoles.^{5,18} The bidentate alcohol L^2 was synthesized by a modification of the method described by Breslow and co-workers.⁴ The bidentate alkane L^3 was prepared following the method of Byers and Canty,¹³ by Wolff–Kishner reduction of L^1 .



Synthesis of metal complexes

Carbonylchlorohydridotris(triphenylphosphine)ruthenium(II)¹⁹ $[\text{Ru}(\text{PPh}_3)_3\text{H}(\text{Cl})(\text{CO})]$ was used as the precursor for the synthesis of ruthenium complexes. We have previously shown that tridentate imidazoles form clean products from this precursor,²⁰ where only one tridentate ligand binds to the metal centre. The synthesis of the metal complexes containing bidentate imidazole ligands L involved refluxing solutions of $[\text{Ru}(\text{PPh}_3)_3\text{H}(\text{Cl})(\text{CO})]$ with each L in toluene solution over a period of hours, and isolation of the products. In all cases a single bidentate imidazole ligand L binds to the metal centre with displacement of PPh_3 and Cl^- from the precursor. The resulting com-

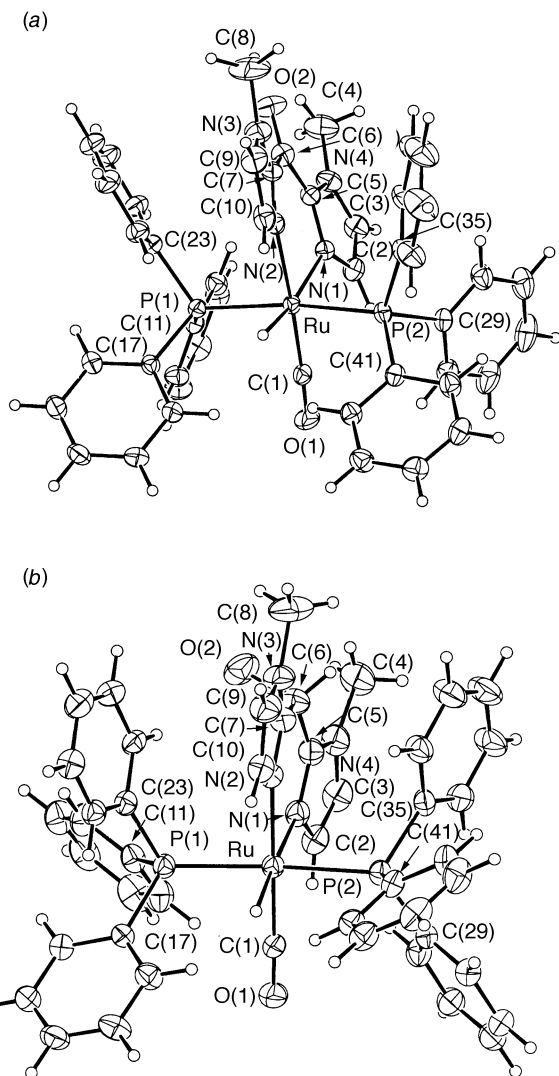


Fig. 1 The ORTEP²¹ plots of (a) $[\text{Ru}(\text{PPh}_3)_2\text{H}(\text{CO})\text{L}^1]\text{BF}_4$ **4** and (b) $[\text{Ru}(\text{PPh}_3)_2\text{H}(\text{CO})\text{L}^2]\text{OH}$ **5** with 30% thermal ellipsoids for the non-hydrogen atoms; hydrogen atoms have an arbitrary radius of 0.1 Å. Both complexes are viewed with the P–Ru–P axis lying horizontal

plexes $[\text{RuL}(\text{PPh}_3)_2\text{H}(\text{CO})]\text{Cl}$ are charged and precipitate directly from the reaction mixture.

Crystals of $[\text{Ru}(\text{PPh}_3)_2\text{H}(\text{CO})\text{L}^1]^+$ containing the ligand L^1 were obtained by addition of sodium tetrafluoroborate to a methanol solution of complex **1**, giving the tetrafluoroborate complex **4**. Crystals of the hydroxide salt, $[\text{Ru}(\text{PPh}_3)_2\text{H}(\text{CO})\text{L}^2]\text{OH}$ **5** were formed on slow crystallisation of $[\text{Ru}(\text{PPh}_3)_2\text{H}(\text{CO})\text{L}^2]\text{Cl}^-$ **2** from methanol–water. Hydroxide resulted from exchange of Cl^- with water during recrystallisation.

The complexes **1–3** have been analysed using NMR spectroscopy. Two-dimensional NMR techniques were used for assigning the resonances and determining the stereochemistry of the products. The structures of **4** and **5** were confirmed using single-crystal X-ray analysis. Projections of the structures of $[\text{Ru}(\text{PPh}_3)_2\text{H}(\text{CO})\text{L}^1]\text{BF}_4$ **4** and $[\text{Ru}(\text{PPh}_3)_2\text{H}(\text{CO})\text{L}^2]\text{OH}$ **5** are shown in Fig. 1. Selected structural parameters are given in Table 1, crystallographic details in Table 2.

Crystal structures

The two complexes **4** and **5** have similar distorted-octahedral geometries about the metal centre. The P–Ru bonds are not collinear, with the P–Ru–P angle distorted by about 10° from linearity [171.6(4) for **4** and 168.9(6)° for **5**]. The bite angle of the bidentate imidazole ligand is small, with bond angles

Table 1 Selected bond distances (Å) and angles (°) for complexes $[\text{Ru}(\text{PPh}_3)_2\text{H}(\text{CO})\text{L}^1]\text{BF}_4$ **4** and $[\text{Ru}(\text{PPh}_3)_2\text{H}(\text{CO})\text{L}^2]\text{OH}$ **5**

	4	5
Ru–N(1)	2.176(3)	2.181(5)
Ru–N(2)	2.135(3)	2.139(5)
Ru–P(1)	2.357(1)	2.336(2)
Ru–P(2)	2.356(1)	2.385(2)
Ru–CO	1.829(4)	1.845(7)
Ru–H	1.66(4)	1.77(5)
P(1)–Ru–P(2)	171.61(4)	168.96(6)
P(1)–Ru–N(1)	94.18(9)	98.3(1)
P(1)–Ru–N(2)	91.91(9)	92.4(1)
P(1)–Ru–C(1)	85.9(1)	88.1(2)
P(2)–Ru–C(1)	89.9(1)	92.8(2)
N(1)–Ru–N(2)	83.2(1)	84.7(2)

Table 2 Crystallographic data* for $[\text{Ru}(\text{PPh}_3)_2\text{H}(\text{CO})\text{L}^1]\text{BF}_4$ **4** and $[\text{Ru}(\text{PPh}_3)_2\text{H}(\text{CO})\text{L}^2]\text{OH}$ **5**

	4	5
Empirical formula	$\text{C}_{46}\text{H}_{41}\text{BF}_4\text{N}_4\text{O}_2\text{P}_2\text{Ru}$	$\text{C}_{46}\text{H}_{42}\text{N}_4\text{O}_4\text{P}_2\text{Ru}$
<i>M</i>	931.68	877.88
Crystal colour, habit	Red, prism	Colourless, prism
Crystal dimensions/mm	0.48 × 0.20 × 0.20	0.43 × 0.32 × 0.11
<i>a</i> /Å	22.314(5)	28.919(9)
<i>b</i> /Å	14.745(3)	20.550(5)
<i>c</i> /Å	26.887(6)	18.910(4)
β /°	103.19(2)	119.57(2)
<i>U</i> /Å ³	8612(3)	9774(4)
<i>D_c</i> /g cm ⁻³	1.437	1.193
<i>F</i> (000)	3808.00	3616.00
μ /cm ⁻¹	4.99	35.51
$2\theta_{\text{max}}$ /°	49.9	120.5
<i>hkl</i> ranges	–26 to 26, 0–17, 0–32	0–32, 0–23, –21 to 18
No. reflections measured; total, unique (<i>R_{int}</i>)	8046, 7906 (0.020)	7718, 7547 (0.032)
Transmission factors	0.91–0.92	0.35–0.70
No. observations [<i>I</i> > 2.50σ(<i>I</i>)]	5603	5760
No. variables	540	527
Reflection/parameter ratio	10.38	10.93
Residual <i>R</i> , <i>R'</i>	0.044, 0.041	0.053, 0.061
Goodness of fit	2.12	3.89
Maximum, minimum peaks in final difference map/e Å ⁻³	0.55, –0.59	0.58, –0.86

* Details in common: monoclinic, space group *C2/c* (no. 15); *Z* = 8; 21 °C; function minimised $\sum w(|F_o| - |F_c|)^2$; $w^{-1} = 4F_o^2/\sigma^2(F_o)$; anomalous dispersion on all non-hydrogen atoms; maximum shift/error in final cycle 0.00.

N–Ru–N of 83.2(1)° in **4** and 84.7(2)° in **5**. The two triphenylphosphine ligands lean towards the CO ligand and away from the imidazolyl rings of the ligand, with the angles between the P–Ru and C–Ru bonds on average less than 90° [85.9(1), 89.9(1) in **4**, 88.1(2) and 92.8(2)° in **5**], and the angles between the P–Ru and N–Ru bonds larger than 90° [94.18(2) and 91.91(9) in **4**, 98.3(1) and 92.4(1)° in **5**].

The imidazolyl rings of complex **4** are planar to within 0.01 Å and form dihedral angles of 21.3 and 18.6° with the co-ordination plane defined by N(1)–N(2)–C(1) and H(Ru). The metal ion is slightly displaced from the co-ordination plane, by 0.03 Å. Atoms N(1), N(2) and C(1) reside on the least-squares plane, whereas H(1Ru) deviates from it by 0.02 Å. The imidazolyl rings of **5** are also planar to within 0.01 Å and form dihedral angles of 9.7 and 11.0° with the co-ordination plane defined by N(1), N(2), C(1) and H(Ru). The metal ion is 0.02 Å out of this plane. Atoms N(1), N(2) and C(1) of **5** reside on the least-squares plane, whereas H(Ru) deviates from it by 0.03 Å.

The deviation from coplanarity of the components of the bidentate imidazole ligands of complexes **4** and **5**, provides a minor extension of the limited bite of the ligand co-ordinated to the large ruthenium ion. The larger deviation from coplanarity evident in **4** is probably driven by contact between the carbonyl O(2) atom and the methyl C(4) and C(8) atoms. The distance between O(2) and C(4) is 2.801(8) Å, and that between O(2) and C(8) is 2.770(8) Å. The O(2) to C(4) and C(8) distances in **5** are 3.24(1) and 3.28(1) Å.

There are several close contacts between the imidazolyl rings of the bidentate imidazole ligand and the triphenylphosphine ligands. For example in complex **4** the N(1) to C(12) distance is 3.299(5) Å, N(2) to C(40) is 3.044(5) Å, N(2) to C(24) is 3.193(5) Å, N(2) to C(35) is 3.195(5) Å and N(2) to C(23) is 3.269(5) Å. Similar contacts are found in the structure of **5**.

In complex **5** the OH⁻ counter ion is hydrogen bonded to the metal carbonyl ligand while the solvent of crystallisation (H₂O) is hydrogen bonded to the OH group on the ligand backbone.

The Ru–P bond lengths in complex **4** are almost identical at 2.357(1) and 2.356(1) Å, and very similar to those in **5** [2.336(2) and 2.385(2) Å]. Comparison with the other known ruthenium complexes containing polydentate nitrogen donor ligands, tridentate imidazole-based ligands,²⁰ tris(pyrazol-1-yl)methane and tris(pyrazol-1-yl)borane complexes, reveals very similar Ru–P bond lengths ranging between 2.33 and 2.37 Å.^{22,23} The Ru–N bond lengths are almost identical in **4** and **5**, at 2.176(3) and 2.135(3) in **4** and 2.181(5) and 2.139(5) Å in **5**. In each complex that opposite the metal-bound hydride is longer [2.176(3) and 2.181(5) Å] than the one opposite the metal-bound carbonyl [2.135(3) and 2.139(5) Å]. Again, other known complexes of tridentate imidazole ligands and tris(pyrazol-1-yl)methane and tris(pyrazol-1-yl)borate complexes with Ru have very similar Ru–N bond lengths, ranging between 2.12 and 2.17 Å.^{22,23}

NMR Assignment of complexes 1–3

The ¹H, ³¹P and ¹³C NMR spectra were completely assigned for complexes **1–3**, using two-dimensional methods. In each of the complexes, the two imidazolyl rings in the ligand are non-equivalent, with one (A) *trans* to the hydride ligand and the other (B) *trans* to the carbonyl ligand. The assignment of protons to the heterocyclic rings A or B was achieved using two-dimensional ¹H nuclear Overhauser effect spectroscopy (NOESY). One imidazolyl ring (B) is directed towards the metal-bound hydride and a NOESY interaction between H_B⁴ and the metal-bound hydride is observed, while the protons (H⁴ and H⁵) on the other imidazolyl ring (A) do not interact with the hydride ligand. The assignments of the resonances of the two methyl groups on nitrogen to their respective imidazolyl rings was also achieved using the ¹H NOESY NMR spectrum; NOESY interactions were observed between each methyl group and the proton H⁵ on the same imidazolyl ring. For complexes **1** and **3** the two *trans* triphenylphosphine ligands appear as a singlet in the ³¹P-¹H NMR spectrum. In the case of [Ru(PPh₃)₂H(CO)L²]Cl **2** the two *trans* triphenylphosphine ligands are non-equivalent. The ³¹P-¹H NMR resonances for **2** appear as two tented doublets with a large ²J_{PP} coupling constant of 287 Hz, characteristic of the *trans* disposition of the phosphines.

Although no crystal structure was obtained for [Ru(PPh₃)₂H(CO)L³]Cl **3**, the NMR data indicate that the structure is analogous to those of **1** and **2**. In **3**, the two triphenylphosphine ligands are mutually *trans* and equivalent, as in **1**, and the two imidazolyl rings of the ligand were assigned to A and B positions using the ¹H NOESY NMR spectrum.

Conclusion

Three new ruthenium(II) complexes containing bidentate imidazole-based ligands L¹–L³ have been synthesized and char-

acterised. Reaction of the appropriate bidentate L with [Ru(PPh₃)₃H(CO)] in toluene solvent led to the formation of [Ru(PPh₃)₂H(CO)L¹]Cl **1**, [Ru(PPh₃)₂H(CO)L²]Cl **2** and [Ru(PPh₃)₂H(CO)L³]Cl **3**, in good yields of between 65 and 88%. The complexes contain a single bidentate imidazole ligand, two triphenylphosphines, a hydride and a carbonyl. X-Ray analysis shows that they are essentially octahedral. Distortion from perfect octahedral symmetry is primarily due to steric effects of the triphenylphosphine ligands and the small bite angle of the bidentate imidazole ligands.

Experimental

All manipulations of metal complexes and air-sensitive reagents were carried out using standard Schlenk or vacuum techniques,²⁴ or in a Vacuum Atmospheres argon-filled dry-box.

Ruthenium(III) trichloride hydrate was obtained from both Aldrich and Johnson Matthey, and used without further purification. *n*-Butyllithium was used as a solution in hexane (≈2.4 mol dm⁻³) as supplied by Aldrich and was titrated immediately prior to use against 2,5-dimethoxybenzyl alcohol.²⁵ *N*-Methylimidazole was obtained from Aldrich and used without further purification. Tetrahydrofuran and toluene were stored over sodium wire and distilled under nitrogen immediately prior to use from sodium-benzophenone ketyl. Light petroleum refers to the fraction with bp 60–80 °C.

The mass spectra of organic compounds were recorded on a Kratos MS9/MS50 double-focusing mass spectrometer, those of organometallic complexes on a Finnigan MAT TSG-46 mass spectrometer (San Jose, CA, USA). In the case of organometallic complexes in which the overall mass spectrum is predominantly that of the ligands, spectra were recorded by scanning mass ranges greater than that of the free L, typically *m/z* >250. Peaks with low intensity are not quoted unless deemed significant. Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrophotometer. Melting points were determined using a Gallenkamp apparatus and are uncorrected. The ¹H, ³¹P and ¹³C NMR spectra were recorded on Bruker AMX400 and AMX600 spectrometers at 300 and 303 K respectively. Chemical shifts are internally referenced to residual solvent in the case of ¹H and ¹³C, and to external neat trimethyl phosphite (δ 140.85) in the case of ³¹P spectra.

Carbonylchlorohydridotris(triphenylphosphine)ruthenium(II) was prepared by the method of Ahmad *et al.*¹⁹

Crystallography

A red prismatic crystal of complex **4** was attached to a thin glass fibre, and mounted on an Enraf-Nonius CAD4 diffractometer employing graphite-monochromated Mo-Kα radiation (λ 0.710 93 Å). C-Centred monoclinic cell constants were obtained from a least-squares refinement using the setting angles of 25 machine-centred reflections in the range 19.6 < 2θ < 24.2°. Data were collected using ω–θ scans with a scan width of (1.50 + 1.05 tan θ)°. The intensities of three representative reflections measured every 60 min decreased by 3.2%, and a linear correction was accordingly applied to the data. The crystal faces were indexed and an analytical absorption correction was applied to the data.

A colourless prismatic crystal of complex **5** was attached to a thin glass fibre and mounted on a Rigaku AFC7R diffractometer employing graphite-monochromated Cu-Kα radiation (λ 1.541 78 Å) from a 12 kW direct drive rotating-anode generator. C-Centred monoclinic cell constants were obtained from a least-squares refinement using the setting angles of 25 automatically centred reflections in the range 90.42 < 2θ < 97.63°. Omega scans of several intense reflections made prior to data collection had an average width at half-height of 0.24°. Data were collected using ω–2θ scans with a scan width of (1.68 + 0.35 tan θ)°. The intensities of three representative

reflections measured every 150 decreased by 3.3% during the data collection, and a linear correction was applied to the data. Other details as for **4**.

All calculations were performed using the TEXSAN²⁶ crystallographic software package. The data were corrected for Lorentz-polarisation effects. The data obtained from both complexes **4** and **5** showed systematic absences of hkl ($h + k \neq 2n$) and $h0l$ ($l \neq 2n$), and the structures were solved in the space group $C2/c$ (no. 15). The structures were solved by direct methods²⁷ and expanded using Fourier-difference maps.²⁸ The non-hydrogen atoms were refined anisotropically, and the hydrides were refined isotropically. The remaining hydrogen atoms were included in the full-matrix least-squares refinements at calculated positions with group thermal parameters. The tetrafluoroborate anion of **4** proved to be disordered and was refined with eight fluorine sites of equal occupancy. After several cycles of refinement the positions of the fluorine atoms were fixed. The crystal structure for complex **5** was modelled as $[\text{Ru}(\text{PPh}_3)_2\text{H}(\text{CO})\text{L}^2]\text{OH}\cdot\text{H}_2\text{O}$, with no hydrogens attached to the oxygen atoms, and the water oxygen equally distributed between two lattice sites. The residual weighting scheme was based on counting statistics and included a statistical uncertainty factor ($p = 0.001$ for **4** and 0.003 for **5**). Neutral atom scattering factors were taken from Cromer and Waber.²⁹ Anomalous dispersion effects were included in the structure-factor calculation,³⁰ and the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.³¹ The values for the mass-attenuation coefficients were those of Creagh and Hubbell.³²

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/495.

Synthesis of bidentate imidazoles

Bis(1-methylimidazol-2-yl) ketone L¹. There have been several reports of the synthesis of compound **L¹**,^{9,13,17} a modification of the method described by Lippard and co-workers.¹⁷ was used. *n*-Butyllithium (110 mmol) was added to a solution of 1-methylimidazole (10 cm³, 125 mmol) in tetrahydrofuran (thf) (150 cm³) at -78°C under nitrogen. The solution was stirred for 1 h at -78°C after which time diethyl carbonate (6 cm³, 50 mmol) was added. The solution changed from pale yellow to purple and thickened. It was allowed to warm to -40°C over several hours, quenched by addition of solid carbon dioxide and then allowed to warm to room temperature. Water (100 cm³) was added and the product obtained by continuous liquid-liquid extraction into ethyl acetate (600 cm³) for 10–12 h. The ethyl acetate solvent was removed and the residue recrystallised from acetone. The product **L¹** was obtained as a colourless crystalline solid (6.6 g, 63%), m.p. $154\text{--}155.5^\circ\text{C}$ (lit.,¹³ $145\text{--}148^\circ\text{C}$). δ_{H} (400 MHz, CDCl₃) 7.31 (s, 1 H, H⁴), 7.09 (s, 1 H, H⁵) and 4.02 (s, 3 H, NCH₃); $\delta_{\text{C-(H)}}(100\text{ MHz, CDCl}_3)$ 174.4 (C=O), 143.4 (C²), 130.7 (C⁴), 127.2 (C⁵) and 36.6 (NCH₃); m/z 191 (11, $[M + 1]^+$), 190 (88, M^+), 162 (19), 161 (70), 109 (100), 96 (22), 95 (32), 82 (60), 54 (30), 53 (10), 52 (11), 42 (17) and 40 (14%). High-resolution mass spectrum (M^+): m/z 190.0845; C₉H₁₀N₄O requires 190.0855.

Bis(1-methylimidazol-2-yl)methanol L². This compound was synthesized using a modification of the procedure described by Breslow and co-workers.⁴ *n*-Butyllithium (40 mmol) was added to 1-methylimidazole (6.6 cm³, 83 mmol) in thf (200 cm³) at -78°C under nitrogen. The solution was stirred for 1.5 h after which time ethyl formate (3 cm³) was added. The solution was allowed to warm to $10\text{--}20^\circ\text{C}$ over several hours, quenched with water (100 cm³) followed by continuous liquid-liquid extraction into ethyl acetate (400 cm³) for 10–12 h. The ethyl acetate sol-

vent was removed and the residue recrystallised from acetone to yield **L²** as a white crystalline solid (2.7 g, 70%), m.p. $199\text{--}202^\circ\text{C}$ (lit.,⁴ $188\text{--}189.5^\circ\text{C}$). δ_{H} (400 MHz, CDCl₃) 6.90 [d, 2 H, $^3J(\text{H}^4\text{H}^5) = 1.2$, H⁴], 6.82 [d, 2 H, $^3J(\text{H}^4\text{H}^5) = 1.2$ Hz, H⁵], 6.02 (s, 1 H, CHOH) and 3.59 (s, 6 H, NCH₃); $\delta_{\text{C-(H)}}(100\text{ MHz, CDCl}_3)$ 146.6 (C²), 127.4 (C⁴), 123.3 (C⁵), 65.1 (COH) and 33.9 (NCH₃); m/z 193 (10, $[M + 1]^+$), 192 (51, M^+), 191 (39), 175 (8), 163 (10), 111 (42), 109 (35), 96 (100), 95 (22), 83 (100), 82 (39), 81 (27), 56 (17), 55 (11), 54 (17), 52 (10), 42 (51) and 41 (10%).

Bis(1-methylimidazol-2-yl)methane L³. This compound was prepared using a modification of the method described by Byers and Canty.¹³ The ketone **L¹** (3.50 g, 18 mmol) was placed in a glass-sleeved stainless-steel reaction bomb (600 cm³) with hydrazine hydrate³³ (10.0 cm³, 194 mmol) and sodium hydroxide (1.50 g, 37.5 mmol). The vessel was sealed and heated to 150°C for 4 h after which it was cooled to room temperature and opened carefully. The product was extracted into acetone and the solvent removed under vacuum. Compound **L³** was recrystallised from acetone as a cream solid (1.27 g, 39%), m.p. $152\text{--}154^\circ\text{C}$ (lit.,⁷ $143\text{--}148^\circ\text{C}$). δ_{H} (400 MHz, CDCl₃) 6.84 [d, 1 H, $^3J(\text{H}^4\text{H}^5) = 1.2$, H⁴], 7.09 [d, 1 H, $^3J(\text{H}^4\text{H}^5) = 1.2$ Hz, H⁵], 4.16 (s, 1 H, CH₂) and 3.59 (s, 3 H, NCH₃); $\delta_{\text{C-(H)}}(400\text{ MHz, CDCl}_3)$ 144.2 (C²), 127.9 (C⁴), 122.1 (C⁵), 33.8 (NCH₃) and 27.5 (CH₂); m/z 177 (10, $[M + 1]^+$), 176 (75), 175 (27), 161 (20), 134 (10), 107 (13), 96 (65), 95 (100), 81 (23), 55 (12), 54 (38), 53 (10) and 52 (14%). High-resolution mass spectrum (M^+): m/z 176.1062; C₉H₁₂N₄ requires 176.1062.

Synthesis of ruthenium complexes

[Ru(PPh₃)₂H(CO)L¹]Cl **1**. A mixture of $[\text{Ru}(\text{PPh}_3)_3\text{H}(\text{Cl})\text{-(CO)}]$ (0.61 g, 0.64 mmol) and **L¹** (0.16 g, 0.82 mmol) in toluene (40 cm³) was refluxed for 2 h. The orange solution was allowed to cool to room temperature and the yellow precipitate which formed was filtered off and washed with hexane (20 cm³). The crude product was recrystallised from methanol to give $[\text{Ru}(\text{PPh}_3)_2\text{H}(\text{CO})\text{L}^1]\text{Cl}$ **1** as orange plates (0.50 g, 88%), m.p. 107°C (decomposed without melting). δ_{H} (600 MHz, CDCl₃) 7.71 (s, 1 H, H²_A), 7.36–7.23 (m, 31 H, PPh₃ and H⁴_A), 7.09 (s, 1 H, H⁵_B), 6.50 (s, 1 H, H⁴_B), 3.97 (s, 3 H, NCH_{3A}), 3.84 (s, 3 H, NCH_{3B}) and -11.63 [t, 1 H, $^2J(\text{H-Ru-P}) = 18.7$ Hz, RuH]; $\delta_{\text{C-(H,P)}}(100\text{ MHz, CDCl}_3)$ 204.9 (RuCO), 166.7 (CO of L¹), 140.0, 139.4 (C²_{A,B}), 136.6 (C⁴_B), 134.6 (C⁴_A), 133.8 (PPh₃), 132.4 (PPh₃), 131.0 (PPh₃), 130.7 (C⁵_B), 129.5 (C⁵_A), 128.9 (PPh₃) and 39.9 (NCH_{3A,B}); δ_{P} (162 MHz, CDCl₃) 47.11 (s); FAB mass spectrum m/z 847 (15, $[M + 2]^+$), 846 (13, $[M + 1]^+$), 845 (22, M^+), 844 (19), 843 (13), 842 (14), 586 (12), 585 (33), 584 (35), 583 (100), 582 (35), 581 (89), 580 (60), 579 (38), 578 (34), 577 (12), 575 (13), 556 (11), 555 (19), 554 (19), 553 (23), 552 (17) and 551 (14%); $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (Nujol) 1929m (Ru–C=O), stretch corresponding to Ru–H not observed.

Crystals of the complex $[\text{Ru}(\text{PPh}_3)_2\text{H}(\text{CO})\text{L}^1]\text{BF}_4$ **4** suitable for structure analysis were obtained by addition of a methanol solution of NaBF₄ to a methanol solution of **1** followed by slow evaporation of the solvent.

[Ru(PPh₃)₂H(CO)L²]Cl **2**. A mixture of $[\text{Ru}(\text{PPh}_3)_3\text{H}(\text{Cl})\text{-(CO)}]$ (0.36 g, 0.38 mmol) and **L²** (0.13 g, 0.68 mmol) in toluene (40 cm³) was refluxed for 2 h. The clear solution was allowed to cool to room temperature, the solvent removed and the residue dissolved in acetone. Light petroleum was added causing the precipitation of a white solid which was filtered off. The crude product was recrystallised from methanol to give $[\text{Ru}(\text{PPh}_3)_2\text{H}(\text{CO})\text{L}^2]\text{Cl}$ **2** as colourless needles (0.22 g, 65%), m.p. 140°C (decomposed without melting). δ_{H} (400 MHz, CDCl₃) 7.42–7.11 (m, 30 H, PPh₃), 6.69 (s, 1 H, H⁴_A), 6.59 (s, 1 H, H⁵_A), 5.95 (s, 1 H, H⁵_B), 5.83 (s, 1 H, H⁴_B), 5.31 (s, 1 H, CHOH), 3.74 (s, 3 H, NCH_{3A}), 3.69 (s, 3 H, NCH_{3B}) and -11.91 [dd, 1 H, $^2J(\text{H-Ru-P}) = 17.4, 22.0$ Hz, RuH]; $\delta_{\text{C-(H,P)}}(100\text{ MHz, CDCl}_3)$

205.7 (RuCO), 145.1, 144.7 (C²_{A,B}), 134.5 (PPh₃), 134.0 (PPh₃), 133.7 (C⁴_B), 133.4 (C⁴_A), 128.6 (PPh₃), 128.4 (PPh₃), 123.2 (C⁵_A), 122.2 (C⁵_B), 57.0 (COH) and 36.3 (NCH_{3A,B}); δ_p (162 Hz, CDCl₃) 47.7 [d, ²J(P–Ru–P) = 287] and 44.3 [d, ²J(P–Ru–P) = 287 Hz]; FAB mass spectrum *m/z* 849 (12, [M + 2]⁺), 848 (11, [M + 1]⁺), 847 (32, M⁺), 845 (17), 587 (24), 586 (28), 585 (80), 584 (56), 583 (100), 582 (67), 581 (47), 580 (37), 579 (13), 577 (16), 569 (17), 568 (16), 567 (21), 566 (18), 565 (13), 564 (10), 557 (15), 556 (14), 555 (29), 554 (21), 553 (20), 552 (14), 540 (11), 539 (15), 538 (13), 537 (14) and 536 (11%); $\tilde{\nu}_{\max}/\text{cm}^{-1}$ (Nujol) 2014w (Ru–H), 1927m (Ru–C=O).

Crystals of the complex [Ru(PPh₃)₂H(CO)L²]OH **5** suitable for structure analysis were obtained by slow evaporation of a methanol–water (99:1) solution of **2**.

[Ru(PPh₃)₂H(CO)L³]Cl **3.** A mixture of [Ru(PPh₃)₃H(Cl)(CO)] (0.50 g, 0.52 mmol) and L³ (0.12 g, 0.68 mmol) in toluene (30 cm³) was refluxed for 3 h during which time a precipitate formed. The mixture was cooled to room temperature and the precipitate filtered off and washed with hexane (10 cm³). Complex **3** was obtained as a white solid (0.39 g, 86%), m.p. 215 °C (decomposed without melting). δ_H (400 MHz, CDCl₃) 7.38–7.25 (m, 30 H, PPh₃), 6.66 [d, 1 H, ³J(H⁴_AH⁵_A) = 1.7, H⁵_A], 6.58 [d, 1 H, ³J(H⁴_AH⁵_A) = 1.7, H⁴_A], 6.12 [d, 1 H, ³J(H⁴_BH⁵_B) = 1.7, H⁴_B], 6.08 [d, 1 H, ³J(H⁴_BH⁵_B) = 1.7, H⁵_B], 3.83 (s, 3 H, NCH_{3A}), 3.68 (s, 2 H, CH₂), 3.66 (s, 3 H, NCH_{3B}) and –11.82 [t, 1 H, ²J(H–Ru–P) = 19.5 Hz, RuH]; $\delta_{C-(H,P)}$ (100 MHz, CDCl₃) 205.2 (RuCO), 142.1, 142.0 (C²_{A,B}), 134.2 (PPh₃), 133.9 (PPh₃), 133.6 (C⁴_B), 132.74 (C⁴_A), 130.5 (PPh₃), 128.7 (PPh₃), 122.6 (C⁵_A), 121.4 (C⁵_B), 35.9 (NCH_{3A,B}) and 24.5 (CH₂); δ_p (162 MHz, CDCl₃) 45.1 (s); FAB mass spectrum *m/z* 831 (3, M⁺), 657 (14), 655 (25), 654 (14), 640 (25), 638 (15), 607 (16), 606 (27), 605 (70), 604 (49), 603 (100), 602 (69), 601 (49), 600 (39), 599 (14), 597 (15), 569 (22), 568 (16), 567 (30), 566 (24), 565 (14), 564 (12), 525 (28), 524 (30), 519 (15), 518 (44), 517 (34), 516 (77), 515 (51), 514 (43), 513 (31) and 512 (15%); $\tilde{\nu}_{\max}/\text{cm}^{-1}$ (Nujol); 1919m (Ru–C=O), stretch corresponding to Ru–H not observed (Found: C, 61.4; H, 5.4; N, 6.2. Calc. for C₄₆H₄₃ClN₄OP₂Ru·2H₂O: C, 61.23; H, 5.25; N, 6.21%).

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