

Oxalate complexes of the $(\eta^6\text{-}p\text{-cymene})\text{ruthenium(II)}$ fragment: $\mu\text{-oxalato-}\kappa^2\text{O}^1,\text{O}^2:\kappa^2\text{O}^{1'},\text{O}^{2'}$ -bis[$(\eta^6\text{-}p\text{-cymene})(\text{triphenylphosphine-}\kappa\text{P})\text{-ruthenium(II)}$] bis(tetrafluoroborate) and $(\eta^6\text{-}p\text{-cymene})(\text{oxalato-}\kappa^2\text{O},\text{O}')$ -(pyridine-3,5-dicarboxylic acid- $\kappa\text{N})\text{-ruthenium(II)}$

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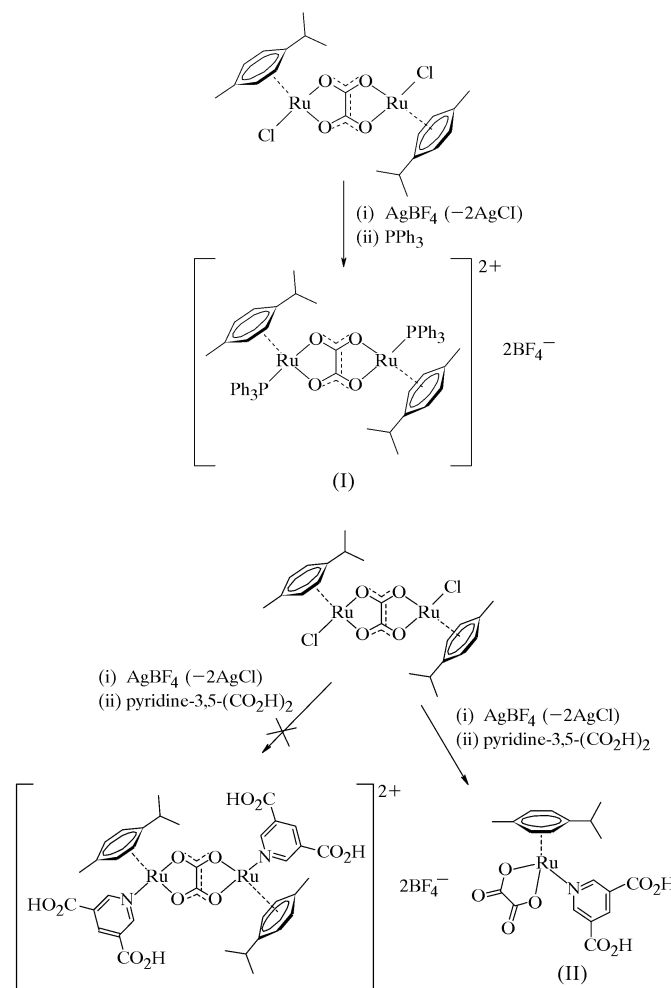
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The crystal structure of dimeric $\mu\text{-oxalato-bis}[(\eta^6\text{-}p\text{-cymene})\text{-}(\text{triphenylphosphine})\text{ruthenium(II)}]$ bis(tetrafluoroborate), $[\text{Ru}_2(\text{C}_2\text{O}_4)(\text{C}_{10}\text{H}_{14})_2(\text{C}_{18}\text{H}_{15}\text{P})_2](\text{BF}_4)_2$, has the cation lying on an inversion centre. The complex demonstrates the *trans* bond-weakening influence, with the longest Ru—C($\eta^6\text{-}p\text{-cymene}$) bonds in the complex lying *trans* to the phosphine group. The related mononuclear species $(\eta^6\text{-}p\text{-cymene})\text{-}(\text{oxalato})(\text{pyridine-3,5-dicarboxylic acid})\text{ruthenium(II)}$, $[\text{Ru}(\text{C}_2\text{O}_4)(\text{C}_{10}\text{H}_{14})(\text{C}_7\text{H}_5\text{NO}_4)]$, crystallizes as hydrogen-bonded tapes linked through O—H...O hydrogen bonds.

Comment

Using a synthetic method first introduced by Winkhaus & Singer (1967) and later adapted by others (Iwata & Ogata, 1973; Bennett & Smith, 1974; Bennett *et al.*, 1982), the reaction of cyclohexa-1,3-dienes with $\text{RuCl}_2 \cdot x\text{H}_2\text{O}$ *via* a reductive dehydrogenation reaction in a mixed EtOH—H₂O solvent affords air-stable $[\text{RuCl}_2(\eta^6\text{-arene})]_2$ chloro-bridged dimer complexes. These dimeric starting materials can be reacted with a wide variety of ligands, resulting in mononuclear half-sandwich ‘piano-stool’ complexes (Bennett & Smith, 1974; Maitlis, 1981). Such $(\eta^6\text{-arene})\text{ruthenium}$ complexes have been shown to have both stoichiometric (Pigge & Coniglio, 2001) and catalytic (Ogo *et al.*, 2002; Hafner *et al.*, 1997; Akiyama & Kobayashi, 2002) applications in organic chemistry. More recently, $(\eta^6\text{-arene})\text{ruthenium}$ complexes have been shown to exhibit antibacterial, antiviral and anticancer properties (Allardyce *et al.*, 2003; Morris *et al.*, 2001; Wang *et al.*, 2002).

Yan and co-workers have investigated the synthesis of dimeric $(\eta^6\text{-arene})\text{ruthenium}$ complexes. The oxalate ($\text{C}_2\text{O}_4^{2-}$) ligand replaces the bridging Cl^- ligands upon reaction with $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2$, producing the dimeric compound



$\{\text{Ru}(\eta^6\text{-}p\text{-cymene})\}_2(\mu\text{-oxalato})\text{Cl}_2$ (Yan *et al.*, 1997). The Cl^- anions of this compound can be displaced by PPh_3 , producing the cation $[\{\text{Ru}(\eta^6\text{-}p\text{-cymene})\}_2(\mu\text{-oxalato})(\text{PPh}_3)_2]^{2+}$, and may also be removed upon reaction with Ag^+ salts before addition of a monodentate ligand. This latter reaction was used to synthesize the ‘molecular box’, $[\{\text{Ru}(\eta^6\text{-}p\text{-cymene})\}_4(\mu\text{-oxalato})_2(\mu\text{-4,4'-bipy})_2]^{4+}$. Our investigations have continued from this work, with the aim of introducing ligands bearing hydrogen-bonding functionality to the $[\{\text{Ru}(\eta^6\text{-arene})\}_2(\mu\text{-oxalato})]^{2+}$ fragment. Initial reactions introduced PPh_3 to the system through the prior removal of the Cl^- anions using Ag^+ salts, allowing the crystallization of the $[\{\text{Ru}(\eta^6\text{-}p\text{-cymene})\}_2(\mu\text{-oxalato})(\text{PPh}_3)_2]^{2+}$ cation as its BF_4^- salt, (I). [Yan *et al.* (1997) synthesized the cation as its trifluoromethanesulfonate salt, but did not crystallographically characterize the compound.] The reaction of $\{\text{Ru}(\eta^6\text{-}p\text{-cymene})\}_2(\mu\text{-oxalato})\text{Cl}_2$ with Ag^+ , followed by addition of the monodentate ligand pyridine-3,5-dicarboxylic acid, resulted in an ambiguous mixture of compounds (spectroscopic data were inconclusive). However, one crystal

was grown from the recrystallization of the mixture, from which the structure of $\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{oxalato})(\text{pyridine-3,5-dicarboxylic acid})$, (II), was determined, rather than the intended dimeric compound $[\{\text{Ru}(\eta^6\text{-}p\text{-cymene})\}_2(\mu\text{-oxalato})\text{-}(\text{pyridine-3,5-dicarboxylic acid})_2](\text{BF}_4)_2$.

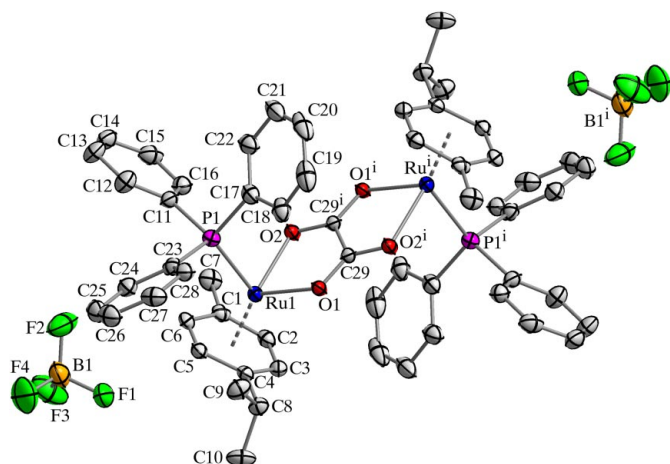


Figure 1
A view of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms and the minor disorder component have been omitted for clarity. The η^6 -binding mode of the *p*-cymene ligands is represented by heavy dashed lines between the Ru atoms and the centroids of the aromatic ring. [Symmetry code: (i) $-x + 1, -y, -z + 1$.]

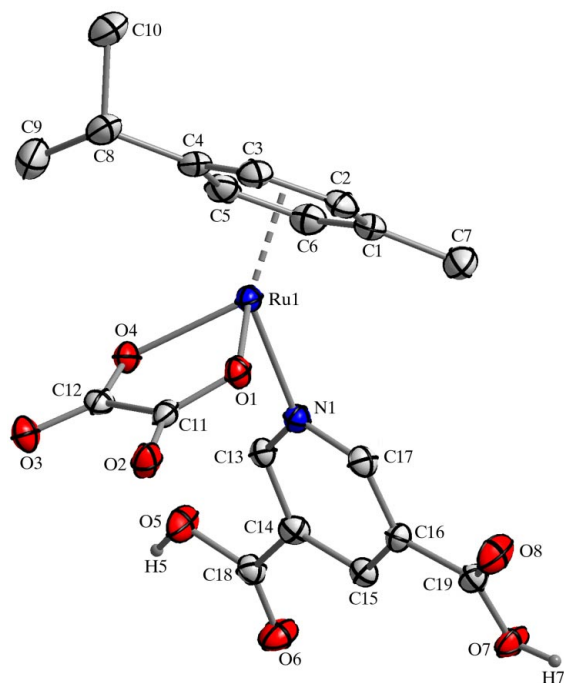


Figure 2
A view of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms, except those of hydroxyl groups, have been omitted for clarity. The η^6 -binding mode of the *p*-cymene ligand is represented by a heavy dashed line between the Ru atom and the centroid of the aromatic ring.

Compound (I), $[\{\text{Ru}(\eta^6\text{-}p\text{-cymene})\}_2(\mu\text{-oxalato})(\text{PPh}_3)_2](\text{BF}_4)_2$, has the cation positioned on an inversion centre (Fig. 1). The compound represents only the fifth oxalato-bridged (η^6 -arene)ruthenium complex to be structurally characterized to date. The original four complexes were characterized by Yan *et al.* (1997), with Cl^- (two conformational isomers), methanol and 4,4'-bipyridine ligands filling the remaining coordination sites of the Ru^{II} ions.

The geometry of the cation in (I) is summarized in Table 1. Table 5 shows the results of a search of the Cambridge Structural Database (CSD; Version 5.27 plus one update, January 2006; Allen, 2002) for (oxalato)ruthenium complexes in the presence and absence of η^6 -arene ligands. The bond lengths within the oxalate ligand are in good agreement with the results of the CSD survey, with little difference observed in the C—C and C—O bond lengths whether an η^6 ligand is present or not. Ru—O bond lengths appear to be slightly shorter in the presence of an η^6 -arene ligand, and the O—Ru—O angle slightly narrower, whereas in the case of (I), the Ru—O bond lengths are longer than the averages in Table 5 and the O—Ru—O angle narrower still. This is presumably due to the steric and electronic effects of the PPh_3 ligand. The average Ru—P bond length from 60 $\text{Ru}(\eta^6\text{-arene})(\text{PPh}_3)$ structures in the CSD is 2.35 (3) Å (range 2.262–2.404 Å), showing good agreement with that observed in (I).

The Ru—C bond lengths in (I) [2.184 (3)–2.256 (3) Å] are average-to-long compared with the search statistics (Table 5). Complexes containing η^6 -arene and phosphine ligands have been shown to demonstrate the *trans* bond-weakening influence, in which the Ru—C bonds positioned *trans* to the

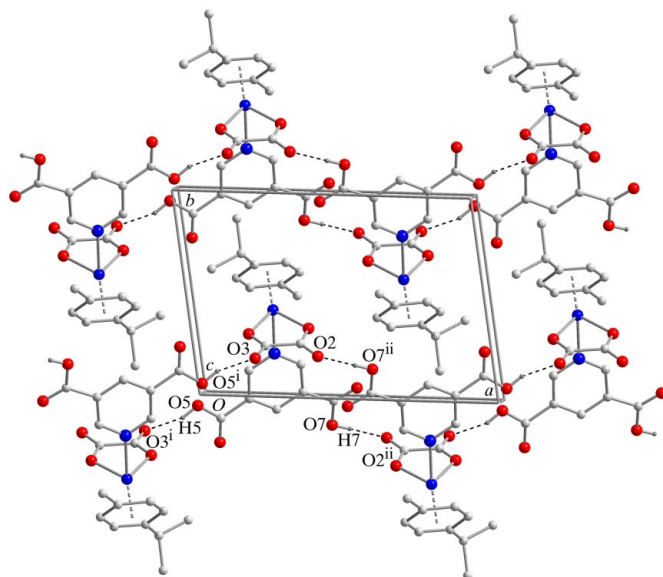


Figure 3
A packing plot, showing the close-packing of two hydrogen-bonded tapes of (II), viewed along the crystallographic *c* axis (*a* axis horizontal). Hydrogen bonds are shown as thin dashed lines. The η^6 -binding mode of the *p*-cymene ligands is represented by heavy dashed lines between the Ru atoms and the centroids of the aromatic ring. [Symmetry codes: (i) $-x, -y, -z$; (ii) $-x + 1, -y, -z + 1$.]

phosphine group are elongated with respect to the others (Bennett *et al.*, 1972; Elsegood & Tocher, 1995). The *trans* influence is observed in compound (I), where atoms C2 and C3, having the longest Ru—C bond lengths within the η^6 -coordination of the arene ligand, lie *trans* to the phosphine ligand. The distance between the Ru^{II} ion and the least-squares plane of the *p*-cymene aromatic ring is 1.6971 (13) Å. The cations and anions are linked together into a three-dimensional structure through a series of weak C—H...F hydrogen bonds (Table 2).

Compound (II), Ru(η^6 -*p*-cymene)(oxalato)(pyridine-3,5-dicarboxylic acid), crystallizes with the asymmetric unit comprising one formula unit (Fig. 2). The compound represents only the second Ru(η^6 -arene)(oxalato)*L* complex (*L* is a monodentate ligand) to be structurally characterized to date, the other being an η^6 -*p*-cymene-PPh₃ complex (Yan *et al.*, 1997). The C—O and C—C bond lengths of the oxalate ligand show good agreement with those observed in (oxalato)-ruthenium complexes in both the presence and absence of an η^6 -arene ligand. The data shown in Table 5 indicate that the presence of an η^6 -arene narrows the O—Ru—O angle, as observed in oxalate dimeric complexes, whereas in the case of monomeric complexes, the presence of an η^6 -arene ligand increases the Ru—O bond lengths. The geometry of compound (II) therefore shows closer agreement with that of a monomeric complex than the dimeric species. However, it is unclear why the monomeric species has formed. The average Ru—N(pyridyl) bond length from 119 Ru(η^6 -arene)(PPh₃) structures in the CSD is 2.12 (3) Å (range 2.054–2.189 Å), showing good agreement with that observed in (II). The Ru—C bond lengths are in the range 2.164 (3)–2.218 (3) Å, with the longest bond lying *trans* to the pyridyl N atom. The distance between the Ru^{II} ion and the least-squares plane of the *p*-cymene aromatic ring is 1.6650 (11) Å.

The presence of the two carboxylic acid groups on opposite sides of the pyridine ring in (II) allows the formation of hydrogen-bonded tapes, propagating in the [101] direction (Table 4 and Fig. 3). Each CO₂H group forms an O—H...O hydrogen bond to a terminal O atom of an oxalate ligand in a neighbouring complex. Close packing of the chains is aided by the alternation of the bulky *p*-cymene ligands above and below the hydrogen-bonded tapes.

We are continuing our work towards the synthesis and structural characterization of dimeric [$\{\text{Ru}(\eta^6\text{-}p\text{-cymene})_2(\mu\text{-oxalato})L_2\}^{n+}$] complexes containing monodentate ligands *L* bearing hydrogen-bonding groups, with the aim of creating extended supramolecular arrays.

Experimental

[RuCl₂(η^6 -*p*-cymene)]₂ was prepared from RuCl₃·*x*H₂O according to the literature method of Bennett *et al.* (1982). {Ru(η^6 -*p*-cymene)}₂(μ -oxalato)Cl₂ was prepared using a method adapted from the literature (Yan *et al.*, 1997). To a stirred solution of [RuCl₂(η^6 -*p*-cymene)]₂ (300 mg, 0.490 mmol) in dichloromethane (20 ml) at room temperature was added sodium oxalate (66 mg, 0.49 mmol) in H₂O (5 ml). The resulting biphasic mixture was stirred vigorously for 4 h,

producing a red-to-yellow colour change. The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 × 10 ml). The organic extracts were combined, dried (Na₂SO₄), filtered and evaporated to dryness to produce an orange solid (280 mg, 91%). Spectroscopic data for {Ru(η^6 -*p*-cymene)}₂(μ -oxalato)Cl₂ were identical to those determined previously (Yan *et al.*, 1997).

For the preparation of compound (I), AgBF₄ (19 mg, 0.098 mmol, 2 equivalents) was added to a stirred solution of {Ru(η^6 -*p*-cymene)}₂(μ -oxalato)Cl₂ (30 mg, 0.048 mmol) in acetone (10 ml) at room temperature under N₂. After stirring for 18 h, the AgCl precipitate was removed by filtration through a pad of Celite and PPh₃ (25 mg, 0.095 mmol, 2 equivalents) was added to the resulting yellow solution. Following further stirring for 6 h at room temperature, the yellow–orange solution was evaporated to dryness, yielding an orange solid (51 mg, 91%). The sample was observed to decompose at temperatures in excess of 503 K. X-ray quality crystals of (I) were grown by the slow diffusion of Et₂O vapour into an MeOH–dichloromethane (approximately 1:1) solution of (I). IR (KBr, ν_{max} , cm⁻¹): 3077 and 3062 (Ar C—H), 2967, 2926 and 2863 (*sp*³ C—H), 1621 (CO₂⁻), 1482, 1471 and 1438 (*sp*³ C—H), 1082 and 1060 (BF₄⁻), 910, 862, 754, 698 (Ar C—H), 531, 509 and 488. Other spectroscopic data were found to be identical to those of the previously reported trifluoromethanesulfonate salt (Yan *et al.*, 1997).

For the preparation of compound (II), AgBF₄ (46 mg, 0.24 mmol, 2 equivalents) was added to a stirred solution of {Ru(η^6 -*p*-cymene)}₂(μ -oxalato)Cl₂ (75 mg, 0.12 mmol) in acetone (10 ml) at room temperature under N₂. After stirring for 6 h, the AgCl precipitate was removed by filtration through a pad of Celite and pyridine-3,5-dicarboxylic acid (40 mg, 0.24 mmol, 2 equivalents) was added to the resulting yellow solution. After stirring for a further 18 h at room temperature, the yellow–orange solution was evaporated to dryness. One X-ray quality crystal of (II) was grown by the slow evaporation of a methanolic solution of the crude reaction mixture.

Compound (I)

Crystal data

[Ru ₂ (C ₂ O ₄)(C ₁₀ H ₁₄) ₂ (C ₁₈ H ₁₅ P) ₂](BF ₄) ₂	<i>D</i> _x = 1.563 Mg m ⁻³
<i>M</i> _r = 1256.74	Mo K α radiation
Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>	Cell parameters from 6070 reflections
<i>a</i> = 9.4503 (6) Å	θ = 2.4–28.0°
<i>b</i> = 16.8493 (10) Å	μ = 0.70 mm ⁻¹
<i>c</i> = 16.8539 (10) Å	<i>T</i> = 150 (2) K
β = 95.815 (2)°	Needle, red
<i>V</i> = 2669.9 (3) Å ³	0.59 × 0.09 × 0.05 mm
<i>Z</i> = 2	

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	6006 independent reflections
ω rotation scans with narrow frames	4296 reflections with <i>I</i> > 2 σ (<i>I</i>)
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	<i>R</i> _{int} = 0.050
<i>T</i> _{min} = 0.683, <i>T</i> _{max} = 0.966	θ_{max} = 27.5°
22839 measured reflections	<i>h</i> = -12 → 12
	<i>k</i> = -21 → 20
	<i>l</i> = -21 → 21

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0204P)^2 + 4.902P]$
$R[F^2 > 2\sigma(F^2)] = 0.036$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.082$	(Δ/σ) _{max} = 0.001
<i>S</i> = 1.03	$\Delta\rho_{\text{max}} = 0.65 \text{ e } \text{Å}^{-3}$
6006 reflections	$\Delta\rho_{\text{min}} = -0.49 \text{ e } \text{Å}^{-3}$
374 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °) for (I).

Ru1—C1	2.184 (3)	Ru1—P1	2.3713 (10)
Ru1—C2	2.238 (4)	Ru1—O1	2.137 (2)
Ru1—C3	2.256 (3)	Ru1—O2	2.131 (2)
Ru1—C4	2.204 (3)	O1—C29	1.252 (4)
Ru1—C5	2.187 (3)	O2—C29 ⁱ	1.258 (4)
Ru1—C6	2.185 (3)	C29—C29 ⁱ	1.530 (6)
P1—Ru1—O1	91.69 (7)	O1—Ru1—O2	77.16 (8)
P1—Ru1—O2	87.34 (7)		

Symmetry code: (i) $-x + 1, -y, -z + 1$.

Table 2
Hydrogen-bond geometry (Å, °) for (I).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C13—H13...F2 ⁱⁱ	0.95	2.56	3.354 (7)	141
C20—H20...F4 ⁱⁱⁱ	0.95	2.87	3.481 (10)	124
C21—H21...F1 ⁱⁱⁱ	0.95	2.45	3.358 (5)	159
C24—H24...F2	0.95	2.52	3.305 (8)	140
C27—H27...F1 ^{iv}	0.95	2.65	3.479 (5)	146

Symmetry codes: (ii) $-x + 1, -y + 1, -z + 1$; (iii) $x + 1, -y + \frac{1}{2}, z + \frac{1}{2}$; (iv) $x, -y + \frac{1}{2}, z + \frac{1}{2}$.

Compound (II)

Crystal data

[Ru(C ₂ O ₄)(C ₁₀ H ₁₄)(C ₇ H ₅ NO ₄)]	Mo <i>K</i> α radiation
<i>M_r</i> = 490.42	Cell parameters from 4500 reflections
Triclinic, <i>P</i> 1̄	$\theta = 2.3$ – 28.2°
<i>a</i> = 7.8754 (5) Å	$\mu = 0.90$ mm ⁻¹
<i>b</i> = 9.0005 (6) Å	<i>T</i> = 150 (2) K
<i>c</i> = 13.6905 (9) Å	Block, yellow
$\alpha = 98.647$ (2)°	0.24 × 0.22 × 0.08 mm
$\beta = 106.062$ (2)°	
$\gamma = 90.165$ (2)°	
<i>V</i> = 920.92 (10) Å ³	
<i>Z</i> = 2	
<i>D_x</i> = 1.769 Mg m ⁻³	

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	3166 reflections with <i>I</i> > 2σ(<i>I</i>)
ω rotation scans with narrow frames	<i>R</i> _{int} = 0.019
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$\theta_{\max} = 26.0^\circ$
<i>T</i> _{min} = 0.813, <i>T</i> _{max} = 0.931	<i>h</i> = -9 → 9
7288 measured reflections	<i>k</i> = -11 → 11
3583 independent reflections	<i>l</i> = -16 → 16

Table 3
Selected geometric parameters (Å, °) for (II).

Ru1—C1	2.199 (3)	C11—O1	1.278 (3)
Ru1—C2	2.175 (3)	C11—O2	1.229 (3)
Ru1—C3	2.185 (3)	C11—C12	1.552 (3)
Ru1—C4	2.218 (3)	C12—O3	1.234 (3)
Ru1—C5	2.165 (3)	C12—O4	1.273 (3)
Ru1—C6	2.164 (3)	C18—O5	1.317 (3)
Ru1—O1	2.0798 (18)	C18—O6	1.205 (3)
Ru1—O4	2.0827 (17)	C19—O7	1.319 (3)
Ru1—N1	2.131 (2)	C19—O8	1.207 (3)
O1—Ru1—O4	78.70 (7)	O4—Ru1—N1	83.63 (7)
O1—Ru1—N1	83.27 (7)		

Table 4
Hydrogen-bond geometry (Å, °) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O5—H5...O3 ⁱ	0.84	1.76	2.563 (3)	160
O7—H7...O2 ⁱⁱ	0.84	1.77	2.613 (2)	179

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x + 1, -y, -z + 1$.

Table 5
Statistics (Å, °) from a CSD search for (oxalato)ruthenium complexes.

Fragment	Ru—O	C—O	C—C(ox)	O—Ru—O	Ru—C
(i)	2.097–2.182 [2.13 (2)]	1.24–1.27 [1.255 (8)]	1.532–1.551 [1.539 (8)]	77.0–79.8 [78.6 (11)]	
(ii)	2.100–2.142 [2.126 (11)]	1.240–1.271 [1.255 (7)]	1.518–1.555 [1.535 (15)]	77.8–78.2 [77.92 (13)]	2.137–2.191 [2.168 (16)]
(iii)	2.079–2.084 [2.081 (14)]	1.221–1.300 [1.25 (4)]	1.549	78.6	2.190–2.223 [2.206 (11)]
(iv)	2.011–2.108 [2.05 (3)]	1.162–1.389 [1.25 (4)]	1.500–1.572 [1.544 (17)]	78.4–83.6 [80.8 (12)]	

Notes: search carried out using CSD (Version 5.27, plus one update, January 2006; Allen, 2002). Value ranges are shown, with mean averages in square brackets directly below. In the search for the Ru(κ^2 -ox) fragment, the terminal O atoms of the oxalate ligands were restrained to be bonded to only one atom each. Fragments: (i) Ru(κ^4 -ox)Ru, four structures; (ii) (Ar)Ru(κ^4 -ox)Ru(Ar), four structures; (iii) (Ar)Ru(κ^2 -ox), one structure; (iv) Ru(κ^2 -ox), 13 structures. Structures containing η^6 -arene ligands were omitted from the searches for Ru(κ^4 -ox)Ru and Ru(κ^2 -ox) fragments. Abbreviations: ox = oxalate and Ar = η^6 -arene.

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0239P)^2 + 0.8593P]$
$R[F^2 > 2\sigma(F^2)] = 0.026$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.061$	$(\Delta/\sigma)_{\max} = 0.001$
<i>S</i> = 1.07	$\Delta\rho_{\max} = 0.53$ e Å ⁻³
3583 reflections	$\Delta\rho_{\min} = -0.35$ e Å ⁻³
267 parameters	
H-atom parameters constrained	

All H atoms in title compounds (I) and (II) were placed in geometrically calculated positions and refined using a riding model, with C—H distances in the range 0.95–1.00 Å and O—H distances of 0.84 Å. *U*_{iso}(H) values were set at 1.2*U*_{eq}(C) for aryl and methine H atoms, 1.5*U*_{eq}(C) for methyl H atoms and 1.5*U*_{eq}(O) for carboxyl H atoms. The tetrafluoroborate anion in (I) was found to be disordered and was modelled as disordered over two sets of positions bearing one coincident B—F bond [major refined occupancy = 65.0 (17)%]. Restraints were applied to the anisotropic displacement parameters of the B and F atoms.

The data sets were truncated at $2\theta = 55^\circ$ for (I) and at $2\theta = 52^\circ$ for (II), as only statistically insignificant data were present above these limits.

For both compounds, data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2000); program(s) used to refine structure: SHELXTL; molecular graphics: DIAMOND (Brandenburg, 2001); software used to prepare material for publication: SHELXTL and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1886). Services for accessing these data are described at the back of the journal.

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