BINUCLEAR DI-μ-HYDROXO- AND DI-μ-METHOXO-PENTAMETHYLCYCLOPENTADIENYL DERIVATIVES OF RHODIUM AND IRIDIUM WITH PYRIDINE TYPE LIGANDS. CRYSTAL STRUCTURE OF [{(C$_5$Me$_5$)Rh(py)}$_2$(μ-OH)$_2$][ClO$_4$]$_2$ (py = PYRIDINE) *

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Summary

The reaction of [{(C$_5$Me$_5$)M}$_2$(μ-OH)$_3$]$^+$ cations (M = Rh, Ir) with aqueous perchloric or tetrafluoroboric acids and pyridine type ligands (L) yields the binuclear cationic complexes [{(C$_5$Me$_5$)ML}$_2$(μ-OH)$_2$]$^{2+}$, when acetone is used as solvent, but the di-μ-methoxo complexes, [{(C$_5$Me$_5$)M(py)}$_2$(μ-OMe)$_2$]$^{2+}$, in methanol. The structure of the di-μ-hydroxorhodium complex was determined by X-ray crystallography and has an internal symmetry centre and an intermetallic separation of 3.308(1) Å.

Introduction

The tri-μ-hydroxo cations [{(C$_5$Me$_5$)M}$_2$(μ-OH)$_3$]$^+$ (M = Rh or Ir), first prepared by Maitlis et al. [1] are valuable starting materials for the synthesis of binuclear complexes containing a variety of bridging ligands containing oxygen or nitrogen donors [2]. In particular we recently reported the synthesis and structural

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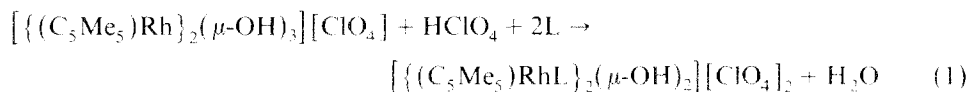* Dedicated to Professor Rafael Usón on the occasion of his 60th birthday.
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characterisation of several mixed-bridged hydroxo- and methoxo-pyrazolate compounds [2c]. The proposed mechanism of the reactions used in the preparations involves the protonation of the μ-hydroxo groups by weak acids such as aniline [2b], pyrazole [2c,d] or alcohols [2a,c]. Wieghardt et al. have shown that the related tri-μ-hydroxo cation $[\{(tacn)Rh\}_2(\mu\text{-}OH)_3]^3$ (tacn = 1,4,7-triazacyclononane) can be protonated in aqueous solution and that this leads to formation of the di-μ-hydroxo solvated cation $[\{(tacn)Rh(H_2O)\}_2(\mu\text{-}OH)_2]^{4-}$ [3].

The present paper presents the results of an investigation on the reaction of the tri-μ-hydroxo complexes $[\{(C_5Me_5)M\}_2(\mu\text{-}OH)_3]^{-}$ (M = Rh or Ir) with strong mineral acids ($HClO_4$, HBF_4) in the presence of pyridine type ligands.

Results and discussion

The tri-μ-hydroxorhodium perchlorate complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OH)_3][ClO_4]$ [2c] reacts in acetone with aqueous perchloric acid in the presence of pyridine type ligands to give di-μ-hydroxo compounds according to eq. 1:

$$[\{(C_5Me_5)Rh\}_2(\mu\text{-}OH)_3][ClO_4] + HClO_4 + 2L \rightarrow$$

$$[\{(C_5Me_5)RhL\}_2(\mu\text{-}OH)_2][ClO_4]_2 + H_2O \qquad (1)$$

(L = pyridine (py) (I), 2-methylpyridine (2 Mepy) (II), 3-methylpyridine (3 Mepy) (III), 4-ethylpyridine (4 Etpy) (IV), 4-n-propylpyridine (4 Pr^{n}py) (V), 4-benzylpyridine (4 Bzpy) (VI), 2-methoxypyridine (2 MeOPy) (VII))
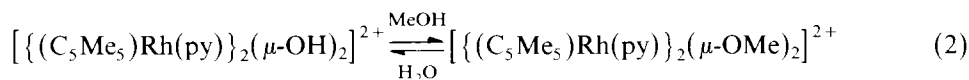
The IR spectra of the solids show a new band, in the 1580–1620 cm^{-1} region, assigned to the ν(CN) vibration of the coordinated pyridine ligand, along with a strong absorption at ca. 3500 cm^{-1} attributed to the remaining μ-hydroxo groups, as well as the typical perchlorate bands of T_d symmetry at ca. 1100 and 620 cm^{-1}. The ^{1}H NMR spectra of the soluble complexes, III and V, show the presence of coordinated pyridine (ring protons: 9.06, 8.98, 8.14 and 7.35 ppm (III) and 9.05 and 7.80 ppm (V)), the C_5Me_5 groups (1.20 (III) and 1.18 ppm (V)), as well as the bridging hydroxo ligands (δ 3.79 ppm for III and V). These spectroscopic observations and the microanalytical results (Table 1) suggest that the products should be formulated as di-μ-hydroxo dicationic complexes with a pyridine ligand coordinated to each pentamethylcyclopentadienylrhodium moiety. The conversion can be compared with the formation of the cations $[\{(C_5Me_5)M(Hdmpz)\}_2(\mu\text{-}OH)_2]^{2-}$ (Hdmpz = 3,5-dimethylpyrazole, M = Rh [2c], Ir [4]) from the corresponding tri-μ-hydroxo complexes $[\{(C_5Me_5)M\}_2(\mu\text{-}OH)_3]^{-}$, and with the preparation of the aquo complex $[\{(tacn)Rh(H_2O)\}_2(\mu\text{-}OH)_2]^{4+}$ from $[\{(tacn)Rh\}_2(\mu\text{-}OH)_3]^3$ [3]. The proposed formulation was confirmed by diffraction studies on complex I (see below). The iridium complex $[\{(C_5Me_5)Ir\}_2(\mu\text{-}OH)_3][BF_4]$ reacts in similar fashion with HBF_4 and pyridine in acetone to give the di-μ-hydroxo complex $[\{(C_5Me_5)Ir(py)\}_2(\mu\text{-}OH)_2][BF_4]_2$ (IX).

Interestingly, the reaction of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OH)_3][ClO_4]$ with $HClO_4$ and pyridine, or $[\{(C_5Me_5)Ir\}_2(\mu\text{-}OH)_3][BF_4]$ with HBF_4 and pyridine, in methanol as solvent, gave the di-μ-methoxo complexes $[\{(C_5Me_5)M(py)\}_2(\mu\text{-}OMe)_2][A]_2$ (M = Rh, A = ClO_4 (VIII); M = Ir, A = BF_4 (X)). The IR spectra of complexes VIII and X do not show the strong ν(OH) band typical of hydroxo complexes, but there is a

TABLE 1

ANALYSES, COLOURS AND YIELDS OF THE COMPLEXES PREPARED

Complex	Analysis (Found(calcd.)(%))			Colour	Yield (%)
	C	H	N		
[{(C$_5$Me$_5$)Rh(py)}$_2$(μ-OH)$_2$][ClO$_4$]$_2$ (I)	41.85 (41.5)	5.1 (4.9)	3.7 (3.2)	Orange	74
[{(C$_5$Me$_5$)Rh(2 Mepy)}$_2$(μ-OH)$_2$][ClO$_4$]$_2$ (II)	42.7 (42.9)	5.4 (5.2)	3.4 (3.1)	Orange	68
[{(C$_5$Me$_5$)Rh(3 Mepy)}$_2$(μ-OH)$_2$][ClO$_4$]$_2$ (III)	42.9 (42.9)	5.3 (5.2)	3.2 (3.1)	Orange	81
[{(C$_5$Me$_5$)Rh(4 Etpy)}$_2$(μ-OH)$_2$][ClO$_4$]$_2$ (IV)	43.4 (44.2)	5.8 (5.5)	3.05 (3.0)	Orange	73
[{(C$_5$Me$_5$)Rh(4 Pr^{n}py)}$_2$(μ-OH)$_2$][ClO$_4$]$_2$ (V)	45.4 (45.4)	6.15 (5.7)	2.7 (2.9)	Orange	55
[{(C$_5$Me$_5$)Rh(4 Bzpy)}$_2$(μ-OH)$_2$][ClO$_4$]$_2$ (VI)	49.6 (50.45)	5.4 (5.2)	2.95 (2.7)	Orange	61
[{(C$_5$Me$_5$)Rh(2 MeOpy)}$_2$(μ-OH)$_2$][ClO$_4$]$_2$ (VII)	41.7 (41.4)	5.4 (5.0)	3.1 (3.0)	Orange	65
[{(C$_5$Me$_5$)Rh(py)}$_2$(μ-OMe)$_2$][ClO$_4$]$_2$ (VIII)	42.7 (42.9)	5.6 (5.2)	3.2 (3.1)	Orange	75
[{(C$_5$Me$_5$)Ir(py)}$_2$(μ-OH)$_2$][BF$_4$]$_2$ (IX)	35.2 (35.3)	4.0 (4.15)	2.7 (2.7)	Yellow	60
[{(C$_5$Me$_5$)Ir(py)}$_2$(μ-OMe)$_2$][BF$_4$]$_2$ (X)	36.2 (36.65)	4.25 (4.4)	2.7 (2.7)	Yellow	65

strong band at 505 (VIII) or 520 cm^{-1} (X) assigned to ν(M–O–M) [2c–5]. The complexes are readily hydrolyzed by traces of water from the solvents. Unfortunately their low solubility has prevented NMR studies. These methoxo complexes may be formed either (i) by protonation of a methoxo group of the intermediate cation [{(C$_5$Me$_5$)M}$_2$(μ-OMe)$_3$]$^+$ formed by the reaction of the corresponding tri-μ-hydroxo cation with methanol [2c,5a,6], followed by the displacement of the methanol by the pyridine ligands, or, (ii), by initial formation of complexes I and IX according to eq. 1 and subsequent reaction with methanol to form the bridging methoxo groups. When complex I was stirred for a week in methanol at room temperature, complex VIII was in fact, isolated from the solution in 75% yield. Complex I was regenerated by treating complex VIII with acetone/water, 2/1 (eq. 2).

$$\left[\{(C_5Me_5)Rh(py)\}_2(\mu\text{-OH})_2\right]^{2+} \underset{H_2O}{\overset{MeOH}{\rightleftharpoons}} \left[\{(C_5Me_5)Rh(py)\}_2(\mu\text{-OMe})_2\right]^{2+} \qquad (2)$$

Analogously, the di-μ-methoxoiridium complex (X) in dichloromethane/water forms the di-μ-hydroxo complex IX. However, the formation of complex X was not observed by refluxing a solution of complex IX in methanol. Thus, the equilibrium depicted for rhodium in eq. 2 between the di-μ-hydroxo and di-μ-methoxo species lies over to the di-μ-hydroxo cation for iridium.

The synthetic method described in this paper may have wider implications for the preparation of related complexes. Although a variety of μ-hydroxo-rhodium and -iridium complexes have been reported, there are still relatively few μ-methoxo complexes of these metals [7].
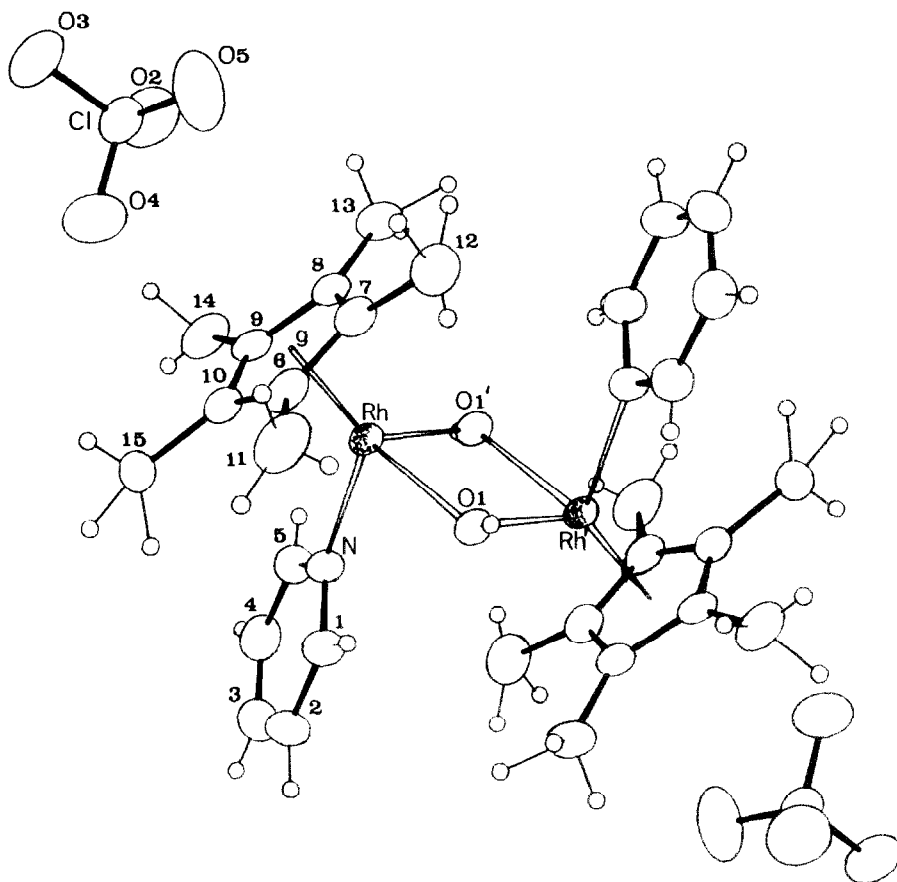
Fig. 1. A view of the dinuclear complex showing the atomic numbering.

Molecular structure of $[\{(C_5Me_5)Rh(py)\}_2(\mu\text{-}OH)_2][ClO_4]_2$

The structure of the cation is illustrated in Fig. 1 which shows the atom numbering scheme. Selected geometrical parameters are given in Table 2. The complex has an internal crystallographic centre of symmetry relating the two halves of the cation. The whole cation is composed of two rhodium atoms, each bonded to a C_5Me_5 (η^5-coordinated) and a pyridine ligand, bridged by two hydroxo groups. The coordination around the rhodium atoms is pseudo-octahedral, the C_5Me_5 occupying three *fac* coordination sites. The separation between the rhodium atoms is 3.308(1) Å a value which rules out any significant metal–metal interaction [2b]. The distance of the metal atom to the least-squares plane through the C_5 ring is 1.769(1) Å, and falls in the range of found for $Rh^{III}(C_5Me_5)$ complexes [2c,8]. The pyridine ligand is coordinated through its nitrogen atom, and the Rh–N distance is comparable with those in the related complex $[\{(C_5Me_5)Rh(Hdmpz)\}_2(\mu\text{-}OH)_2][BF_4]_2$ (Hdmpz = 3,5-dimethylpyrazol), 2.120(5) Å [2c], and in the pyridazine (pydz) compound $[\{(C_5Me_5)Rh\}_2(\mu\text{-}Cl)_2(\mu\text{-}pydz)][ClO_4] \cdot H_2O$, mean value 2.170(7) Å [9], and is similar to that in the pyridine-rhodium(III) complex $[Rh\{CH_2CH_2\text{-}C(CF_3)=C(CF_3)\}(Me_3CCOCHCOCMe_3)(py)_2]$ for the rhodium–nitrogen bond *trans*

TABLE 2

SELECTED BOND LENGTHS (Å) AND ANGLES (°) [a]

Rh–O(1)	2.109(4)	g–Rh–O(1)	133.3(1)
Rh–O(1′)	2.113(4)	g–Rh–O(1′)	130.2(1)
Rh–N	2.141(4)	g–Rh–N	126.7(1)
Rh–g	1.770(1)	O(1)–Rh–N	83.1(2)
Rh–C(6)	2.144(6)	O(1)–Rh–O(1′)	76.8(2)
Rh–C(7)	2.139(6)	N–Rh–O(1′)	89.2(2)
Rh–C(8)	2.164(6)	Rh–O(1)–Rh′	103.1(2)
Rh–C(9)	2.145(6)		
Rh–C(10)	2.149(6)		
Rh–Rh′	3.308(1)		

[a] g Represents the centroid of the C_5 independent ring.

TABLE 3

DETAILS OF THE DATA COLLECTION AND REFINEMENT

Crystal data	
Formula	$C_{30}H_{42}N_2O_{10}Cl_2Rh_2$
Crytal habit	Yellow, irregular shape
Crystal size (mm)	Max-min dimensions: 0.08–0.37
Symmetry	Monoclinic, $P2_1/n$
Unit cell determination:	Least-squares fit from 64 reflexions ($\theta < 45°$)
Unit cell dimensions	12.5006(3), 12.7910(2), 11.2378(2) Å; 90, 102.615(2), 90°
Packing: $V(Å^3)$, Z	1753.5(1), 2
$D_c(g\,cm^{-3})$, M, $F(000)$	1.643, 867.39, 880
Experimental data	
Technique	Four circle diffractometer: Philips PW1100
	Bisectins geometry
	Graphite oriented monochromator: Cu-K_α
	ω-2θ scans, scan width: 1.5°
	Detector apertures $1 \times 1°$, $\mu p\ \theta_{max}$ 65° 1 min/reflex.
Number of reflections:	
Independent	2965
Observed	2709 (3 $\sigma(I)$ criterion)
Standard reflections:	2 reflections every 90 minutes
	Variation: no
Solution and refinement	
Solution	Patterson
Refinement	L.S. on Fobs with 1 block
Parameters:	
Number of variables	276 (16 H-parameters fixed)
Ratio of freedom	9.8
H atoms	Difference map
Final shift/error	0.06
ω-scheme	Empirical as to give no trends in
	$\langle \omega\Delta^2 F \rangle$ versus $\langle |F_0| \rangle$ and $\langle \sin\theta/\lambda \rangle$
Max. thermal value	$U_{11}(05)$ 0.206(9) $Å^2$
Final ΔF peaks	0.97 eA^{-3} near the Rh atom
Final R and R_w	0.050, 0.060
Computer and programs	Vax 11/750, X-ray 76 [11]
Scattering factors	Int. Tables for X-ray crystallography [12]

to a carbon atom, 2.145(6) Å [10]. The two (η^5-C$_5$Me$_5$)Rh(py) fragments are linked via the hydroxo groups, Rh–O(1) 2.109(4) and Rh–O(1′) 2.113(4) Å, which complete the coordination spheres of the rhodium atoms. The value of the Rh–O–Rh′ angle, 103.1(2)°, is similar to those in the related di-μ-hydroxo complexes [{(C$_5$-Me$_5$)Rh(Hdmpz)}$_2$(μ-OH)$_2$][BF$_4$]$_2$, 101.0(2)° [2c] and [{(tacn)Rh(H$_2$O)}$_2$(μ-OH)$_2$][ClO$_4$]$_4$ · 4H$_2$O (tacn = 1,4,7-triazacyclononane), 100.5(3)° [3].

No special features were detected in the geometry of the C$_5$Me$_5$ and pyridine ligands or the perchlorate anion. A hydrogen bond links the bridging OH group with an oxygen of the anion: O(1)...O(3i) 2.970(8), H(1)–O(1) 0.80(9), O(3i)...H(1) 2.18(8) Å ($i = -\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$), O(1)–H(1)...O(3i) 171(7)°.

Experimental

C, H and N analyses were carried out with a Perkin–Elmer 240B microanalyzer. IR spectra were recorded on a Perkin–Elmer 1330 spectrophotometer in the range 4000–200 cm^{-1}, using Nujol mulls between polyethylene sheets. ^{1}H NMR spectra were recorded in (CD$_3$)$_2$CO at room temperature on a Varian XL 200 spectrometer, with SiMe$_4$ as internal standard. Solvents were dried and distilled before use.

Preparation of the hydroxo-complexes [{(C$_5$Me$_5$)ML}$_2$(μ-OH)$_2$][A]$_2$ (I–VII, IX)

The appropriate pyridine ligand L (0.20 mmol) and aqueous HA (0.10 mmol) were added to a solution of [{(C$_5$Me$_5$)M}$_2$(μ-OH)$_3$][A] (M = Rh, A = ClO$_4$; M = Ir,

TABLE 4

FRACTIONAL ATOMIC COORDINATES

Atom	x/a	y/b	z/c
Rh	0.04971(3)	0.04748(3)	0.38628(3)
Cl	0.4251(1)	0.1656(1)	0.2194(2)
O(1)	−0.0482(3)	0.0898(3)	0.5095(4)
O(2)	0.4302(7)	0.0552(4)	0.2115(9)
O(3)	0.4960(6)	0.2129(5)	0.1510(7)
O(4)	0.3164(5)	0.2004(6)	0.1675(8)
O(5)	0.4533(9)	0.1993(7)	0.3403(6)
N(1)	−0.1045(3)	0.0022(4)	0.2738(4)
C(1)	−0.1920(5)	0.0630(6)	0.2667(7)
C(2)	0.2906(6)	0.0427(8)	0.1847(8)
C(3)	0.2990(7)	−0.0445(9)	0.1128(8)
C(4)	−0.2091(7)	−0.1068(8)	0.1200(7)
C(5)	0.1138(6)	0.0824(6)	0.2016(6)
C(6)	0.1186(5)	0.1949(4)	0.3513(6)
C(7)	0.1956(5)	0.1385(5)	0.4418(5)
C(8)	0.2232(4)	0.0436(5)	0.3887(6)
C(9)	0.1601(4)	0.0380(5)	0.2649(6)
C(10)	0.0990(4)	0.1334(5)	0.2429(5)
C(11)	0.0692(8)	0.2981(6)	0.3663(9)
C(12)	0.2464(10)	0.1783(9)	0.5670(8)
C(13)	0.3010(7)	−0.0373(8)	0.4497(10)
C(14)	0.1689(8)	0.0435(8)	0.1760(10)
C(15)	0.0268(6)	0.1642(8)	0.1228(7)

A = BF$_4$) (0.10 mmol) in acetone (5 ml). When M = Rh and L = py, 2-Mepy, 4-Etpy, 2-MeOpy or M = Ir and L = py, the corresponding complexes separated out immediately; the resulting suspensions were stirred for 20 min and the complexes were filtered off, washed with diethyl ether, and dried in vacuum. When M = Rh and L = 3-Mepy, 4-Pr^{n}py, or 4-Bzpy, the solutions were stirred for 20 min and concentrated under vacuum to ca. 1 ml; addition of diethyl ether produced precipitates of the corresponding complexes. Recrystallization from dichloromethane/diethyl ether gave crystalline solids in all cases.

Preparation of the methoxo-complexes [{(C$_5$Me$_5$)M(py)}$_2$(μ-OMe)$_2$][A]$_2$ (VIII, X)

To solutions of [{(C$_5$Me$_5$)M}$_2$(μ-OH)$_3$][A] (M = Rh, A = ClO$_4$; M = Ir, A = BF$_4$) (0.10 mmol), in methanol (5 ml) were added pyridine (15.5 μl, 0.20 mmol) and 0.10 mmol of the relevant acid HA. The separation of a solid began immediately, and the resulting suspensions were stirred for 20 min. The solids were filtered off, washed with diethyl ether, and dried in vacuum.

X-Ray crystallography

Table 3 presents details of the analysis. μ was 96.96 cm^{-1}, and the irregular shape of the sample prevented any absorption correction; 25 strong low order reflections appeared to be affected by extinction and were considered unobserved in the final cycles of refinement. Table 4 lists the final atomic coordinates. Lists of structure factors, hydrogen parameters and anisotropic thermal parameters are available from the authors on request.

Acknowledgements

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