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Syntheses and molecular structures of 6-halogeno-pyridin-2-olate complexes with the diruthenium(2+) core

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Abstract

The complexes $[Ru_2(CO)_5(\mu\text{-FpyO})_2]_2$ (**1**), $[Ru_2(CO)_4(\mu\text{-ClpyO})_2]_2$ (**2**), and $[Ru_2(CO)_4(\mu\text{-BrpyO})_2]_2$ (**3**) were prepared from $Ru_3(CO)_{12}$ and 6-fluoro-2-hydroxypyridine (FpyOH), 6-chloro-2-hydroxypyridine (ClpyOH) and 6-bromo-2-hydroxypyridine (BrpyOH), respectively, in hot toluene. Compounds **1**–**3** are coordination dimers with a *cyclo*-RuORuO motif. By carrying out the reaction in hot methanol, the dinuclear complexes $[Ru_2(CO)_4(\mu\text{-ClpyO})_2(CH_3OH)]$ (**4**) and $[Ru_2(CO)_4(\mu\text{-BrpyO})_2(CH_3OH)]$ (**5**), respectively, were obtained. Treatment of **2** and **3** with triphenylphosphane provided the complexes $[Ru_2(CO)_4(\mu\text{-ClpyO})_2(PPh_3)]$ (**6**) and $[Ru_2(CO)_4(\mu\text{-BrpyO})_2(PPh_3)]$ (**7**), respectively. The solid-state structures of complexes **1**, **2**, **4**, **6**, and **7** were determined by single crystal X-ray diffraction. In all cases, a head–head coordination of the two 6-halopyridinolate ligands at the Ru_2^{2+} core was found. In all chlorine- or bromine-containing complexes, the axial coordination site at the ruthenium atom neighbored by two Cl or Br atoms remains unoccupied due to steric shielding by the halogen atom. In the fluoropyridinolate complex **1**, the same coordination site is occupied by a carbonyl ligand.

Keywords: Dinuclear complexes; Pyridonate ligand; Ruthenium compounds; X-ray crystal structures

1. Introduction

For studies on the subject of ruthenium-catalyzed carbene transfer reactions with diazo compounds, we became interested recently in dinuclear ruthenium(I,I) compounds in which the Ru_2^{2+} core is bridged by two 6-substituted pyridin-2-olate (2-pyridonate) ligands. So far, only complexes of this type containing the parent 2-pyridonate ligand have been reported. Thus, the reaction of 2-hydroxypyridine with $Ru_3(CO)_{12}$ in hot toluene generated the complex $[Ru_2(CO)_4(\mu\text{-pyO})_2]_n$ (pyO = 2-pyridinolate) as a coordination polymer, which was found to be insoluble in all common solvents with no Lewis base properties but could be depolymerized by the addition of donor ligands such as carbon monoxide, acetonitrile, triphenylphosphane, triphenyl phosphite, and 2-hydroxypyridine [1,2]. Recently, we have found that the reaction of $Ru_3(CO)_{12}$ with 6-methyl- or 6-phenyl-2-hydroxypyridine provides complexes that are different in composition and structure from the desired complexes $[Ru_2(CO)_4(\mu\text{-MepyO})_2]$ and $[Ru_2(CO)_4(\mu\text{-PhpyO})_2]$ [3]. In contrast to the current situation with Ru_2^{2+} complexes, a number of 6-R-pyridonate (RpyO, R = Me, F, Cl, Br) complexes with the Ru_2^{4+} and Ru_2^{5+} core, having the general composition $[Ru_2(\mu\text{-RpyO})_4]$ [4–8]

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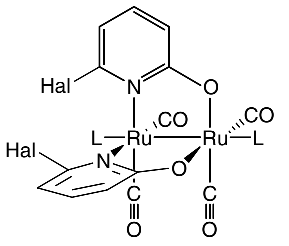
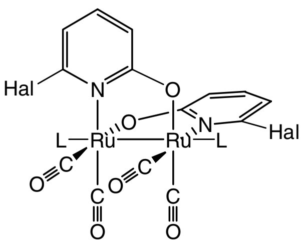
and [$Ru_2(\mu\text{-}RpyO)_4X$] (see, e.g. [7,9–11]), respectively, have been synthesized and structurally characterized.

In this communication, we report on the synthesis and structure determination of the first Ru_2^{2+} complexes with 6-halogeno-pyridin-2-olate ligands. Because of the unsymmetrically bridging pyridonate ligands, the two regioisomers[1] **I** and **II** can be expected, to which we refer here as the head–head (or 0,2) and the head–tail (or 1,1) isomer, respectively. For complexes of the type [$Ru_2(\mu\text{-}RpyO)_4$] and [$Ru_2(\mu\text{-}RpyO)_4X$] (R = Me, Hal), the three possible regioisomers (0,4, 1,3, 2,2) have all been obtained, and it has been stated that no general criteria exist to predict the preferred arrangement in an individual case [7]. For the Ru_2^{2+}/bis(6-halogeno-pyridin-2-olate) complexes reported here, the head–head (or 0,2) regioisomer **I** was obtained uniformly.



I



II

2. Experimental

2.1. General remarks

All solvents were distilled prior to use. 6-Fluoro- [12] and 6-bromo-2-hydroxypyridine [13] were prepared by published procedures, 6-chloro-2-hydroxypyridine was purchased and used as received. Nuclear magnetic resonance spectra in solution were recorded using a Bruker DRX 400 spectrometer (^1H: 400.13 MHz, ^{13}C: 100.62 MHz, ^{19}F: 376.47 MHz). ^1H NMR spectra were referenced to TMS, ^{13}C NMR spectra to the solvent signal ($\delta(CDCl_3) = 77.0$, $\delta(CD_3CN) = 118.26$ ppm), and ^{19}F spectra to external $CFCl_3$ ($\delta = 0$ ppm). IR spectra: Bruker Vector 22 FTIR; Mass spectra: MALDI: Bruker Daltonic Reflex III; ESI: Waters micromass ZMD. The reported m/z values for complexes **1**–**7** refer to the most intense peak of a multiple-line isotope pattern; the experimental and calculated intensity distribution agree with each other. Microanalyses were carried out with a Heraeus CHN–O–Rapid instrument in the Division of Analytical Chemistry, University of Ulm.

2.2. Preparation of bis(μ-6-fluoropyridin-2-olato-1κO:2κN)-pentacarbonyl-1κ²C:2κ³C–diruthenium(Ru–Ru) dimer, [$Ru_2(CO)_5(\mu\text{-}FpyO)_2]_2$ (1)

A solution of $Ru_3(CO)_{12}$ (100 mg, 0.16 mmol) and 6-fluoro-2-hydroxypyridine (53 mg, 0.47 mmol) in toluene (10 ml) was heated at reflux for 5 h. Crystals started to appear at the end of the reaction. After cooling to r.t., the orange-yellow precipitate was filtered off, washed with a small volume of cold toluene, and dried at 0.001 mbar. Yield: 72 mg (0.064 mmol, 54% based on Ru). Decomposition of the complex, indicated by color change to brown and black, started above 235 °C. The complex is air-sensitive and was stored, therefore, at 8 °C under argon. IR (KBr): 2035 s, 1998 s, 1991 s, 1951 s, 1927 s, 1621 s, 1551 m, 1433 s, 1347 m, 1246 m, 1028 s, 785 m, 573 w cm^{-1}. ^1H NMR (CD_3CN): $\delta = 6.13$ (ddd, $J_{H,H} = 7.5$, 0.9 Hz, $|J_{H,F}| = 1.9$ Hz, 5-H_{py}), 6.19 (d, $J_{H,H} = 8.3$ Hz, long-range coupling not resolved, 3-H_{py}), 7.47 (dt, $J_{H,H} \approx J_{H,F} \approx 8.6$ Hz, $J_{H,H} = 7.6$ Hz, 4-H_{py}). ^{13}C NMR (CD_3CN): $\delta = 93.32$ ($J_{C,F} = 30.7$ Hz), 111.94 ($J_{C,F} = 4.4$ Hz), 142.5 ($J_{C,F} = 11.7$ Hz), 164.39 ($J_{C,F} = 249.6$ Hz), 175.73 ($J_{C,F} = 5.1$ Hz), 202.48, 204.62 (d, $J_{C,F} = 5.1$ Hz). MS (MALDI-TOF, dithranol): $m/z = 1136.3$ (M^+), 1050.5 ($M^+ - 3$ CO). *Anal.* Calc. for $C_{30}H_{12}F_4N_4O_{14}Ru_4$ (1132.7): C, 31.81; H, 1.07; N, 4.95. Found: C, 31.62; H, 1.19; N, 4.98%.

2.3. Preparation of bis(μ-6-chloropyridin-2-olato-1κO:2κN)-tetracarbonyl-1κ²C:2κ²C–diruthenium(Ru–Ru) dimer, [$Ru_2(CO)_4(\mu\text{-}ClpyO)_2]_2$ (2)

A solution of $Ru_3(CO)_{12}$ (100 mg, 0.16 mmol) and 6-chloro-2-hydroxypyridine (61 mg, 0.47 mmol) in toluene (10 ml) was heated at reflux for 2.5 h. After cooling to r.t., the red precipitate was filtered off, washed with a small volume of cold toluene, and dried at 0.001 mbar. Yield: 118 mg (0.10 mmol, 88% based on Ru). Decomposition of the complex started at 328 °C. IR (KBr): 2035 s, 1991 s, 1958 s, 1938 s, 1601 m, 1463 s, 1433 s, 1330 m, 1177 m, 1015 m, 931 m, 785 m cm^{-1}. MS (MALDI-TOF, dithranol): $m/z = 1114.5$ ($M^+ - CO$). *Anal.* Calc. for $C_{28}H_{12}Cl_4N_4O_{12}Ru_4$ (1142.5): C, 29.44; H, 1.06; N, 4.90. Found: C, 29.43; H, 1.13; N, 4.83%.

2.4. Preparation of bis(μ-6-bromopyridin-2-olato-1κO:2κN)-tetracarbonyl-1κ²C:2κ²C–diruthenium(Ru–Ru) dimer, [$Ru_2(CO)_4(\mu\text{-}BrpyO)_2]_2$ (3)

The same procedure as in Section 2.3, but with 6-bromopyridine (81.6 mg, 0.47 mmol), furnished a red solid, which started to decompose at 312 °C; yield: 129 mg (0.098 mmol, 83% based on Ru). IR (KBr): 2033 s, 1989 s, 1955 s, 1935 s, 1602 m, 1461 s, 1426 s, 1398 m, 1331 m, 1173 w, 1011 w, 903 w, 781 w cm^{-1}.

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[1] This term, well established in organic chemistry, has been applied appropriately by Cotton et al. to characterize these types of isomeric complexes; see [6].

MS (MALDI-TOF, dithranol): $m/z = 1295.5$ ($M^+ -$ CO). *Anal.* Calc. for $C_{28}H_{12}Br_4N_4O_{12}Ru_4$ (1320.3): C, 25.47; H, 0.92; N, 4.24. Found: C, 25.58; H, 0.98; N, 4.26%.

2.5. Preparation of bis(μ-6-chloropyridin-2-olato-1κO:2κN)-methanol-1κO-tetracarbonyl-1κ²C:2κ²C–diruthenium(Ru–Ru) dimer, [Ru₂(CO)₄(CH₃OH)(μ-ClpyO)₂]₂ (**4**)

A solution of $Ru_3(CO)_{12}$ (100 mg, 0.16 mmol) and 6-chloro-2-hydroxypyridine (61 mg, 0.47 mmol) in methanol (10 ml) was heated at reflux for 48 h. After cooling to r.t., the red precipitate was filtered off, washed with a little cold methanol, and dried at 0.001 mbar. Yield: 72 mg (0.12 mmol, 51% based on Ru). When the complex was heated, extrusion of a liquid was observed at ~235 °C, and a color change to silver-black above 326 °C. ^1H NMR ($CDCl_3$): $\delta = 3.48$ (s, 3 H), 3.50 (s, 3H), 6.47 (d, $J = 7.1$ Hz, 1H), 6.66 (d, $J = 8.6$ Hz, 1H), 6.74 (d, $J = 7.3$ Hz, 1H), 7.25 (d, 1H, partly covered by residual solvent signal), 7.35 (pseudo-t, $J_1 + J_2 = 15.6$ Hz, 1H), 7.60 (pseudo-t, $J_1 + J_2 = 15.9$ Hz, 1H). IR (KBr): 2044 s, 1991 s, 1963 s, 1601 s, 1531 m, 1465 s, 1167 m, 1025 m, 1013 m, 789 m cm^{-1}. MS (ESI): $m/z = 594.5$ ($C_{14}H_6Cl_2N_2O_6Ru_2 + Na$). MS (MALDI-TOF, dithranol): $m/z = 1117.5$ ($2 \cdot C_{14}H_6Cl_2N_2O_6Ru_2 - CO$). *Anal.* Calc. for $C_{30}H_{20}Cl_4N_4O_{14}Ru_4$ (1206.6): C, 29.86; H, 1.67; N, 4.64. Found: C, 29.85; H, 1.72; N, 4.62%.

2.6. Preparation of bis(μ-6-bromopyridin-2-olato-1κO:2κN)-methanol-1κO-tetracarbonyl-1κ²C:2κ²C–diruthenium(Ru–Ru), [Ru₂(μ-BrpyO)₂(CO)₄(CH₃OH)]₂ (**5**)

Following the procedure given in Section 2.5, but with 6-bromo-2-hydroxypyridine (81.6 mmol, 0.47 mmol) and a reaction time of 36 h, 91 mg (0.13 mmol, 56% based on Ru) of a red solid was obtained, which decomposed above 300 °C. IR (KBr): 2032 s, 1989 s, 1954 s, 1936 s, 1602 s, 1523 m, 1461 s, 1427 s, 1331 m, 1174 m, 1011 m, 904 m, 791 m, 781 m cm^{-1}. MS (MALDI-TOF, dithranol): $m/z = 1292.6$ ($M^+ - 2CH_3OH -$ CO). *Anal.* Calc. for $C_{30}H_{20}Br_4N_4\ O_{14}Ru_4$ (1384.4): C, 26.03; H, 1.46; N, 4.05. Found: C, 25.80; H, 1.22; N, 4.13%.

2.7. Preparation of bis(μ-6-chloropyridin-2-olato-1κO:2κN)-tetracarbonyl-1κ²C:2κ²C–triphenylphosphane-1κP–diruthenium(Ru–Ru), [Ru₂(CO)₄(μ-ClpyO)₂(PPh₃)] (**6**)

Complex **2** (29.7 mg, 26 μmol) was suspended in a solution of triphenylphosphane (13.1 mg, 50 μmol) and CH_2Cl_2 (1 ml), and the mixture was stirred until a homogeneous yellow solution had formed (ca. 30 min). It was passed over a plug of silica gel (Si60, 0.063–0.2 mm, 1 g) in order to remove any trace of **2**, evaporated to dryness, and the remaining orange-yellow solid was dried at 0.001 mbar. Yield: 41.7 mg (50 μmol, quantitative based on PPh_3); m.p. 199 °C. ^1H NMR ($CDCl_3$): $\delta = 6.10$ (d, $J = 8.6$ Hz, 2H), 6.39 (d, $J = 7.3$ Hz, 2H), 7.16 (dd, $J = 8.6$, 7.3 Hz, 2H), 7.39–7.49 (m, 9 H), 7.59–7.63 (m, 6H). ^{13}C NMR ($CDCl_3$): $\delta = 110.10$, 113.95, 128.32 (d, $J_{C,P} = 9.5$ Hz), 130.32, 130.35, 131.59 (d, $J_{C,P} = 40.2$ Hz), 133.82 (d, $J_{C,P} = 10.1$ Hz), 139.13, 147.15, 172.91, 172.92, 200.40 (d, $J_{C,P} = 6.6$ Hz), 201.88 (d, $J_{C,P} = 6.6$ Hz). IR (KBr): 2036 s, 1987 s, 1958 s, 1926 s, 1600 m, 1528 w, 1472 s, 1451 m, 1435 m, 1094 w, 1010 w, 694 w cm^{-1}. MS (ESI): $m/z = 834.6$ (M^+). *Anal.* Calc. for $C_{32}H_{21}Cl_2N_2O_6PRu_2$ (833.54): C, 46.11; H, 2.54; N, 3.36. Found: C, 45.90; H, 2.64; N, 3.32%.

2.8. Preparation of bis(μ-6-bromopyridin-2-olato-1κO:2κN)-tetracarbonyl-1κ²C:2κ²C–triphenylphosphane-1κP–diruthenium(Ru–Ru), [Ru₂(CO)₄(μ-BrpyO)₂(PPh₃)] (7)

The same procedure as described in Section 2.7 was carried out with complex **3** (34.3 mg, 26 μmol) and furnished 46.1 mg (50 μmol, quantitative based on PPh_3) of an orange-yellow solid; m.p. 223–224.5 °C. ^1H NMR ($CDCl_3$): $\delta = 6.10$ (dd, $J = 8.5$, 0.8 Hz, 2H), 6.52 (dd, $J = 7.3$, 0.8 Hz, 2H), 7.06 (dd, $J = 8.5$, 7.3 Hz, 2H), 7.38–7.46 (m, 9H), 7.59–7.63 (m, 6H). ^{13}C NMR ($CDCl_3$): $\delta = 114.09$, 114.27, 128.32 (d, $J_{C,P} = 9.5$ Hz), 130.30, 130.32, 131.66 (d, $J_{C,P} = 39.5$ Hz), 133.84 (d, $J_{C,P} = 10.2$ Hz), 138.14, 139.16, 174.00, 174.02, 200.63 (d, $J_{C,P} = 7.3$ Hz), 201.97 (d, $J_{C,P} = 6.6$ Hz). IR (KBr): 2033 s, 1989 s, 1956 s, 1928 s, 1603 s, 1522 m, 1469 s, 1447 m, 1387 w, 1362 w, 1188 w, 1094 w, 1006 w, 906 w, 694 m, 570 w. *Anal.* Calc. for $C_{32}H_{21}Br_2N_2O_6PRu_2$ (922.44): C, 41.67; H, 2.29; N, 3.04. Found: C, 41.44; H, 2.24; N, 2.92%. MS (ESI): $m/z = 945.7$ ($M^+ + Na$), 923.5 (M^+).

2.9. X-ray crystal structure determination for complexes **1**, **2**, **4**, **6**, and 7

Single crystals of **1** were obtained as follows: A part of the boiling reaction solution (toluene, see Section 2.2) was separated after a reaction time of 4 h, filtered hot, and was cooled slowly (10 °C/h) from ~100 °C to r.t. The yellow rod-shaped crystals of **1** were separated manually from the orange crystals of unreacted $Ru_3(CO)_{12}$. Block-shaped red crystals of **2** were obtained by filtration of the hot reaction solution (toluene) to separate already precipitated product, cooling, and crystallization at 8 °C during three days. Dark-red pris-

Table 1
Summary of crystallographic data and structure refinement for compounds **1**, **2**, **4**, **6**, and **7**

	1	**2**	**4**	**6**	**7**
Empirical formula	$C_{30}H_{12}F_4N_4O_{14}Ru_4$[a]	$C_{28}H_{12}Cl_4N_4O_{12}Ru_4$[a]	$(C_{15}H_{10}Cl_2N_2O_7Ru_2)_2$	$C_{32}H_{21}Cl_2N_2O_6P_1Ru_2 \cdot 0.5C_6H_{12}$	$C_{32}H_{21}Br_2N_2O_6P_1Ru_2$
Formula weight	1132.72	1142.50	1206.58	875.60	922.44
Temperature (K)	190(2)	193(2)	190(2)	193(2)	193(2)
Crystal size (mm)	0.23 × 0.10 × 0.08	0.31 × 0.19 × 0.15	0.38 × 0.23 × 0.15	0.31 × 0.23 × 0.15	0.27 × 0.19 × 0.12
Crystal system	monoclinic	monoclinic	orthorhombic	triclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$	*Pbca*	$P\bar{1}$	$P\bar{1}$
a (Å)	8.585(1)	8.376(1)	29.391(2)	9.646(1)	13.962(1)
b (Å)	12.973(1)	9.592(2)	15.498(2)	10.262(1)	14.989(1)
c (Å)	15.610(2)	11.855(2)	8.512(6)	18.920(2)	24.077(2)
α (°)	90	98.83(2)	90	100.66(1)	82.60(1)
β (°)	100.82(2)	100.79(2)	90	102.79(1)	88.25(1)
γ (°)	90	109.36(2)	90	98.68(1)	76.96(1)
Volume ($Å^3$)	1707.5(4)	858.6(2)	3877.4(6)	1758.4(3)	4868.0(7)
Z	2	1	4	2	6
ρ_{calc} (g cm^{-3})	2.203	2.21	2.067	1.654	1.888
μ(Mo Kα) (cm^{-1})	1.83	2.11	1.87	1.10	3.49
F(000)	1088	548	2336	872	2688
θ Range (°)	2.06–25.97	2.31–26.11	1.91–24.09	2.12–25.98	1.92–25.94
Index ranges	$-9 \leqslant h \leqslant 9$ $-15 \leqslant k \leqslant 15$ $-19 \leqslant l \leqslant 19$	$-10 \leqslant h \leqslant 10$ $-11 \leqslant k \leqslant 11$ $-14 \leqslant l \leqslant 14$	$-32 \leqslant h \leqslant 33$ $-17 \leqslant k \leqslant 17$ $-9 \leqslant l \leqslant 9$	$-10 \leqslant h \leqslant 10$ $-12 \leqslant k \leqslant 12$ $-22 \leqslant l \leqslant 23$	$-17 \leqslant h \leqslant 17$ $-18 \leqslant k \leqslant 18$ $-29 \leqslant l \leqslant 29$
Reflections collected	13139	12141	23592	13847	38546
Independent reflections (R_{int})	3108 (0.0335)	3126 (0.0289)	2959 (0.0447)	6387 (0.0261)	17671 (0.0451)
Completeness to θ_{max} (%)	92.8	91.4	96.4	92.7	93.0
Absorption correction		numerical			numerical
Data/restraints/parameters[b]	3108/0/253	3126/0/235	2959/0/258	6387/0/433	17671/0/1216
Goodness-of-fit on F^2	0.880	1.179	1.041	0.939	
Final *R* indices [$I > 2\sigma(I)$]: R_1, wR_2[c]	0.0201, 0.0407	0.0220, 0.0625	0.0217, 0.0591	0.0226, 0.0524	0.0285, 0.0513
R indices (all data): R_1, wR_2[c]	0.0312, 0.0426	0.0282, 0.0750	0.0264, 0.0604	0.0308, 0.0548	0.0536, 0.0561
Largest difference peak and hole (e $Å^{-3}$)	0.53, −0.46	0.52, −0.98	0.346, −0.49	0.477, −0.44	0.74, −0.71

[a] In the solid state, the complex exists as a centrosymmetric coordination dimer.

[b] Refinement based on F^2 values.

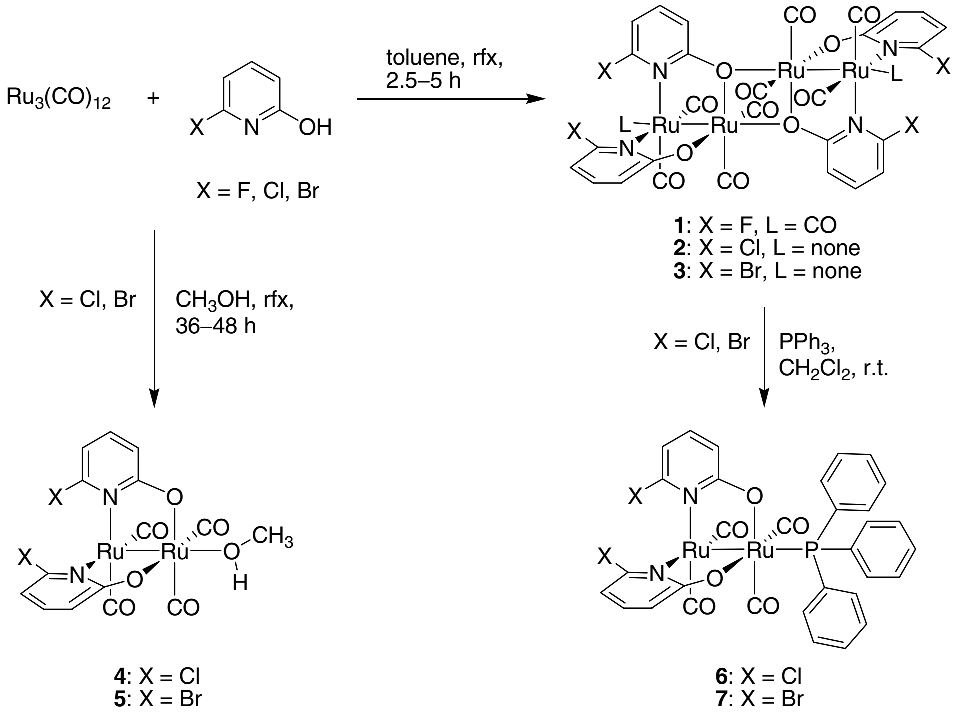
[c] $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$; $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$.

matic crystals of **4** were grown from methanol by using the same procedure as before. Crystallization from hot cyclohexane afforded ruby-red crystals of $\mathbf{6} \cdot 0.5C_6H_{12}$ and orange-yellow crystals of **7**.

Data collection was performed on an image-plate diffractometer (Stoe IPDS) using monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). For **2** and **6**, the positions of the Ru atoms were extracted from a sharpened Patterson map, all other structures were completely solved with direct methods. All structures were refined using a full-matrix least-squares method. Hydrogen atom positions were calculated geometrically and treated as riding on their bond neighbors in the refinement procedure. The position of the methanolic OH proton of **4** was located in a difference Fourier map and was refined freely. The positions of the carbon atoms of the cyclohexane molecule present in the unit cell of **6** were not well defined and the atoms showed large ellipsoids of thermal vibration; therefore, the derived bond lengths and angles are not reasonable. Software for all calculations: SHELX-97 [14]; molecule plots: ORTEP-3 [15]. Crystallographic data and details of the refinement for all structures are given in Table 1.

3. Results and discussion

The syntheses carried out during this study are put together in Scheme 1. Heating of $Ru_3(CO)_{12}$ with three molar amounts of 6-fluoro-, 6-chloro- or 6-bromo-2-hydroxypyridine in boiling toluene furnished the complexes $[Ru_2(CO)_5(\mu\text{-FpyO})_2]_2$ (**1**), $[Ru_2(CO)_4(\mu\text{-ClpyO})_2]_2$ (**2**) and $[Ru_2(CO)_4(\mu\text{-BrpyO})_2]_2$ (**3**), respectively, all of which started to separate already from the hot reaction solution. In contrast to the latter two, complex **1** deteriorates when exposed to air for an



Scheme 1.

extended period of time; the orange color of the solid starts to darken after one day and turns into black after several days. All three complexes are barely soluble in the common non-polar organic solvents, but have a higher solubility in donor solvents such as DMSO or acetonitrile: in each case, ~50 mg of the complex can be dissolved in 1 ml of acetonitrile. These solubility characteristics are a consequence of the solid-state structures of **1**–**3** which, according to X-ray structure analysis of **1** and **2** (vide infra), exist as centrosymmetric coordination dimers made up from two dinuclear monomers and held together by two Ru–O contacts. The coordination dimers are also detected in the MALDI mass spectra. Solvents with Lewis-base properties can easily split up the dimers, thereby replacing the axial Ru–O coordination by a donor molecule. Thus, the reported NMR spectra of **1**, recorded in CD_3CN solution (see Section 2), are in fact those of $[Ru_2(CO)_4(CD_3CN)_2(\mu\text{-FpyO})_2]$; the observation of only two ^{13}C signals for the carbonyl groups, one of which shows a $J_{C,F}$ coupling of 5.1 Hz, most likely excludes the alternative complex $[Ru_2(CO)_5(CD_3CN)(\mu\text{-FpyO})_2]$ which should give rise to at least three CO signals in the ^{13}C NMR spectrum. The axial site at the second ruthenium atom is occupied by a carbonyl ligand in **1** but remains empty in **2** and **3**.

The formation of a coordination dimer can also be suppressed in the presence of the two-electron donor ligands, methanol and triphenylphosphane. Thus, the reaction of $Ru_3(CO)_{12}$ with 6-chloro- or 6-bromopyridine in hot methanol furnished the methanol adducts **4** and **5**, and brief treatment of coordination dimers **2** and **3** with PPh_3 at 20 °C afforded the "monomeric" complexes **6** and **7** which are well soluble in common solvents such as chloroform, toluene, and acetonitrile. Compound **4** was sparingly soluble in chloroform, while **5** was virtually insoluble. Remarkably, the ^1H NMR spectrum of **4** in $CDCl_3$ showed two sets of signals for the pyridonate rings. This magnetic non-equivalence of the

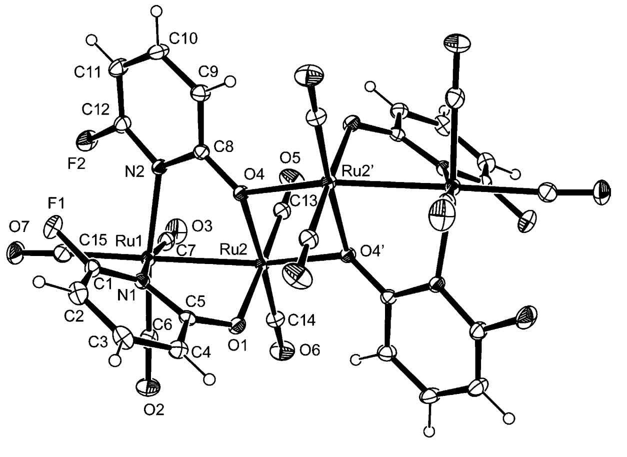


Fig. 1. Molecular structure of **1** in the crystal. Ellipsoids of thermal vibration are shown at the 30% probability level. The coordination dimer has a crystallographic center of symmetry. Geometry of the RuORuO core: Ru2–O4 2.137(2) Å, Ru2–O4 2.283(2) Å, O4–Ru2–O4′ 75.53(7)°, Ru2–O4–Ru2′ 104.47 (7)°, O4–Ru2–O4′–Ru2′ 0.0°.

two pyridonate ligands is due to the formation of a centrosymmetric dimer $[Ru_2(CO)_4(CH_3OH)(\mu\text{-HalpyO})_2]_2$ maintained by two O–H···O hydrogen bonds involving the methanol ligand and one pyridonate ring, as was revealed by X-ray structure determination (vide infra, Fig. 3). This dimer is obviously stable in $CDCl_3$ solution, but not under mass spectrometry conditions: The ESI-MS spectrum of **4** shows a peak corresponding to the "monomeric" dinuclear complex without the methanol ligand, and the MALDI mass spectra of **4** and **5** closely resemble those of the coordination dimers **2** and **3**, respectively.

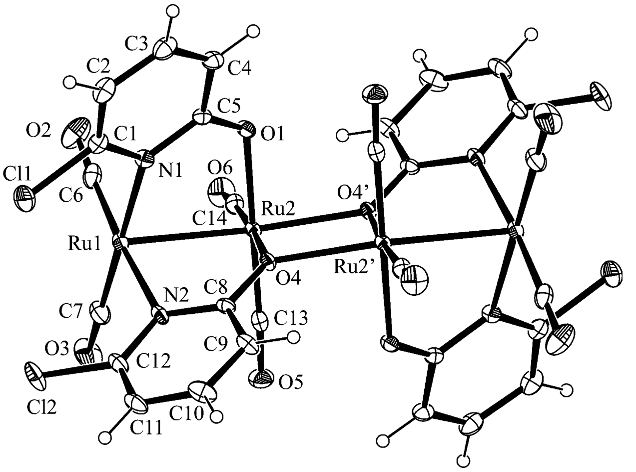


Fig. 2. Molecular structure of **2** in the crystal. Ellipsoids of thermal vibration are shown at the 30% probability level. The coordination dimer has a crystallographic center of symmetry. Geometry of the RuORuO core: Ru2–O4 2.141(2) Å, Ru2–O4′ 2.227(2) Å, O4–Ru2–O4′ 78.24(10)°, Ru2–O4–Ru2′ 101.76(10)°, O4–Ru2–O4′–Ru2′ 0.0°.

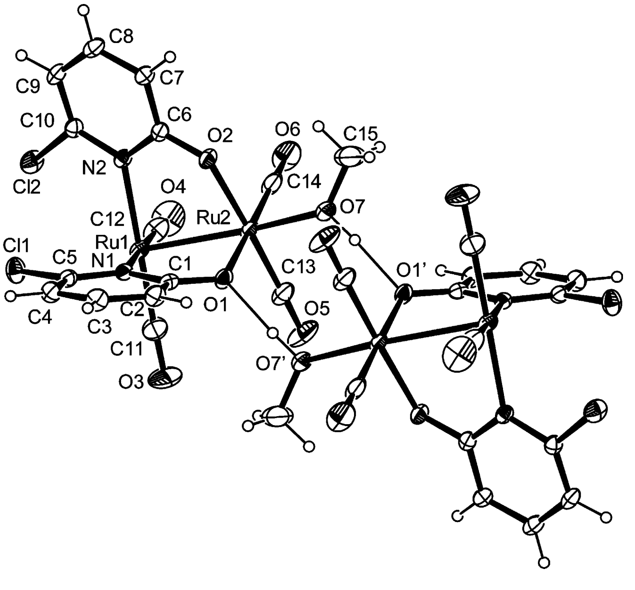


Fig. 3. Molecular structure of **4** in the crystal. Ellipsoids of thermal vibration are shown at the 30% probability level. The hydrogen-bonded dimer has a crystallographic center of symmetry.

The solid-state structures of complexes **1**, **2**, **4**, **6**, and **7** were determined by single-crystal X-ray diffraction analysis. Molecule plots are shown in Figs. 1–5. Selected data of the bond geometry are assembled in Table 2. All complexes feature the head–head (0,2) arrangement of the two pyridonate ligands, i.e., both halogen substituents at C-6 of the two pyridonate rings are neighboring the axial coordination site of the same ruthenium atom. The intramolecular Cl···Cl and Br···Br contacts are somewhat shorter than the sum of van der Waals radii (3.60 Å for Cl···Cl, 4.00 Å for Br···Br), while the F···F distance in **1** is distinctly larger than this sum (3.742 vs. 2.80 Å). As a consequence, the axial coordination site at the ruthenium atom having the halogen neighbors remains unoccupied in the chloro-(**2**, **4**, **6**) and bromo-(**7**) complexes, while in fluoro-complex **1**, the small carbonyl ligand can be accommodated at this

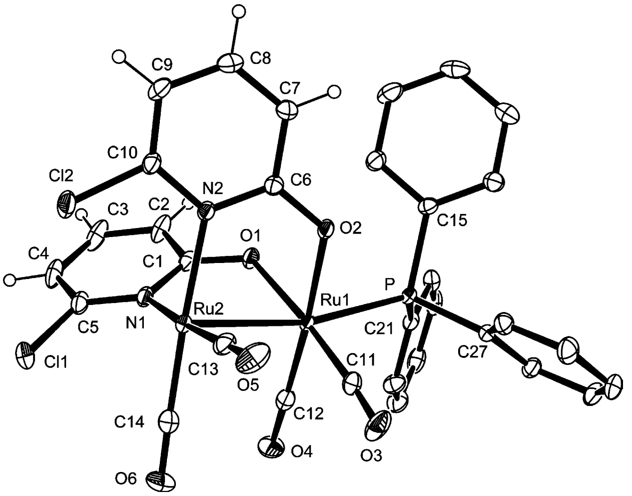


Fig. 4. Molecular structure of **6** in the crystal. Ellipsoids of thermal vibration are shown at the 30% probability level.

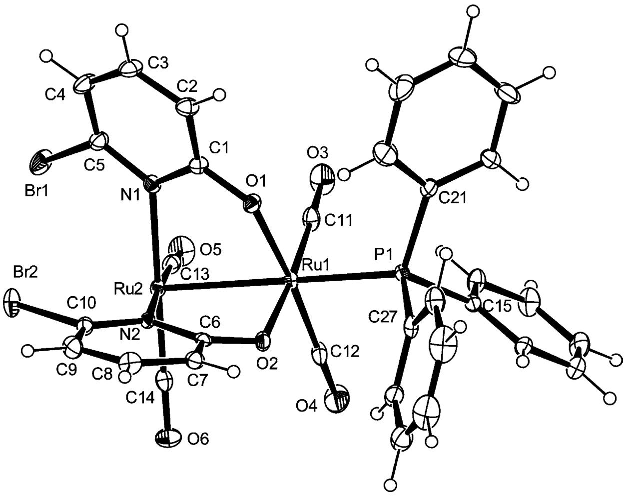
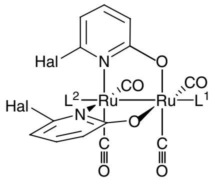


Fig. 5. Molecular structure of **7** in the crystal. Ellipsoids of thermal vibration are shown at the 30% probability level.

Table 2
Selected values of the bond geometry of compounds **1**, **2**, **4**, **6**, and **7**



	1	**2**	**4**	**6**	**7**[b]
Hal	F	Cl	Cl	Cl	Br
L^1	Opy[a]	Opy[a]	HOCH$_3$	PPh$_3$	PPh$_3$
L^2	CO				
Bond lengths (Å)					
Ru–Ru	2.6393(4)	2.6081(8)	2.6281(3)	2.6627(6)	2.6620(5)–2.6738(5)
Ru–N	2.169(2), 2.183(2)	2.119(3), 2.175(3)	2.154(2), 2.157(2)	2.142(2), 2.167(2)	2.139(3)–2.168(3)
Ru–O	2.091(2), 2.137(2)	2.099(2), 2.141(2)	2.098(2), 2.117(2)	2.109(2), 2.120(2)	2.083(2)–2.114(3)
Ru–C$_{\mathrm{carbonyl}}$	1.840(3)–1.886(3)	1.843(4)–1.861(4)	1.839(3)–1.850(3)	1.844(3)–1.853(3)	1.839(5)–1.862(5)
N–C(–O)	1.331(4), 1.368(3)	1.351(5), 1.354(5)	1.361(4), 1.363(3)	1.347(3), 1.355(3)	1.362(5)–1.378(4)
(N–)C–O	1.273(3), 1.302(3)	1.300(4), 1.315(4)	1.290(3), 1.295(3)	1.285(3), 1.290(3)	1.278(4)–1.294(5) 1.362(5)–1.378(4)
Hal···Hal[c]	3.742	3.484	3.387	3.534	3.699–3.726
Ru–L^1	2.283(2)	2.227(2)	2.198(2)	2.414(1)	2.387(1)–2.391(1)
Ru–L^2	1.990(3)				
Bond angles (°)					
Ru$_{\mathrm{O,O}}$–Ru$_{\mathrm{N,N}}$–N	81.07(6), 82.42(6)	83.05(8), 84.08(8)	83.54(6), 85.42(6)	82.62(5), 84.62(5)	83.30(8)–85.35(8)
Ru$_{\mathrm{O,O}}$–Ru$_{\mathrm{N,N}}$–C$_{\mathrm{carbonyl}}$	89.66(9), 89.95(9)	92.94(12), 95.87(13)	93.37(11), 94.25(11)	92.80(3), 95.92(8)	92.89(11)–94.30(12)
Ru$_{\mathrm{N,N}}$–Ru$_{\mathrm{O,O}}$–C$_{\mathrm{carbonyl}}$	94.81(9), 95.94(9)	93.62(11), 94.13(11)	96.04(11), 96.21(11)	93.01(8), 93.79(7)	92.34(11)–96.36(11)
Ru$_{\mathrm{N,N}}$–Ru$_{\mathrm{O,O}}$–O	81.65(5), 83.11(5)	82.38(6), 85.33(7)	82.43(5), 85.21(5)	81.04(5), 83.32(4)	80.12(6)–84.38(7)
N–Ru–N	86.05(8)	87.58(12)	87.06(6)	86.54(7)	87.38(11)–91.40(12)
Ru–Ru–L^1	153.63(5)	158.25(7)	161.63(7)	167.84(2)	168.97(3)–173.40(3)
Torsion angles (°)					
N–Ru–Ru–O	27.9(1), 28.2(1)	19.0(1), 24.5(1)	16.1(1), 19.3(1)	22.0(1), 23.6(1)	15.4(1)–17.1(1) 22.9(1)–27.3(1)
Ru–N–C–O	13.2(3), 15.3(3)	2.2(4), 11.9(4)	−0.6(3), 8.4(3)	0.3(3), 17.6(3)	1.7(5)–7.1(5), 8.5(5)–16.6(4)
C–Ru–Ru–C[d]	30.1(1)	26.1(2)	19.0(1)	25.99(3)	21.4(2)–27.1(2)

[a] Centrosymmetric dimer with *cyclo*-RuORuO core.
[b] The given ranges relate to the three independent molecules in the asymmetric unit of the crystal.
[c] Intramolecular Hal···Hal distance.
[d] The given torsion angles are those involving the two carbonyl groups that point downwards in Figs. 1–5.

site. Steric shielding of the axial site at ruthenium has been observed before in the diruthenium(II,II) complex (2,2)-tetrakis(6-chloropyridin-2-olato)diruthenium [7], where pairs of the pyridonate ligands are in a trans orientation (in contrast to the cis orientation in the present complexes).

The second ruthenium atom in complexes **1** and **2** completes its ligand sphere by axial coordination of a pyridonate oxygen atom of a second dinuclear complex molecule which in turn forms a Ru–O bond with the first molecule. In this manner, a centrosymmetric dimer with a planar cyclo-Ru–O-Ru–O core is built up (see Figs. 1 and 2 for details of the bond geometry). The axial Ru–O bond is longer by 0.09–0.19 Å than the equatorial Ru–O bonds. This dimerization motif is not uncommon in the structural chemistry of dinuclear ruthenium carboxylate and pyridonate complexes [6,7,16].

In complex **4**, the axial coordination site at the O,O-substituted ruthenium atom is occupied by a methanol molecule. In the solid state, a centrosymmetric dimer exists which is held together by two O–H···O hydrogen bonds involving the OH function of methanol and a pyridonate oxygen atom of a second dinuclear complex. The hydrogen bond is almost linear: $\angle(\mathrm{O{-}H\cdots O}) = 166(4)°$, $d(\mathrm{O{-}H}) = 0.92(5)$ Å, $d(\mathrm{O\cdots H}) = 1.71(5)$ Å, $d(\mathrm{O\cdots O}) = 2.610(3)$ Å. Finally, the PPh$_3$ complexes **6** and **7** exist as isolated dinuclear complexes. Notably, the three P–C$_{\mathrm{Ph}}$ bonds are not in a fully staggered conformation with respect to the four equatorial ligands at ruthenium; rather, one P–C$_{\mathrm{Ph}}$ bond is almost colinear with a Ru–C or Ru–O bond (torsion angle in **6**: C11–Ru1–P–C27 5.0(2)°; in **7**: O2–Ru1–P1–C27 5.1(2)°).

The Ru–Ru bond lengths in all five complexes are in the range of single bonds; as Table 2 shows, the shortest distance is found in the coordination dimer **2** (2.608 Å) and the longest one in the PPh_3 complexes (2.663–2.674 Å). For comparison, a Ru–Ru bond length of 2.7108(4) Å was found in the unsubstituted pyridonate complex $[Ru_2(CO)_4(\mu\text{-pyO})_2(PPh_3)_2]$ bearing two axial PPh_3 ligands [17]. All complexes feature the expected deviation from the fully eclipsed conformation around the Ru–Ru bond (see torsion angles given in Table 2); similar geometries have been observed in $[Ru_2(CO)_4(\mu\text{-pyO})_2L_2]$, L = PPh_3 [17] and 2-hydroxypyridine [2]. The torsion angles N–Ru–Ru–O and C–Ru–Ru–C are larger in the fluoropyridonate complex **1** than in **2**, **4**, **6**, and **7**. Another remarkable difference is seen for the torsion angles Ru–N–C–O, which are quite similar in **1** (13.2° and 15.3°) while in the other complexes one torsion angle is close to 0° and the other is larger by ca. 8–17°.

In conclusion, we have succeded in the preparation and structural characterization of several Ru(I,I) complexes of the type $[Ru_2(CO)_4(\mu\text{-HalpyO})_2]$ which bear additional ligands at the axial sites of the ruthenium atoms. All complexes presented here exist as the head–head (or 0,2) regioisomers. We will report in due course that, with different axial ligands, the head–tail regioisomers can also be obtained. The ability of the complexes to catalyze olefin cyclopropanation with diazoacetates is reported elsewhere [18].

4. Supplementary material

CCDC Nos. 273561 (**1**), 273562 (**2**), 273563 (**4**), 273564 (**6**), and 273565 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Director, Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK, fax (int.): +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or at www.ccdc.cam.ac.uk/conts/retrieving.html.

Acknowledgments

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