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Reactions of $[Ru\text{-}(\eta\text{-}C_6H_6)Cl(O_2CCF_3)]$ with α-pyridone and related ligands: X-ray crystal structure of $[Ru(\eta\text{-}C_6H_6)Cl(C_6H_6NO)]$

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Abstract

The reaction of $[Ru(\eta\text{-}C_6H_6)Cl(O_2CCF_3)]$ (**1**) with 6-methyl- or 6-chloro-hydroxypyridine at room temperature gives the products $[Ru(\eta\text{-}C_6H_6)Cl(C_6H_6NO)]$ (**2**) and $[Ru(\eta\text{-}C_6H_6)Cl(C_5H_3NOCl)]$ (**3**), respectively. The structure of **2** has been established by *X*-ray diffraction. The crystals are orthorhombic, space group $P2_12_12_1$ with *a* 6.844(2) *b* 10.975(4) and *c* 15.363(5) Å. In contrast, reaction with the parent α-pyridone at room temperature gives a low yield of $[Ru(\eta\text{-}C_6H_6)Cl_2(C_5H_4NHO)]$ (**4**), in which the ligand is bound to the metal through the pyridone oxygen atom. Prolonged reflux converts **4** into $[Ru(\eta\text{-}C_6H_6)Cl(C_5H_4NO)]$ (**5**), in which the ligand is an anionic chelate. Variable temperature ^1H NMR measurements show that **5** is fluxional in strongly coordinating solvents.

The reactions of $[Ru(\eta\text{-arene})Cl_2]_2$ compounds with a variety of chelating anionic ligands have been studied in recent years. For example, the reaction of $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ with thallium (I) acetylacetonate gives the neutral compound $[Ru(\eta\text{-}C_6H_6)Cl(acac)]$ [1]; the reactions of $[Ru(\eta\text{-arene})Cl_2]_2$ with a variety of dithiophosphinate salts give products of two types, $[Ru(\eta\text{-arene})Cl(S_2PR_2)]$ and $[Ru(\eta\text{-arene})(S_2PR_2)_2]$ [2,3]; recently [4] we reported the preparation of a variety of complexes of the types $[Ru(\eta\text{-arene})Cl(O_2CR)]$ and $[Ru(\eta\text{-arene})(O_2CR_2)_2]$. Several of these complexes have been shown to be fluxional by multinuclear NMR spectroscopy [5]. In an extension to our earlier work we now report the reactions of $[Ru(\eta\text{-}C_6H_6)Cl(O_2CCF_3)]$ with ligands related to α-pyridone.

Results and discussion

Our initial attempts to isolate clean products from the reactions of the dimers $[Ru(\eta\text{-arene})Cl_2]_2$ with α-pyridone and related ligands were unsuccessful. Therefore, as we had previously shown [4,5] that the compound $[Ru(\eta\text{-}C_6H_6)Cl(O_2CCF_3)]$ was

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a useful precursor to a wide variety of mononuclear and binuclear η-benzeneruthenium(II) compounds, all further synthetic procedures utilised this starting material.

On treating **1** with an excess of α-pyridone in methanol at room temperature an orange solution is formed. Concentration and cooling of that solution deposits the product as an orange microcrystalline solid. The infrared spectrum of the product contains bands at 1618 and 3439 cm^{-1} which are assigned to the ν(C=O) and ν(N–H) stretching modes of the ligand coordinated as its neutral pyridone tautomer. The ^1H NMR spectrum contains a singlet resonance at δ 5.98 ppm, due to the π-bonded benzene, and signals due to the aromatic protons of the pyridyl ring at δ 6.16, 6.29 and 7.37 ppm. An additional broad singlet at δ 11.56 ppm is due to a proton bound to the pyridyl nitrogen atom. Integration of the ^1H NMR signals shows the ratio of C_6H_6/C_5H_4NHO is 1/1. These data together with the results of elemental analyses are consistent with the formulation $[Ru(\eta\text{-}C_6H_6)Cl_2(C_5H_4NHO)]$ (**4**). Confirmatory evidence for this formulation is provided by the mass spectrum of the compound, recorded at 70 keV, which exhibits a parent ion peak at *m/e* 345, corresponding to the cation $[Ru(\eta\text{-}C_6H_6)Cl_2(C_5H_4NHO)]^+$; fragmentation peaks due to the successive loss of two chloride ions are also observed.

When **4** is redissolved in methanol and the solution refluxed for 3 h a new compound is formed. The infrared spectrum of this product does not contain bands due to ν(C=O) and ν(N–H) stretching modes. The room temperature ^1H NMR spectrum contains a singlet resonance at δ 5.97 ppm and pyridyl resonances at δ 6.09, 6.47, 7.36 and 7.95 ppm. No resonance due to N*H* could be detected. The highest peak in the mass spectrum was observed at *m/e* 309, and was attributed to the cation $[Ru(\eta\text{-}C_6H_6)Cl(C_5H_4NO)]^+$. These spectroscopic data together with the results of elemental analyses indicate that the product obtained was $[Ru(\eta\text{-}C_6H_6)Cl(C_5H_4NO)]$ (**5**), in which the α-pyridone derived ligand is now an anionic chelate. An identical product is obtained in substantially higher yield by refluxing **1** with an excess of α-pyridone in methanol (see Experimental Section).

Although in the complexes $[Ru(\eta\text{-}C_6H_6)(S\text{–}S)_2]$ ($S\text{–}S = S_2PMe_2$, S_2PPh_2 or $S_2P(OEt)_2$) the unidentate and bidentate dithioacid ligands do not undergo rapid intramolecular exchange on the NMR time scale at room temperature [2], the acetato complexes $[Ru(\eta\text{-arene})Cl(O_2CR)]$ and $[Ru(\eta\text{-}C_6Me_6)(O_2CMe)_2]$ are known to undergo ionic dissociation and temperature-dependent equilibration involving solvent molecules [4]. The ^1H NMR spectrum of $[Ru(\eta\text{-}C_6H_6)Cl(C_5H_4NO)]$ shows only one $\eta\text{-}C_6H_6$ resonance at room temperature, but the behaviour of the spectrum between 25 and −70 °C (four $\eta\text{-}C_6H_6$ resonances, at δ 5.97, 5.78, 5.73 and 5.59 ppm, are observed below −40 °C) indicates that similar scrambling processes are occurring (eq. 1–3).

$$[Ru(\eta\text{-}C_6H_6)Cl(C_5H_4NO)] \rightleftharpoons [Ru(\eta\text{-}C_6H_6)Cl(\sigma\text{-}ONC_5H_4)(S)] \quad (1)$$

$$[Ru(\eta\text{-}C_6H_6)Cl(C_5H_4NO)] \rightleftharpoons [Ru(\eta\text{-}C_6H_6)Cl(\sigma\text{-}NOC_5H_4)(S)] \quad (2)$$

$$[Ru(\eta\text{-}C_6H_6)Cl(C_5H_4NO)] \underset{(S = \text{solvent})}{\rightleftharpoons} [Ru(\eta\text{-}C_6H_6)Cl(S)_2]^+ + [C_5H_4NO]^- \quad (3)$$

On treatment of **1** with an excess of 6-methylhydroxypyridine in methanol, an orange product is formed in moderate (60%) yield. The infrared spectrum contains bands due to the anionic form of the ligand, and a single ν(Ru–Cl) stretch at 281

cm^{-1}. The ^1H NMR spectrum contains a singlet resonance at δ 5.92 ppm, pyridyl resonances at δ 7.23, 6.29 and 5.65 ppm, and a singlet at δ 2.41 ppm due to the methyl group in the six position on the pyridyl ring. Integration of the NMR spectrum indicates a $C_6H_6/[C_6H_6NO]^-$ ratio of 1/1. The mononuclear nature of the product is indicated by the appearance of the parent ion peak in the mass spectrum at *m/e* 323, due to the cation $[Ru(\eta\text{-}C_6H_6)Cl(C_6H_6NO)]^+$; fragmentation patterns corresponding to $[Ru(\eta\text{-}C_6H_6)Cl]^+$, $[Ru(\eta\text{-}C_6H_6)(C_6H_6NO)]^+$ and $[Ru(\eta\text{-}C_6H_6)]^+$ are also observed. These data, together with elemental analyses, indicate that the product of this reaction is $[Ru(\eta\text{-}C_6H_6)Cl(C_6H_6NO)]$ (**2**), in which the anion derived from 6-methylhydroxypyridine is a chelating ligand. The structure of the molecule has been confirmed by X-ray crystallography, vide infra. When the reaction described above is carried out with 6-chlorohydroxypyridine a strictly analogous product, $[Ru(\eta\text{-}C_6H_6)Cl(C_5H_3NOCl)]$ (**3**), is obtained.

Crystal structure of [Ru(η-C_6H_6)Cl(C_6H_6NO)]

Details of the solution of the structure are given in the Experimental Section. Selected bond distances and angles are presented in Table 3 and final atomic coordinates in Table 4. The structure of $[Ru(\eta\text{-}C_6H_6)Cl(C_6H_6NO)]$ is shown in Fig. 1. The geometry about the ruthenium ion is that of a distorted tetrahedron with the η-arene ring and the other ligands adopting a "piano stool" configuration. The complex has a similar arrangement to that of several $[Ru(\eta\text{-arene})Cl_2L]$ and $[Ru(\eta\text{-arene})Cl_2L]^+$ molecules [4,6]. The ring centroid of the η-benzene is 1.64 Å from the ruthenium atom. This compares with values of 1.62–1.68 Å in the (η-benzene)ruthenium(II) complexes $[\{Ru(\eta\text{-}C_6H_6)(OH)\}_4][SO_4]_2 \cdot 12H_2O$ and $[Ru_4(\eta\text{-}C_6H_6)_4(OH)_4(O)][BPh_4]_2 \cdot 2Me_2CO$ [7,8]. The Ru–C bonds lie in the range 2.152–2.175 Å. The Ru–Cl bond length, 2.392(2) Å, is closely similar to that found in related molecules [4,6,9]. The six atoms of the pyridyl ring are coplanar, the

Table 1

Hydrogen-1 NMR data for some ruthenium(II) complexes at 298 K

Compound	Solvent	δ(ppm) [a]	
		η-arene	others
$[Ru(\eta\text{-}C_6H_6)Cl_2(C_5H_4NHO)]$	$(CD_3)_2SO$	5.98(s)	6.16(t) 6.29(d) 7.37(m) [b] 11.56(s,N*H*)
$[Ru(\eta\text{-}C_6H_6)Cl(C_5H_4NO)]$	$CDCl_3$	5.97(s)	6.09(d) 6.47(t) 7.36(t) 7.95(d)
$[Ru(\eta\text{-}C_6H_6)Cl(C_5H_3NOCl)]$	$(CD_3)_2SO$	6.00(s)	5.90(d) 6.67(d) 7.48(t)
$[Ru(\eta\text{-}C_6H_6)Cl(C_6H_6NO)]$	$(CD_3)_2SO$	5.92(s)	5.65(d) 6.29(d) 7.23(t) 2.41(s,CH_3)

[a] Chemical shifts in ppm relative to internal $SiMe_4$. [b] Overlapping doublet and triplet.

Table 2

Microanalytical data for some ruthenium(II) complexes

Compound	Analyses (Found (calcd.) (%))			
	C	H	N	Cl
$[Ru(\eta\text{-}C_6H_6)Cl_2(C_5H_4NHO)]$	37.9	3.2	4.1	20.0
	(38.3)	(3.2)	(4.1)	(20.6)
$[Ru(\eta\text{-}C_6H_6)Cl(C_5H_4NO)]$	40.8	3.2	4.5	11.5
	(42.3)	(3.2)	(4.5)	(11.5)
$[Ru(\eta\text{-}C_6H_6)Cl(C_5H_3NOCl)]$	38.7	3.0	3.9	21.1
	(38.3)	(3.2)	(4.1)	(20.6)
$[Ru(\eta\text{-}C_6H_6)Cl(C_6H_6NO)]$	44.5	3.8	4.3	10.6
	(44.7)	(3.7)	(4.3)	(11.0)

Table 3

Selected bond distances (Å) and angles (°) for the compound $[Ru(\eta\text{-}C_6H_6)Cl(C_6H_6NO)]$ (with standard deviations in parentheses)

Ru(1)-Cl(1)	2.392(2)	Ru(1)-O(1)	2.120(5)
Ru(1)-N(1)	2.091(5)	Ru(1)-C(11)	2.157(8)
Ru(1)-C(12)	2.161(7)	Ru(1)-C(13)	2.166(8)
Ru(1)-C(14)	2.171(7)	Ru(1)-C(15)	2.175(7)
Ru(1)-C(16)	2.152(7)	O(1)-C(1)	1.315(9)
N(1)-C(1)	1.355(8)	N(1)-C(5)	1.337(8)
C(1)-C(2)	1.374(9)	C(2)-C(3)	1.384(10)
C(3)-C(4)	1.405(11)	C(4)-C(5)	1.386(10)
C(5)-C(6)	1.485(11)	C(11)-C(12)	1.395(13)
C(11)-C(16)	1.448(11)	C(12)-C(13)	1.433(13)
C(13)-C(14)	1.417(12)	C(14)-C(15)	1.393(12)
C(15)-C(16)	1.386(11)		
Ru(1)-N(1)-C(1)	93.7(4)	Cl(1)-Ru(1)-N(1)	85.4(1)
Ru(1)-O(1)-C(1)	93.7(4)	Cl(1)-Ru(1)-O(1)	85.9(1)
N(1)-C(1)-O(1)	109.8(5)	N(1)-Ru(1)-O(1)	62.5(2)
N(1)-C(1)-C(2)	122.1(6)	C(4)-C(5)-C(6)	123.7(6)
C(1)-C(2)-C(3)	117.0(7)	C(4)-C(5)-N(1)	118.1(7)
C(2)-C(3)-C(4)	120.2(7)	C(5)-N(1)-C(1)	122.3(6)
C(3)-C(4)-C(5)	120.3(7)	C(5)-N(1)-Ru(1)	143.4(5)

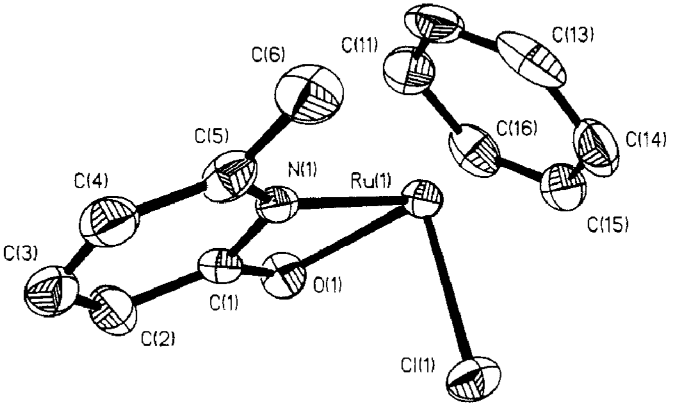


Fig. 1. The molecular structure of $[Ru(\eta\text{-}C_6H_6)Cl(C_6H_6NO)]$.

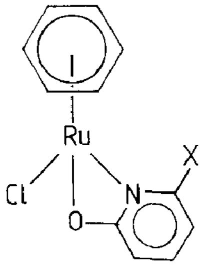
Table 4

Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for the compound $[\text{Ru}(\eta\text{-}C_6H_6)\text{Cl}(C_6H_6NO)]$

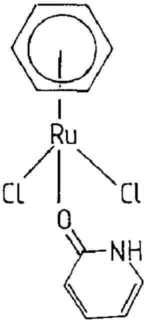
	x	y	z	U_{eq}^{a}
Ru(1)	8539(1)	7437(1)	2157(1)	24(1)
Cl(1)	7526(3)	9077(2)	3078(1)	41(1)
O(1)	11431(7)	7972(4)	2470(3)	32(1)
N(1)	9786(8)	6700(5)	3282(3)	25(1)
C(1)	11458(9)	7352(6)	3202(4)	29(2)
C(2)	12865(11)	7361(7)	3840(5)	41(2)
C(3)	12522(13)	6651(7)	4570(5)	42(2)
C(4)	10785(12)	5976(7)	4641(5)	40(2)
C(5)	9410(12)	6008(6)	3979(4)	34(2)
C(6)	7537(12)	5326(7)	4003(5)	44(2)
C(11)	9338(15)	6385(8)	1026(5)	53(3)
C(12)	8001(14)	5716(7)	1517(5)	48(3)
C(13)	6173(15)	6243(8)	1772(5)	56(3)
C(14)	5713(11)	7449(8)	1516(5)	50(2)
C(15)	7027(13)	8107(7)	1007(5)	43(2)
C(16)	8809(12)	7609(7)	767(5)	43(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

maximum deviation from that plane being 0.005 Å. Both the Ru–O and Ru–N bonds, 2.120(5) and 2.091(5) Å, respectively, are somewhat longer than those observed in compounds in which the anion of 6-methylhydroxypyridine is coordinated in the less sterically demanding bridging mode [10]. The bite angle at ruthenium O(1)–Ru(1)–N(1) (62.5(2)°), is small compared with the angles (Cl(1)–Ru(1)–N(1), (85.4(1)°), and Cl(1)–Ru(1)–O(1), (85.9(1)°). That angle is, however, fairly similar to those in related chelating pyridinethiolate complexes of ruthenium(II) [11]. Finally there are no obvious steric consequences of the methyl group on the pyridyl ring, and we thus assume that the structures of **3** and **5** are closely related to that of **2**.



(2: X = Me;
3: X = Cl;
5: X = H)



(4)

Experimental

Microanalyses were by carried out in the Chemistry Department, University College London. Infrared spectra were recorded in the range 250–4000 cm^{-1} on a Perkin–Elmer 983 grating spectrometer with Nujol mulls on caesium iodide plates. Hydrogen-1 NMR spectra were recorded on a Varian XL200 spectrometer. Mass spectra were determined by the University of London Intercollegiate Research Service at the School of Pharmacy.

Materials

$[Ru(\eta\text{-}C_6H_6)Cl(O_2CCF_3)]$ was prepared from $[Ru(\eta\text{-}C_6H_6)Cl_2]_2$ by a published method [4]. All other reagents were obtained from commercial suppliers.

All reactions were carried out in degassed solvents under nitrogen. ^1H NMR data are presented in Table 1 and analytical data in Table 2.

(η-Benzene)dichloro(hydroxypyridine)ruthenium(II)

$[Ru(\eta\text{-}C_6H_6)Cl(O_2CCF_3)]$ (0.20 g, 0.6 mmol) was added to a solution of 2-hydroxypyridine (0.20 g, 2.1 mmol) in methanol (20 cm^3). The mixture was stirred for 12 h. The orange solution was filtered to remove any unchanged starting materials. The filtrate was evaporated under reduced pressure to ca. half its volume then kept at 0 °C for 6 h, to give crystals of the product, which was filtered off, washed with diethyl ether, and air dried; the yield was 0.08 g (38%) (ν(CO) 1618 cm^{-1}, ν(NH) 3439 cm^{-1}, ν(RuCl) 310 cm^{-1}).

(η-Benzene)chloro(hydroxypyridinato)ruthenium(II)

A suspension of $[Ru(\eta\text{-}C_6H_6)Cl(O_2CCF_3)]$ (0.20 g, 0.6 mmol) in methanol (20 cm^3) containing 2-hydroxypyridine (0.38 g, 4.0 mmol) was refluxed for 7 h. The yellow/brown solution was filtered hot and concentrated to ca. half volume under reduced pressure. A light brown solid which separated was filtered off and dried in vacuo at ca. 90 °C. Yield 0.14 g (66%) (ν(RuCl) 281 cm^{-1}).

(η-Benzene)chloro(6-methylhydroxypyridinato)ruthenium(II)

$[Ru(\eta\text{-}C_6H_6)Cl(O_2CCF_3)]$ (0.20 g, 0.6 mmol) was added to a solution of 6-methyl-2-hydroxypyridine (0.20 g, 1.8 mmol) in methanol (15 cm^3) and the mixture stirred at 22 °C for 16 h. The orange solution was filtered, evaporated under reduced pressure to a volume of 5 cm^3, then kept at 0 °C. The orange precipitate formed was filtered off, washed with cold methanol (2 × 2 cm^3), and dried in vacuo. Yield 0.12 g (60%) (ν(Ru–Cl) 280 cm^{-1}).

(η-Benzene chloro(6-chloro-2-hydroxypyridinato)ruthenium(II)

This complex was prepared similarly by reaction with 6-chloro-2-hydroxypyridine. Yield 0.18 g (85%) (ν(RuCl) 283 cm^{-1}).

Crystal structure determination of $[Ru(\eta\text{-}C_6H_6)Cl(C_6H_6NO)]$

Crystal data: $C_{12}H_{12}NOClRu$, $M = 322.5$, orthorhombic, a 6.844(2), b 10.975(5), c 15.363(5) Å, U 1152 $Å^3$, D_c 1.86 g cm^{-3}, $Z = 4$, μ(Mo-K_α) 15.0 cm^{-1}, $F(000)$ 640, λ(Mo-K_α) 0.71069 Å, space group $P2_12_12_1$ from systematic absences.

Intensities were collected on a Nicolet R3m/V diffractometer for 1223 independent reflections; the solution and refinement are based on 1128 with $|F_o| > 3\sigma|F_o|$. The position of the ruthenium atom was deduced from a Patterson synthesis and the remaining nonhydrogen atoms were located by subsequent difference electron synthesis. Refinement of the structure by full matrix least squares reduced R to 0.043 in four cycles with all nonhydrogen atoms refined anisotropically. A weighting scheme of the form $w = 1/(\sigma^2(F) + 0.00134\ F^2)$ was applied for a final cycle and gave $R = 0.0322$ ($R' = 0.0352$). The maximum shift/error ratio at this stage was 0.04, and no peaks in the final difference electron density synthesis were greater than 0.65 $e\text{Å}^{-3}$. Final fractional coordinates are given in Table 4. Tables of observed and calculated structure factors and a full list of positional and thermal parameters are available on request from the authors. Crystallographic calculations used the SHELXTL PLUS program package [12].

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