Synthesis and reactivity of areneruthenium pyranone and pyridinone complexes †

Glen Capper, Lee C. Carter, David L. Davies,* John Fawcett and David R. Russell

Department of Chemistry, University of Leicester, Leicester LE1 7RH, UK

The complexes [Ru(mes)Cl(L)] (mes = 1,3,5-trimethylbenzene; HL = a pyranone or a pyridinone) have been synthesised and characterised. Reaction of [Ru(mes)Cl(L)] (HL = 2-ethyl-3-hydroxypyran-4-one) with CO in the presence of $AgBF_4$ gave [Ru(mes)L(CO)][BF$_4$]. This carbonyl complex reacts with nucleophiles to give substitution products [Ru(mes)L(L')][BF$_4$] (L' = H_2O or H_2NCH_2Ph). One of the initial complexes, [Ru(mes)Cl(L)] (HL = 2-methyl-3-hydroxypyran-4-one) and the carbonyl complex have been characterised by X-ray diffraction.

Bioorganometallic chemistry is an area which has attracted increasing attention in the last few years.[2] A particular attraction of biological compounds is their solubility in water, as a consequence their complexes may have applications as catalysts in aqueous media.[3] The reaction of [{Ru(C$_6$H$_6$)Cl$_2$}$_2$] with amino acids was reported as long ago as 1977.[4] However, the current interest in bioorganometallic chemistry is manifested by the recent publications concerning the reactions of [{Ru(arene)Cl$_2$}$_2$] dimers with amino acids, peptides and nucleobases.[5]

Pyranones and pyridinones have received a lot of interest in recent years due to their use as chelators in medicine; complexes with Group 13 elements and with iron have been extensively studied.[6] Pyridinones, in particular, are readily tailored to manipulate their hydrophobic/hydrophilic properties.[7] Ruthenium complexes of pyranones and pyridinones have been used as catalysts for the oxidation of alcohols.[8] We have recently reported the synthesis of some areneruthenium[9] and Rh(C$_5$Me$_5$)[1] complexes of pyranones and pyridinones which are soluble in dichloromethane and in water. In this paper we report the synthesis of some more areneruthenium pyranone and pyridinone complexes, their dissolution in water as well as some of their reactivity. Of particular importance is the synthesis of a new water-soluble metal carbonyl complex which has been characterised by X-ray diffraction.

Results and Discussion

The complexes 1–3 were synthesised by treating the relevant compound HL[1–3] and 1 equivalent of sodium methoxide with [{Ru(mes)Cl$_2$}$_2$] (mes = C$_6$H$_3$Me$_3$-1,3,5) as previously reported for complex 4.[9] The complexes are all soluble in dichloromethane and so are easily separated from the sodium chloride by-product.

The complexes were characterised by ^{1}H NMR, mass spectrometry and microanalysis (Table 1). The ^{1}H NMR spectra all show the expected signals due to the arene and the pyranone or pyridinone. The aquation of the complexes was studied by running the NMR spectra in D$_2$O. In each case only one species was observed and the spectra were relatively unaffected by the addition of an excess of chloride (NaCl). We have previously observed the same result for complex 4 and ascribed this to complete aquation having occurred.[9] However, subsequent studies with analogous rhodium complexes have shown this not to be the case.[1] Conductivity measurements on complex 4 (Λ°_m 68.5 S cm^2 mol^{-1}) show that there is in fact an
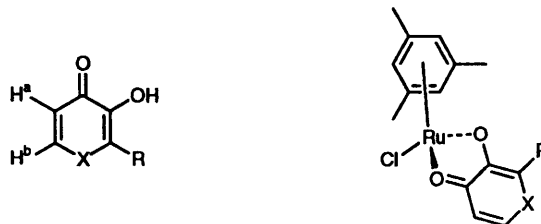
HL^1	X = O,	R = Me	**1**	X = O,	R = Me
HL^2	X = NMe,	R = Me	**2**	X = NMe,	R = Me
HL^3	X = NH,	R = Et	**3**	X = NH,	R = Et
HL^4	X = O,	R = Et	**4**	X = O,	R = Et

equilibrium between co-ordinated water and chloride. The observation of only one set of signals means the equilibrium must be rapid on the NMR time-scale. We believe this is also the case for complexes 1–3. The spectra and conductivity results show that the complexes are soluble in water and that the chloride is easily displaced by other ligands.

Complex **4** reacts with carbon monoxide in the presence of AgBF$_4$ to afford [Ru(mes)L^4(CO)][BF$_4$] **5**. In the ^{1}H NMR spectrum the methylene protons, though formally inequivalent, give rise to a single quartet at δ 2.83. The infrared spectrum exhibits an absorption at 2050 cm^{-1}, which is characteristic of a terminal Ru–CO. The FAB mass spectrum shows a weak cluster at m/z 389 for the molecular ion with the strongest peak being the $M - CO$ fragment at m/z 361.

Complexes **1** and **5** have also been characterised by X-ray diffraction. The molecular structures are shown in Figs. 1 and 2; selected bond lengths and angles are listed in Table 2, with fractional atomic coordinates in Tables 3 and 4. In both complexes the metal atom sits at the centre of a slightly distorted octahedron with the arene being η^6 co-ordinated, the deprotonated pyranonate ligand chelating through two oxygen atoms and the sixth site occupied by Cl or CO, respectively. In each structure two independent molecules are observed in the unit cell.

In complex **1** the Ru–Cl bond length, 2.420(2) Å, is identical in both molecules, and is similar to the Ru–Cl distances found in [Ru(mes)Cl(L)] (HL = amino acid) complexes, 2.439(3) and 2.420(2) Å (L = alaninate[10] or phenylglycinate[11]). In complex **5** the Ru–CO bond distance is 1.89(2) Å (average of the two independent molecules) which is the same as that found in [Ru(C$_6$H$_6$)(CO)(GeCl$_3$)$_2$], 1.87(2) Å,[12] and an average Ru–CO distance of 1.896 Å.[13] The average (terminal) Ru–C(8)–O(4) angle is nearly linear at 175.9(14)°.

In both complexes **1** and **5** the bond lengths of the pyranone

† Bio-organometallic Chemistry. Part 2.[1]

Table 1 Spectroscopic and analytical data for new compounds

		Analysis[b] (%)			
Complex	^{1}H NMR[a] (δ, J/Hz)	C	H	N	Mass spectrum[c]
1	2.25 (9 H, s, C$_6$Me$_3$), 2.40 (3 H, s, Me), 4.92 (3 H, s, C$_6$H$_3$), 6.48 (1 H, d, J 5, H^a), 7.55 (1 H, d, J 5, H^b)	46.60 (47.20)	4.55 (4.50)		382, 347
2	2.24 (9 H, s, C$_6$Me$_3$), 2.39 (3 H, s, Me), 3.56 (3 H, s, NMe), 4.85 (3 H, s, C$_6$H$_3$), 6.33 (1 H, d, J 7, H^a), 6.90 (1 H, d, J 7, H^b)	45.95 (45.30)	4.45 (4.85)	3.55 (3.20)	395, 360
3	1.05 (3 H, t, J 7, Me), 2.20 (9 H, s, C$_6$Me$_3$), 2.72 (2 H, m, CH$_2$), 4.84 (3 H, s, C$_6$H$_3$), 6.60 (1 H, d, J 7, H^a), 6.90 (1 H, d, J 7, H^b), 10.33 (1 H, br, NH)^d	43.65 (43.70)	4.95 (5.75)	3.60 (3.20)	395, 360
5	1.23 (3 H, t, J 7.5, Me), 2.26 (9 H, s, C$_6$Me$_3$), 2.83 (2 H, q, J 7.5, CH$_2$), 5.68 (3 H, s, C$_6$H$_3$), 6.67 (1 H, d, J 5, H^a), 7.85 (1 H, d, J 5, H^b)	42.65 (42.95)	3.65 (4.05)		389, 361
6^e	1.25 (3 H, t, J 7.5, Me), 2.20 (9 H, s, C$_6$Me$_3$), 2.87 (2 H, q, J 7.5, CH$_2$), 5.29 (3 H, s, C$_6$H$_3$), 6.63 (1 H, d, J 5, H^a), 8.03 (1 H, d, J 5, H^b)				
7	1.27 (3 H, t, J 7.5, Me), 2.02 (9 H, s, C$_6$Me$_3$), 2.90 (2 H, m, CH$_2$), 3.45 (3 H, m, NCH$_2$ + NH), 4.70 (3 H, s, C$_6$H$_3$), 6.65 (1 H, d, J 5, H^a), 7.3–7.5 (5 H, m, Ph), 7.81 (1 H, d, J 5, H^b)	49.55 (49.80)	5.20 (5.10)	2.75 (2.50)	468, 361^f

[a] In CDCl$_3$. [b] Calculated values in parentheses. [c] m/z Values for $[M]^+$ and $[M - \text{Cl}]^+$. [d] This resonance disappears on shaking with D$_2$O. [e] Spectrum run in D$_2$O; the complex was only characterised in solution. [f] m/z Values for $[M^+]$ and $[M - \text{NH}_2\text{CH}_2\text{Ph}]^+$.
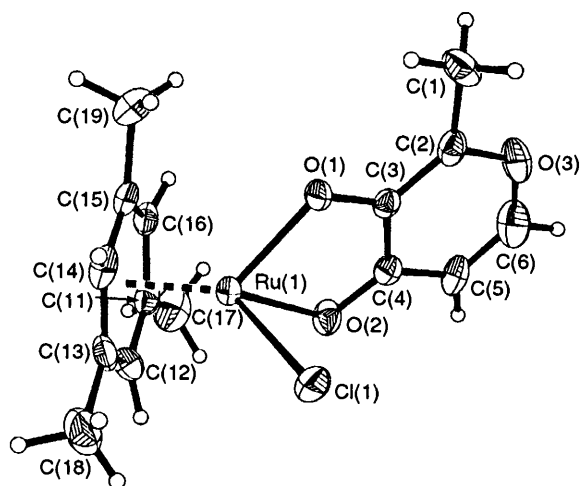
Fig. 1 Molecular structure of [Ru(mes)Cl(L^1)] **1** showing 30% probability displacement ellipsoids for all non-hydrogen atoms
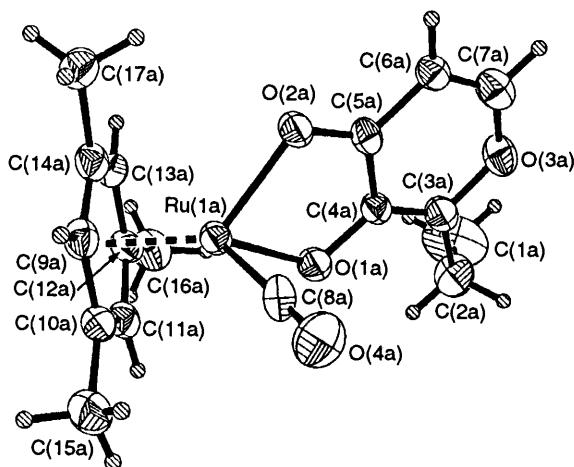
Fig. 2 Molecular structure of the cation [Ru(mes)L^4(CO)]$^+$ **5** showing 30% probability displacement ellipsoids for all non-hydrogen atoms

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1** and **5**

Complex 1

Molecule 1		Molecule 2	
Ru(1)–Cl(1)	2.420(2)	Ru(2)–Cl(2)	2.420(2)
Ru(1)–O(1)	2.091(4)	Ru(2)–O(1a)	2.090(5)
Ru(1)–O(2)	2.106(4)	Ru(2)–O(2a)	2.117(5)
Ru(1)–C(11)	2.158(7)	Ru(2)–C(11a)	2.166(7)
Ru(1)–C(12)	2.179(7)	Ru(2)–C(12a)	2.186(7)
Ru(1)–C(13)	2.197(8)	Ru(2)–C(13a)	2.194(7)
Ru(1)–C(14)	2.182(7)	Ru(2)–C(14a)	2.175(7)
Ru(1)–C(15)	2.165(7)	Ru(2)–C(15a)	2.163(7)
Ru(1)–C(16)	2.156(7)	Ru(2)–C(16a)	2.165(7)
O(1)–C(3)	1.306(8)	O(1a)–C(3a)	1.338(8)
O(2)–C(4)	1.276(8)	O(2a)–C(4a)	1.271(9)
C(3)–C(4)	1.441(9)	C(3a)–C(4a)	1.391(10)
Cl(1)–Ru(1)–O(1)	85.4(1)	Cl(2)–Ru(2)–O(1a)	85.5(1)
Cl(1)–Ru(1)–O(2)	83.6(1)	Cl(2)–Ru(2)–O(2a)	84.8(1)
O(1)–Ru(1)–O(2)	79.2(2)	O(1A)–Ru(2)–O(2a)	78.9(2)

Complex 5

Molecule a		Molecule b	
Ru(1a)–O(1a)	2.059(7)	Ru(1b)–O(1b)	2.085(7)
Ru(1a)–O(2a)	2.079(7)	Ru(1b)–O(2b)	2.105(7)
Ru(1a)–C(8a)	1.906(12)	Ru(1b)–C(8b)	1.870(12)
Ru(1a)–C(9a)	2.214(10)	Ru(1b)–C(9b)	2.187(12)
Ru(1a)–C(10a)	2.221(11)	Ru(1b)–C(10b)	2.291(11)
Ru(1a)–C(11a)	2.195(10)	Ru(1b)–C(11b)	2.270(11)
Ru(1a)–C(12a)	2.312(11)	Ru(1b)–C(12b)	2.214(11)
Ru(1a)–C(13a)	2.265(11)	Ru(1b)–C(13b)	2.221(10)
Ru(1a)–C(14a)	2.212(10)	Ru(1b)–C(14b)	2.244(11)
C(4a)–O(1a)	1.338(12)	C(4b)–O(1b)	1.330(13)
C(5a)–O(2a)	1.296(12)	C(5b)–O(2b)	1.278(12)
C(4a)–C(5a)	1.418(14)	C(4b)–C(5b)	1.433(15)
C(8a)–O(4a)	1.156(16)	C(8b)–O(4b)	1.138(15)
O(1a)–Ru(1a)–O(2a)	79.7(3)	O(1b)–Ru(1b)–O(2b)	80.5(3)
C(8a)–Ru(1a)–O(1a)	90.4(4)	C(8b)–Ru(1b)–O(1b)	92.4(4)
C(8a)–Ru(1a)–O(2a)	89.1(4)	C(8b)–Ru(1b)–O(2b)	89.5(4)
Ru(1a)–C(8a)–O(4a)	177.6(10)	Ru(1b)–C(8b)–O(4b)	174.1(10)

ligand are similar to those in the respective unco-ordinated pyranones[14,15] suggesting no delocalisation around the ring on co-ordination. Only one species is observed in solution and so the observation of two different molecules in the unit cell is presumably due to packing forces.

Attack of nucleophiles at co-ordinated carbon monoxide is well known.[16] For a number of complexes there is a correlation

between the CO stretching frequency and whether attack occurs at the CO; carbonyls having $\tilde{v}$(CO) greater than 2000 cm^{-1} usually react at the carbonyl.[17] The preparation of **5** and some of its reactions with nucleophiles are summarised in Scheme 1. Reaction of **5** with water was studied by dissolving the complex in D$_2$O and running the ^{1}H NMR spectrum. Immediately after dissolution two species are observed in a 1:1 ratio; these correspond to complex **5** and an aqua complex **6** in which the carbon monoxide has been replaced by water. After 2 h the ratio has changed to 1:2 in favour of **6** and after 2 d only **6** is observed. The identity of **6** has been confirmed by treating an aqueous solution of **4** with AgBF$_4$. Thus in the case of water as

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

Atom	x	y	z	Atom	x	y	z
Ru(1)	8 612(1)	1 825(1)	7 213(1)	Ru(2)	8 924(1)	1 902(1)	10 190(1)
Cl(1)	7 135(1)	2 071(1)	6 956(1)	Cl(2)	10 364(1)	2 141(1)	10 505(1)
O(1)	8 147(3)	2 182(3)	7 883(1)	O(1a)	9 484(3)	2 207(4)	9 536(2)
O(2)	8 665(3)	3 382(3)	7 190(2)	O(2a)	8 867(3)	3 468(3)	10 180(2)
O(3)	7 804(3)	4 561(4)	8 414(2)	O(3a)	9 765(3)	4 539(4)	8 950(2)
C(1)	7 548(5)	2 992(6)	8 788(2)	C(1a)	10 116(5)	2 980(7)	8 637(2)
C(2)	7 839(4)	3 552(5)	8 361(3)	C(2a)	9 780(5)	3 555(6)	9 039(3)
C(3)	8 107(4)	3 138(5)	7 947(2)	C(3a)	9 487(4)	3 183(5)	9 455(2)
C(4)	8 386(4)	3 774(5)	7 569(2)	C(4a)	9 156(4)	3 817(6)	9 795(3)
C(5)	8 332(5)	4 804(5)	7 648(3)	C(5a)	9 144(5)	4 860(6)	9 692(3)
C(6)	8 043(5)	5 140(6)	8 053(3)	C(6a)	9 433(5)	5 185(6)	9 287(3)
C(11)	9 920(4)	1 764(5)	6 948(3)	C(11a)	7 595(5)	1 899(6)	10 432(2)
C(12)	9 376(5)	1 405(6)	6 601(3)	C(12a)	8 113(5)	1 493(6)	10 789(2)
C(13)	8 791(5)	616(6)	6 705(3)	C(13a)	8 676(5)	699(6)	10 691(3)
C(14)	8 777(5)	223(5)	7 167(3)	C(14a)	8 712(5)	312(5)	10 229(3)
C(15)	9 331(5)	611(5)	7 521(2)	C(15a)	8 195(5)	718(5)	9 865(2)
C(16)	9 901(4)	1 367(5)	7 405(3)	C(16a)	7 627(4)	1 508(5)	9 970(2)
C(17)	10 512(5)	2 633(7)	6 856(3)	C(17a)	7 035(5)	2 773(6)	10 529(3)
C(18)	8 184(6)	224(7)	6 343(3)	C(18a)	9 252(5)	264(7)	11 063(3)
C(19)	9 262(6)	259(6)	8 019(3)	C(19a)	8 286(6)	362(6)	9 367(3)
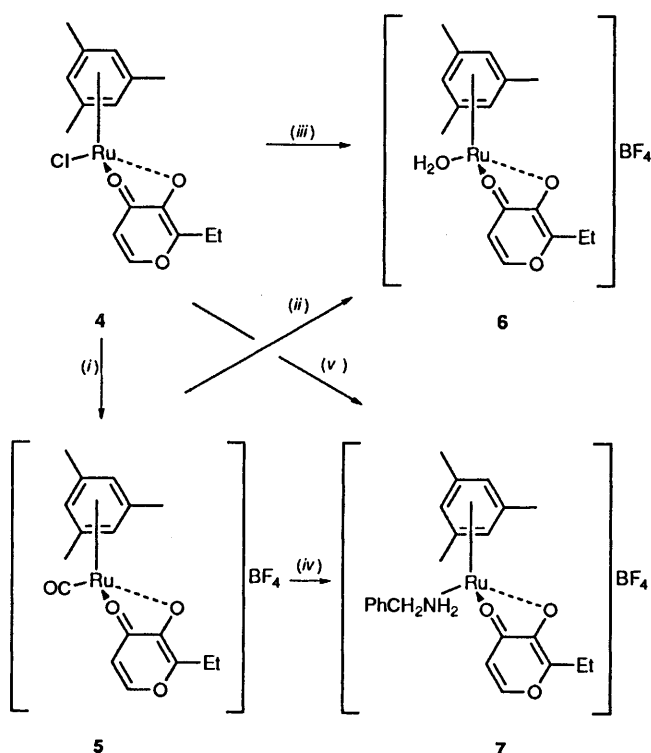
Scheme 1 (i) CO, AgBF$_4$; (ii) D$_2$O; (iii) D$_2$O, AgBF$_4$; (iv) PhCH$_2$-NH$_2$, Na$_2$CO$_3$; (v) PhCH$_2$NH$_2$, AgBF$_4$

a nucleophile, rather surprisingly given that $\tilde{v}$(CO) is at 2050 cm^{-1}, substitution rather than attack at carbonyl appears to have occurred. To test the generality of this observation a reaction with a nitrogen-based nucleophile was attempted.

Complex **5** was stirred with 1 equivalent of benzylamine in the presence of sodium carbonate. The infrared spectrum showed no absorptions between 2100 and 1700 cm^{-1} suggesting that substitution of the carbonyl has also occurred in this case. The ^{1}H NMR spectrum of the product displays signals due to the mesitylene protons at δ 2.02 and 4.70, a triplet at δ 1.27 and a complex multiplet at δ 2.90 due to the ethyl group, and two mutually coupled doublets at δ 7.81 and 6.65 also of the pyranone ligand. In addition, there is a multiplet at δ 3.45 (3 H) due to overlapping NH and CH$_2$ and a complex signal at δ 7.4 (5 H) indicating the presence of a benzylamine. The FAB mass spectrum shows a cluster at m/z 468 which corresponds to the

cation [Ru(mes)L^4(NH$_2$CH$_2$Ph)]$^+$. This confirms that the carbonyl has been replaced by the amine to form complex **7**. The complex can be synthesised independently by reaction of **4** with benzylamine in the presence of AgBF$_4$ and has an identical ^{1}H NMR spectrum to the sample prepared from **5**.

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 compound HL^3 was prepared using literature procedures[18] as were [{Ru(mes)Cl$_2$}$_2$][19] and [Ru(mes)-Cl(L^4)].[9] The reactions described were carried out under nitrogen; however, once isolated as pure solids the compounds are air-stable and precautions for their storage are unnecessary.

Proton NMR spectra were recorded on a Bruker AM300 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, infrared spectra on a Perkin-Elmer 580 spectrometer in dichloromethane solution.

Preparations

[Ru(mes)Cl(L^1)] 1. Sodium methoxide (18 mg, 0.34 mmol) and HL^1 (43 mg, 0.34 mmol) were added to a suspension of [{Ru(mes)Cl$_2$}$_2$] (100 mg, 0.17 mmol) in methanol–water (1:1) (30 cm^3) and the mixture was refluxed for 3 h. The solvent was removed and the residue dissolved in dichloromethane and filtered through Celite. The solvent was evaporated to give an orange-brown solid [Ru(mes)Cl(L^1)] **1** (102 mg, 77%).

[Ru(mes)Cl(L^2)] 2 and [Ru(mes)Cl(L^3)] 3. The procedure was the same as for complex **1** using [{Ru(mes)Cl$_2$}$_2$] (50 mg, 0.086 mmol) and gave orange-brown solids [Ru(mes)Cl(L^2)] **2** (126 mg, 93%) and [Ru(mes)Cl(L^3)] **3** (100 mg, 74%), respectively.

[Ru(mes)L^4(CO)][BF$_4$] 5. A solution of complex **4** (252 mg, 0.64 mmol) in dichloromethane (50 cm^3) was cooled to −78 °C and purged with carbon monoxide for 15 min. The salt AgBF$_4$ (124 mg, 0.64 mmol) was then added with carbon monoxide still bubbling through. The mixture was allowed to warm to room temperature and stirred for 2 h. It was then filtered and the solvent removed. The residue was recrystallised from

Table 4 Fractional atomic coordinates ($\times 10^4$) for complex **5**

Atom	x	y	z	Atom	x	y	z
Ru(1a)	0.441 06(10)	0.651 01(6)	0.410 84(2)	C(1b)	0.771(3)	0.988 0(18)	0.200 1(8)
Ru(1b)	0.983 99(10)	0.989 56(6)	0.373 47(2)	C(2b)	0.854 2(16)	1.046 9(17)	0.224 5(3)
O(1a)	0.519 3(9)	0.650 2(5)	0.351 77(19)	C(3b)	0.979 2(14)	0.981 4(10)	0.244 6(3)
O(2a)	0.475 4(8)	0.808 0(5)	0.402 12(19)	C(4b)	1.001 4(11)	0.971 8(8)	0.286 6(3)
O(3a)	0.610 6(9)	0.864 7(6)	0.286 84(22)	C(5b)	1.129 7(12)	0.924 0(9)	0.302 2(3)
O(4a)	0.134 3(11)	0.674 5(8)	0.377 0(3)	C(6b)	1.225 4(14)	0.882 3(9)	0.272 8(3)
C(1a)	0.784 8(24)	0.695 4(15)	0.256 4(7)	C(7b)	1.193 2(16)	0.891 7(12)	0.233 4(4)
C(2a)	0.626 5(18)	0.687 8(11)	0.268 2(3)	C(8b)	0.894 1(13)	0.861 2(10)	0.378 0(3)
C(3a)	0.588 2(14)	0.764 9(9)	0.299 4(3)	C(9b)	0.860 1(13)	1.116 8(9)	0.399 2(3)
C(4a)	0.539 7(12)	0.746 0(7)	0.337 6(3)	C(10b)	0.981 8(16)	1.165 0(9)	0.382 1(3)
C(5a)	0.517 8(11)	0.829 2(8)	0.365 2(3)	C(11b)	1.115 8(13)	1.129 1(8)	0.393 0(3)
C(6a)	0.541 9(11)	0.931 1(8)	0.350 7(3)	C(12b)	1.133 7(13)	1.047 4(8)	0.422 02(29)
C(7a)	0.586 5(13)	0.941 3(10)	0.312 4(4)	C(13b)	1.013 0(13)	1.006 3(8)	0.441 4(3)
C(8a)	0.250 9(14)	0.667 7(9)	0.389 5(3)	C(14b)	0.875 1(12)	1.041 7(9)	0.431 1(3)
C(9a)	0.371 3(14)	0.602 7(8)	0.472 9(3)	C(15b)	0.961 2(20)	1.247 7(10)	0.350 1(5)
C(10a)	0.366 0(13)	0.514 6(8)	0.445 9(3)	C(16b)	1.285 6(13)	1.006 9(10)	0.432 4(4)
C(11a)	0.492 9(14)	0.489 2(8)	0.424 5(3)	C(17b)	0.743 7(14)	0.994 8(11)	0.451 1(4)
C(12a)	0.625 3(13)	0.541 7(8)	0.430 9(3)	B(1a)	0.982 4(18)	0.232 2(12)	0.001 2(5)
C(13a)	0.623 5(13)	0.628 7(8)	0.457 09(29)	F(1a)	1.109 8(10)	0.283 6(6)	−0.004 29(28)
C(14a)	0.499 8(13)	0.660 4(8)	0.477 2(3)	F(2a)	0.878 7(11)	0.300 9(7)	0.010 7(3)
C(15a)	0.229 9(15)	0.454 8(11)	0.440 2(4)	F(3a)	0.937 8(13)	0.188 1(9)	−0.035 1(3)
C(16a)	0.754 6(15)	0.512 6(10)	0.407 2(4)	F(4a)	0.999 2(12)	0.156 2(8)	0.028 2(3)
C(17a)	0.501 9(17)	0.757 3(9)	0.503 9(3)	B(1b)	0.511 5(13)	0.252 0(7)	0.351 20(28)
O(1b)	0.908 2(8)	1.010 3(6)	0.313 06(20)	F(1b)	0.555 3(13)	0.179 8(7)	0.322 89(28)
O(2b)	1.151 8(8)	0.919 2(6)	0.341 27(20)	F(2b)	0.526 6(13)	0.212 7(7)	0.390 72(28)
O(3b)	1.077 5(11)	0.939 9(8)	0.218 39(24)	F(3b)	0.370 4(13)	0.276 1(7)	0.343 55(28)
O(4b)	0.841 5(10)	0.783 7(7)	0.384 2(3)	F(4b)	0.593 5(13)	0.339 2(7)	0.347 64(28)

dichloromethane–diethyl ether to give **5** as red crystals (251 mg, 88%).

Reaction of complex 5 with water. A sample of complex **5** was dissolved in D_2O and the reaction was monitored by ^1H NMR spectroscopy. The first spectrum indicated the presence of $[Ru(mes)L^4(CO)]^+$ and $[Ru(mes)L^4(D_2O)]^+$ in 1:1 ratio; after 2 h this had changed to 1:2 and after 2 d only $[Ru(mes)L^4(D_2O)]^+$ was visible in the NMR spectrum.

Reaction of complex 5 with benzylamine. Benzylamine (23 mg, 0.21 mmol) was added to a stirred solution of complex **5** (102 mg, 0.21 mmol) in dichloromethane (50 cm³); Na_2CO_3 (32 mg, 0.21 mmol) was then added and the mixture stirred for 1 h. It was then filtered and the residue recrystallised from methanol–diethyl ether to give $[Ru(mes)L^4(NH_2CH_2Ph)][BF_4]$ **7** as an orange crystalline solid (86 mg, 72%).

Complex **7** can also be prepared as follows. The salt $AgBF_4$ (51 mg, 0.26 mmol) was added to a solution of complex **4** (103 mg, 0.26 mmol) in dichloromethane (50 cm³), followed by addition of benzylamine (28 mg, 0.26 mmol). The mixture was stirred for 0.5 h and then filtered. The solvent was removed to afford **7** as an orange solid (117 mg, 90%).

Crystallography

Crystals of complex **1** were grown from dichloromethane–light petroleum and those of **5** from dichloromethane–diethyl ether.

Complex 1. *Crystal data.* $C_{15}H_{17}ClO_3Ru$, $M = 381.8$, orthorhombic, space group *Pbca*, $a = 15.448(2)$, $b = 13.505(1)$, $c = 28.431(2)$ Å, $U = 5931.4(9)$ Å³ (by least-squares refinement of optimised setting angles for 52 centred reflections with $4.75 < \theta < 12.5°$), $\lambda(Mo-K\alpha) = 0.7107$ Å, $Z = 16$ ($Z = 8$ for each unique molecule), $D_c = 1.710$ g cm⁻³, $F(000) = 3072$. Orange needle, crystal size $0.56 \times 0.23 \times 0.11$ mm, $\mu(Mo-K\alpha) = 12.4$ cm⁻¹.

Data collection and processing. Siemens P4 diffractometer, ω mode with ω-scan width $= 0.8°$, ω-scan speed 3.0–30.0° min⁻¹; 6240 reflections measured $(4.0 \leqslant 2\theta \leqslant 49°$; $−1 \leqslant h \leqslant 19$,

$−1 \leqslant k \leqslant 15$, $−36 \leqslant l \leqslant 1$), 5071 independent reflections (merging $R_{int} = 0.033$) giving 3285 with $F > 4\sigma(F)$.

Structure analysis and refinement. Direct methods. Full-matrix least-squares refinement based on F using the program package SHELXTL-PC[20] with all non-hydrogen atoms anisotropic and hydrogens in calculated positions (C–H 0.96 Å) with one overall fixed U_{iso} ($= 0.08$ Å²). The weighting scheme $w = 1/[\sigma^2(F) + 0.0003F^2]$ gave final values of $R = 0.0426$ and $R' = 0.0457$.

Complex 5. *Crystal data.* $C_{17}H_{19}BF_4O_4Ru$, $M = 475.21$, monoclinic, space group $P2_1/c$, $a = 12.960(5)$, $b = 32.38(2)$, $c = 9.33(1)$ Å, $\beta = 91.03(5)°$, $U = 3915(7)$ Å³ (by least-squares refinement of optimised setting angles of 474 zero- and upper-layer reflections), $\lambda(Mo-K\alpha) = 0.7107$ Å, $Z = 8$ ($Z = 4$ for each unique molecule), $D_c = 1.61$ g cm⁻³, $F(000) = 1904$. Orange needle, crystal size $0.96 \times 0.24 \times 0.20$ mm, $\mu(Mo-K\alpha) = 7.66$ cm⁻¹.

Data collection and processing. Stoe STADI-2 diffractometer, ω mode with ω-scan width $= 2.1 + 0.7 \sin (\mu)/\tan (\nu)$, ω-scan speed 15° min⁻¹ minimum (increased above 1000 cycles s⁻¹ in order to optimise the data collection time and maintain constant precision); 9544 reflections measured $(7 \leqslant 2\theta \leqslant 50°$; $0 \leqslant h \leqslant 10$, $0 \leqslant k \leqslant 15$, $−38 \leqslant l \leqslant 38$), 6618 independent reflections (merging $R_{int} = 0.022$), 4000 data used with $I > 2.5\sigma(I)$.

Structure analysis and refinement. Direct methods, SHELXS 86.[21] Full-matrix least-squares refinement based on F using the program package SHELX 76[21] with all non-hydrogen atoms anisotropic and hydrogens in calculated positions (C–H 0.95 Å) with group isotropic displacement parameters. One of the BF_4 ions was approximately ordered, the other gave high isotropic displacement parameters and apparent alternative sites. Refinement of a disordered model marginally improved the R factor but gave further alternative sites. The coordinates of BF_4 (b) are the dominant positions of a disordered ion. The weighting scheme $w = 1/[\sigma^2(F) + 0.0113F^2]$ gave final values of $R = 0.0676$ and $R' = 0.0708$.

Complete atomic coordinates, thermal parameters and bond

lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Acknowledgements

References

1 A. P. Abbott, G. Capper, D. L. Davies, J. Fawcett and D. R. Russell, *J. Chem. Soc., Dalton Trans.*, 1994, 3709.

2 G. Jaouen, A. Vessieres and I. S. Butler, *Acc. Chem. Res.*, 1993, **26**, 361; G. Jaouen and A. Vessieres, *Pure Appl. Chem.*, 1989, **61**, 565.

3 M. Barton and J. D. Atwood, *J. Coord. Chem.*, 1991, **24**, 43.

4 D. F. Dersnah and M. C. Baird, *J. Organomet. Chem.*, 1977, **127**, C55.

5 R. Krämer, K. Polborn, H. Wanjek, I. Zahn and W. Beck, *Chem. Ber.*, 1990, **123**, 767; W. Beck and R. Krämer, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1467; R. Krämer, M. Maurus, R. Bergs, K. Polborn, K. Sünkel, B. Wagner and W. Beck, *Chem Ber.*, 1993, **126**, 1969; D. Carmona, A. Medoza, F. J. Lahoz, L. A. Oro, M. P. Lamata and E. San Jose, *J. Organomet. Chem.*, 1990, **396**, C17; W. S. Sheldrick and S. Heeb, *J. Organomet. Chem.*, 1989, **377**, 357; *Inorg. Chim. Acta*, 1990, **168**, 93.

6 W. O. Nelson, T. B. Karpishin, S. J. Rettig and C. Orvig, *Inorg. Chem.*, 1988, **27**, 1045; M. W. Finnegan, S. J. G. Lutz, W. O. Nelson and C. Orvig, *Inorg. Chem.*, 1987, **26**, 2171; R. C. Hider and A. D. Hall, *Prog. Med. Chem.*, 1991, **28**, 41.

7 R. C. Hider and A. D. Hall, *Perspect. Bioinorg. Chem.*, 1991, **1**, 209.

8 A. M. El-Hendawy, *Transition Met. Chem.*, 1992, **17**, 250.

9 L. C. Carter, D. L. Davies, J. Fawcett and D. R. Russell, *Polyhedron*, 1993, **12**, 1599.

10 L. C. Carter, D. L. Davies, K. T. Duffy, J. Fawcett and D. R. Russell, *Acta Crystallogr., Sect. C*, 1994, **50**, 1559.

11 G. Capper, D. L. Davies, J. Fawcett and D. R. Russell, unpublished work.

12 L. Y. Y. Chan and W. A. G. Graham, *Inorg. Chem.*, 1975, **14**, 1778.

13 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1989, S1.

14 J. Burgess, J. Fawcett, M. A. Llewellyn, S. A. Parsons and D. R. Russell, unpublished work.

15 S. D. Brown, J. Burgess, J. Fawcett, S. A. Parsons, D. R. Russell and E. Waltham, *Acta Crystallogr., Sect. C*, 1995, **51**, 1335.

16 P. C. Ford and A. Rokicki, *Adv. Organomet. Chem.*, 1988, **28**, 139.

17 R. J. Angelici, *Acc. Chem. Res.*, 1972, **5**, 335; R. J. Angelici, P. A. Christian, B. D. Dombek and G. A. Pfeffer, *J. Organomet. Chem.*, 1974, **67**, 287.

18 W. O. Nelson, T. B. Karpishin, S. J. Rettig and C. Orvig, *Can. J. Chem.*, 1988, **66**, 123.

19 J. W. Hull, jun. and W. L. Gladfelter, *Organometallics*, 1984, **3**, 605.

20 G. M. Sheldrick, SHELXTL-PC. Release 4.2, Siemens Analytical X-Ray Instruments Inc., Madison, WI, 1991.

21 G. M. Sheldrick, programs for crystal structure determination, SHELX 76, University of Cambridge, 1976; SHELXS 86, University of Göttingen, 1986.