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Mono-, di- and tetra-nuclear *p*-cymeneruthenium complexes containing oxalato ligands

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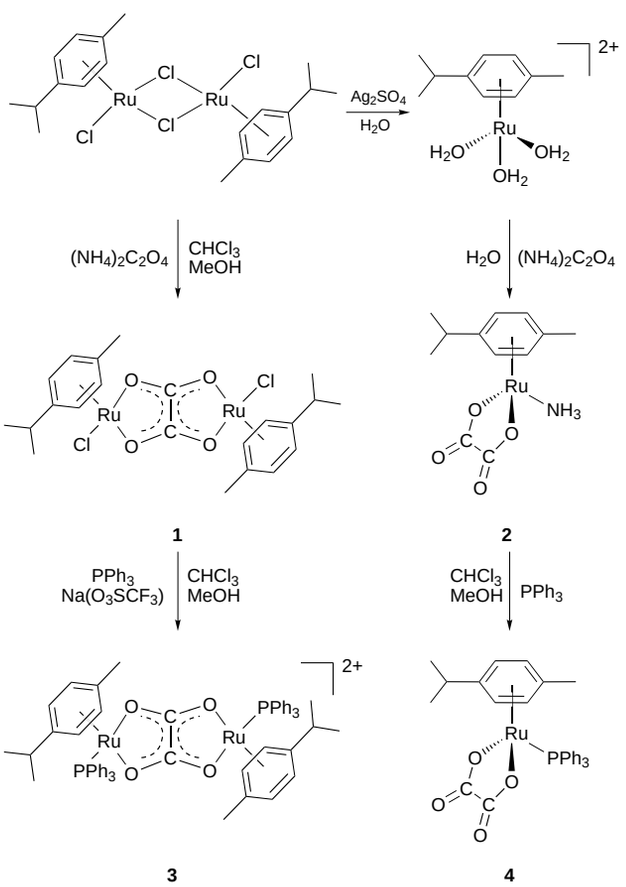
The oxalato complexes $[Ru_2(\mu\text{-}\eta^4\text{-}C_2O_4)Cl_2(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)_2]$ **1** and $[Ru(\eta^2\text{-}C_2O_4)(NH_3)(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)]$ **2** have been prepared from the reaction of ammonium oxalate with $[\{RuCl_2(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)\}_2]$ and $[Ru(H_2O)_3(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)]^{2+}$, respectively. With triphenylphosphine, **1** reacted to give $[Ru_2(\mu\text{-}\eta^4\text{-}C_2O_4)(PPh_3)_2(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)_2]^{2+}$ **3**, while **2** gave $[Ru(\eta^2\text{-}C_2O_4)(PPh_3)(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)]$ **4**. The dichloro complex **1** can also be converted into the cationic dimethanol complex $[Ru_2(\mu\text{-}\eta^4\text{-}C_2O_4)(MeOH)_2(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)_2]^{2+}$ **5** by precipitation of the chloride with a silver salt in methanol. Complex **5** reacted with 4,4′-bipyridine to afford a novel tetranuclear metallomacrocycle $[Ru_4(\mu\text{-}\eta^4\text{-}C_2O_4)_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-bipy})_2(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)_4]^{4+}$ **6** with alternating oxalato and 4,4′-bipyridine bridges. The reaction between **1** and azide yielded the known azido-bridged complex $[\{Ru(\mu\text{-}\eta^1\text{-}N_3)Cl(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)\}_2]$ **7**. The molecular structures of **1** (two conformational isomers), **4**, **5** and **6** have been solved by X-ray crystallography.

Many organorhodium complexes containing bidentate oxygen ligands such as β-diketonate,[1] tropolonate (the anion of 2-hydroxycyclohepta-2,4,6-trienone),[2] oxalate,[3] chloranilate (the dianion of 2,5-dichloro-3,6-dihydroxy-*p*-benzoquinone),[4] squarate (3,4-dihydroxycyclobut-3-ene-1,2-dionate),[5] pyronate and pyridinonate[6] anions are known. In contrast, organoruthenium complexes containing bidentate oxygen ligands have not been extensively studied.[7] Half-sandwich ruthenium complexes containing oxalato ligands have not been reported so far.

It is well known that ruthenium complexes are versatile compounds, able to catalyse various organic reactions.[8,9] In recent years there has been an increasing interest in mononuclear half-sandwich ruthenium complexes containing a chloride ligand and a chelating ligand, because the labile chloride can be readily displaced by small molecules such as H_2, N_2, O_2, CO, CO_2 and $CH_2{=}CH_2$.[7b,10–19] The co-ordination of such molecules is interesting with respect to activation for catalytic transformations. Thus, a half-sandwich cationic complex $[Ru(\eta^5\text{-}C_5Me_5)\{\eta^1\text{-}PPh_2CH_2\overline{CHO(CH_2)_3O}\}\{\eta^2\text{-}PPh_2CH_2\overline{CHO(CH_2)_3O}\}]^+$ was found to catalyse the hydrogenation of hex-1-ene to *n*-hexane.[18c] In this paper we report on mono-, di- and tetra-nuclear *p*-cymeneruthenium complexes containing bidentate and bis-bidentate oxalato ligands.

Results and Discussion

The *p*-cymene complex $[\{RuCl_2(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)\}_2]$ reacts with $(NH_4)_2C_2O_4$ in chloroform–methanol solution at 60 °C to give the dinuclear complex $[Ru_2(\mu\text{-}\eta^4\text{-}C_2O_4)Cl_2(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)_2]$ **1** (Scheme 1) as the only product. Complex **1** is soluble in CH_2Cl_2 and water. In the infrared spectrum it gives rise to only one very strong absorption at 1614 cm^{-1} for the C=O stretching of the oxalato ligand. The ^{13}C NMR spectrum shows, apart from the resonances of the *p*-cymene ligands, only one signal at δ 171.2 for the oxalato ligand. Depending on the solvent, **1** crystallizes in two quite different crystalline forms. The single-crystal X-ray analysis shows two conformational isomers **1a** (monoclinic crystals from $CHCl_3$) and **1b** (orthorhombic crystals from $CHCl_3$–MeOH–Et_2O) as represented in Fig. 1. No significant differences in bond lengths and angles of the two structures are observed (Table 1), even though **1b** is the sterically less favourable conformer. However, as the orientation of the isopropyl group of the *p*-cymene ligand is different with respect to the chloride co-ordination, the torsion angles about bonds



Scheme 1

Ru(1)–C(2) and Ru(1)–C(5) are quite different, see Table 1. Compared to mononuclear half-sandwich ruthenium chloro complexes (Ru–Cl bond length range: 2.42–2.47 Å),[7,12–16,20] **1a** and **1b** have shorter Ru–Cl bond distances [2.394(1) Å in **1a** and 2.391(1) Å in **1b**].

The mononuclear oxalato complex $[Ru(\eta^2\text{-}C_2O_4)(NH_3)(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)]$ **2** was prepared by the reaction of $[Ru(H_2O)_3(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)]^{2+}$ with $(NH_4)_2C_2O_4$ in an aqueous solution at pH 6–9 and 70 °C (Scheme 1). Complex **2** is also soluble in both CH_2Cl_2 and water. The ^{13}C NMR spectrum

Table 1 Selected bond lengths (Å) and angles (°) for compounds **1a** and **1b**

1a		**1b**	
Ru(1)–Cl(1)	2.3945(14)	Ru(1)–Cl(1)	2.3913(9)
Ru(1)–O(1)	2.127(3)	Ru(1)–O(1)	2.128(2)
Ru(1)–O(2a)	2.129(3)	Ru(1)–O(2b)	2.134(2)
O(1)–C(1)	1.252(5)	C(1)–O(1)	1.255(4)
O(2)–C(1)	1.256(6)	C(1)–O(2)	1.256(4)
C(1)–C(1a)	1.530(9)	C(1)–C(1b)	1.536(7)
Ru · · · Ru	5.500(6)	Ru · · · Ru	5.506(5)
O(1)–Ru(1)–O(2a)	77.99(12)	O(1)–Ru(1)–O(2b)	77.83(9)
C(1)–O(2)–Ru(1a)	112.6(3)	C(1)–O(1)–Ru(1)	112.6(2)
C(1)–O(1)–Ru(1)	112.6(3)	C(1)–O(2)–Ru(1b)	112.4(2)
O(1)–C(1)–C(1a)	117.5(5)	O(1)–C(1)–C(1b)	117.1(3)
O(2)–C(1)–C(1a)	117.0(5)	O(2)–C(1)–C(1b)	117.0(4)
O(1)–C(1)–O(2)	125.5(4)	O(1)–C(1)–O(2)	125.9(3)
O(1)–Ru(1)–Cl(1)	84.72(10)	O(1)–Ru(1)–Cl(1)	83.94(7)
O(2a)–Ru(1)–Cl(1)	82.90(11)	O(2b)–Ru(1)–Cl(1)	84.37(7)

Torsion angles	**1a**	**1b**
Cl(1)–Ru(1)–C(2)–C(8)	103.3(5)	34.3(4)
Cl(1)–Ru(1)–C(5)–C(11)	19.8(6)	85.7(4)

Symmetry operations: a $-x, -y + 1, -z$; b $-x, -y, -z$.

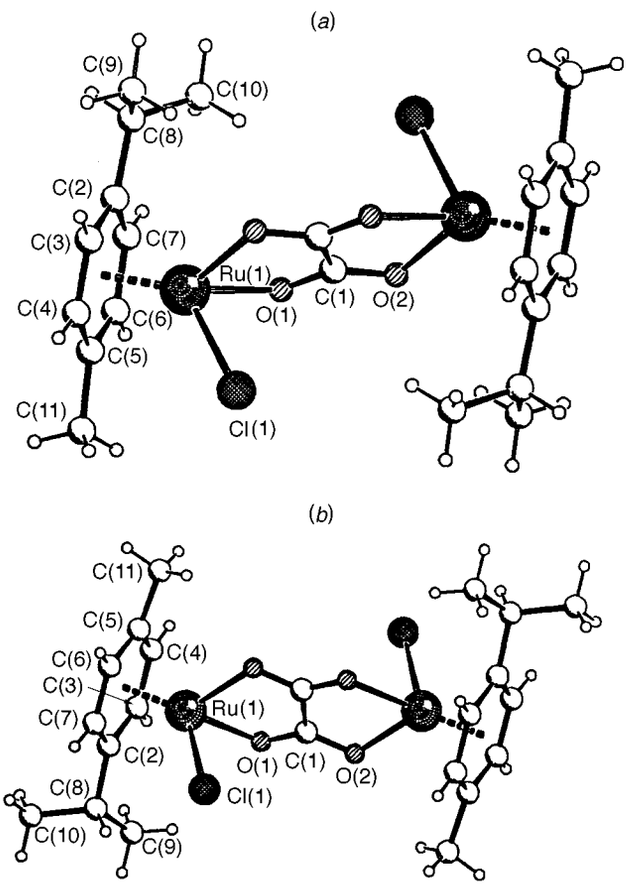


Fig. 1 View of the structures of $[Ru_2(\mu\text{-}\eta^4\text{-}C_2O_4)Cl_2(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)_2]$ **1** with two conformational isomers **1a** (*a*) and **1b** (*b*)

shows one peak at δ 167.9 revealing two equivalent C atoms of the oxalato ligand. The infrared spectrum displays two different C=O absorptions at 1701 and 1665 cm^{-1}, corresponding to the stretching vibrations of the C=O bonds with co-ordinated and free oxygen atoms of the oxalato ligand. The bands of a NH_3 ligand and a H_2O of crystallization appear in the 3177–3300 cm^{-1} region. The presence of the NH_3 ligand and the H_2O molecule of crystallization is also confirmed by the microanalytical data. The mass spectrum shows the molecular ion peak without

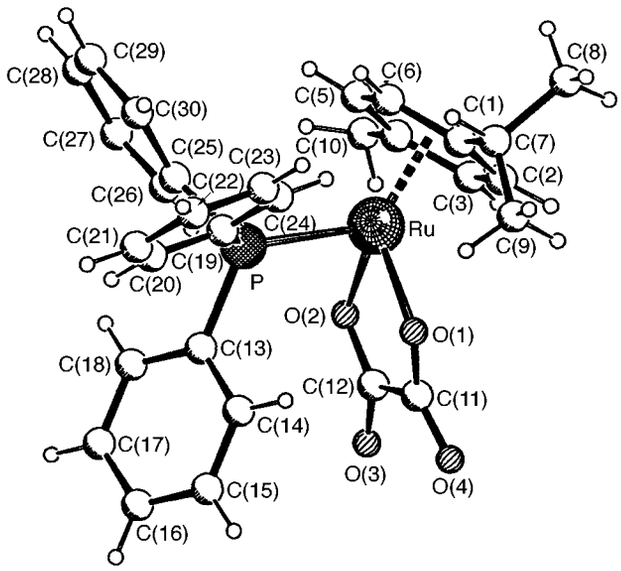


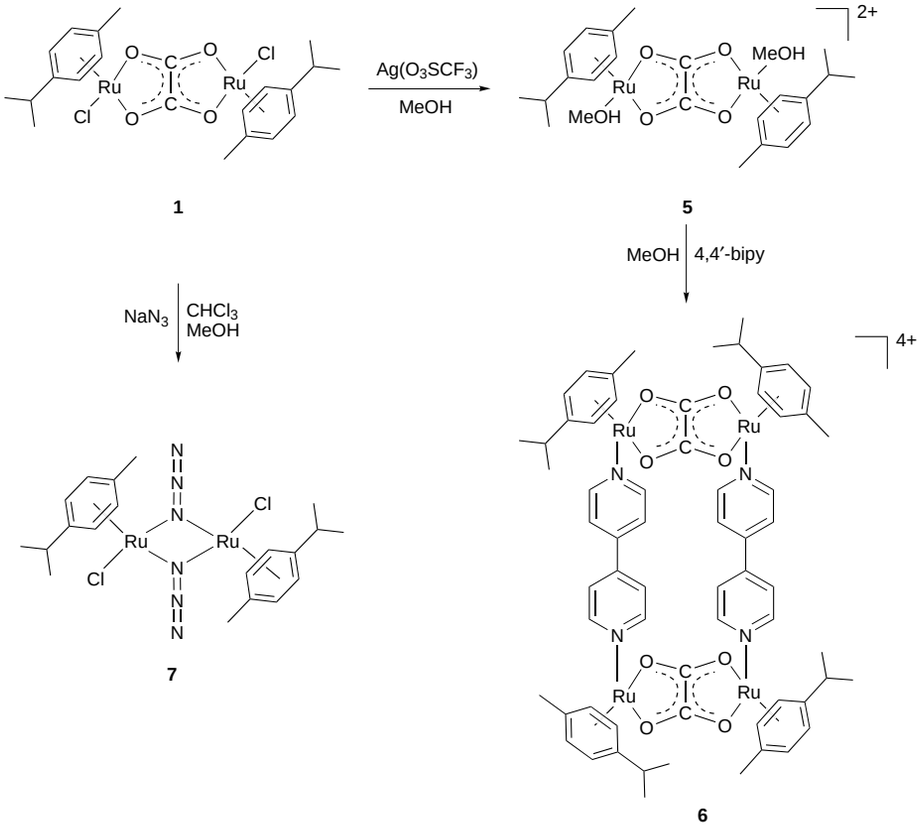
Fig. 2 View of the structure of $[Ru(\eta^2\text{-}C_2O_4)(PPh_3)(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)]$ **4**

a water of crystallization. The spectroscopic and analytical data are consistent with the formulation $[Ru(\eta^2\text{-}C_2O_4)(NH_3)(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)]\cdot H_2O$, in which the NH_3 ligand stems from ammonium oxalate. Further evidence for the co-ordination of NH_3 rather than H_2O comes from the following experiment: replacing $(NH_4)_2C_2O_4$ by $Na_2C_2O_4$ does not give **2**. The analogous complex $[Ru(\eta^2\text{-}C_2O_4)(H_2O)(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)]$ forms presumably, but the co-ordination of the H_2O is too weak for isolation of the complex. In addition, it is noteworthy that in aqueous solution the oxalate group does not link two ($\eta^6\text{-}p\text{-}Pr^iC_6H_4Me$)Ru units to form a dinuclear complex.

Chloride abstraction from complex **1** with equal amounts of PPh_3 in the presence of $Na[O_3SCF_3]$ leads to formation of the complex $[Ru_2(\mu\text{-}\eta^4\text{-}C_2O_4)(PPh_3)_2(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)_2]^{2+}$ **3** as the only product (Scheme 1). The ^{31}P NMR spectrum of **3** shows only one peak at δ 32.1, the IR spectrum displays one strong absorption at 1626 cm^{-1} indicating the presence of the symmetrical oxalato ligand. In the mass spectrum two strong characteristic fragments $[Ru(PPh_3)(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)]^+$ and $[Ru(PPh_3)]^+$ can be observed. The constitution of **3** is proposed on the basis of the microanalytical and spectroscopic data.

The mononuclear complex $[Ru(\eta^2\text{-}C_2O_4)(PPh_3)(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)]$ **4** was prepared from **2** by substitution of NH_3 with PPh_3 (Scheme 1). In the IR spectrum of **4** two absorptions at 1694 and 1672 cm^{-1} indicate two inequivalent C=O stretching vibrations of the oxalato ligand. In the ^{31}P NMR spectrum only one resonance was found at δ 30.4, while in the mass spectrum the molecular ion peak was observed. The molecular structure of **4** was solved by a single-crystal X-ray analysis and is shown in Fig. 2, with selected bond lengths and angles listed in Table 2. The Ru–P bond length [2.367(2) Å] in **4** is comparable to that found in related Ru–PPh_3 complexes.[14b,21] The oxalate is co-ordinated by two vicinal oxygen atoms giving rise to the formation of a five-membered metallacycle. The C–O distances of the co-ordinated oxygen atoms [C(11)–O(1) 1.330(6), C(12)–O(2) 1.271(6) Å] are as expected longer than those of the non-co-ordinated oxygen atoms [C(11)–O(4) 1.221(7), C(12)–O(3) 1.226(6) Å]. The O–C–C angles of the oxalato ligand are also smaller for the co-ordinated compared to the free oxygen atoms: O(1)–C(11)–C(12) 114.1(5), O(2)–C(12)–C(11) 115.9(5); O(4)–C(11)–C(12) 121.4(6), O(3)–C(12)–C(11) 120.0(6)°. This is in contrast to complex **1** in which the oxalate is co-ordinated on both sides to ruthenium atoms, giving rise to the equivalence of all four C–O bonds [1.256(5) Å] and of all four O–C–C angles [117.2(4)°].

The dinuclear cation $[Ru_2(\mu\text{-}\eta^4\text{-}C_2O_4)(MeOH)_2(\eta^6\text{-}p\text{-}Pr^iC_6\text{-}$



1 **5** **7** **6**

Scheme 2

Table 2 Selected bond lengths (Å) and angles (°) for compounds **4** and **5**

4		**5**	
Ru–P	2.367(2)	Ru(1)–O(3)	2.104(5)
Ru–O(2)	2.080(3)	Ru(1)–O(1)	2.120(4)
Ru–O(1)	2.084(4)	Ru(1)–O(2a)	2.130(4)
C(11)–O(4)	1.221(7)	C(1)–O(2)	1.258(7)
C(11)–O(1)	1.300(6)	C(1)–O(1)	1.260(7)
C(11)–C(12)	1.548(8)	C(1)–C(1a)	1.519(14)
C(12)–O(3)	1.226(6)	O(3)–C(13)	1.348(10)
C(12)–O(2)	1.271(6)	Ru · · · Ru	5.548(5)
O(2)–Ru–O(1)	78.6(2)	O(3)–Ru(1)–O(1)	82.2(2)
O(2)–Ru–P	84.41(11)	O(3)–Ru(1)–O(2a)	83.5(2)
O(1)–Ru–P	90.46(12)	O(1)–Ru(1)–O(2a)	77.8(2)
O(4)–C(11)–O(1)	124.5(6)	O(2)–C(1)–O(1)	125.7(6)
O(4)–C(11)–C(12)	121.4(6)	O(2)–C(1)–C(1a)	117.4(6)
O(1)–C(11)–C(12)	114.1(5)	O(1)–C(1)–C(1a)	116.9(7)
O(3)–C(12)–O(2)	124.1(6)	C(1)–O(1)–Ru(1)	114.2(4)
O(3)–C(12)–C(11)	120.0(6)	C(1)–O(2)–Ru(1a)	113.6(4)
O(2)–C(12)–C(11)	115.9(5)	C(13)–O(3)–Ru(1)	130.3(6)
C(11)–O(1)–Ru	114.2(4)		
C(12)–O(2)–Ru	114.9(4)		

Symmetry operation: a $-x, -y + 2, -z + 2$.

$H_4Me)_2]^{2+}$ **5** was obtained by using Ag^+ to remove the chloride ligands of **1** in methanolic solution (Scheme 2) and isolated as the triflate (O_3SCF_3) salt. The IR spectrum of **5** displays only one strong absorption at 1631 cm^{-1} for the co-ordinated oxalate. In the ^1H NMR spectrum the methanol ligands could not be found in CD_3OD. However, the co-ordination of methanol was unambiguously revealed by a single-crystal X-ray structural analysis of the CF_3SO_3 salt of **5** (Fig. 3). Complex **5** retains the conformation of **1**, and there are no apparent changes in bond lengths and angles except a slightly increased angle of C(1)–O(1)–Ru(1) from 112.6(2) to 114.2(4)°. A slightly increased Ru · · · Ru distance in **5** [5.548(5) Å] is also found compared to that in **1** [mean 5.503(6) Å] (Table 2).

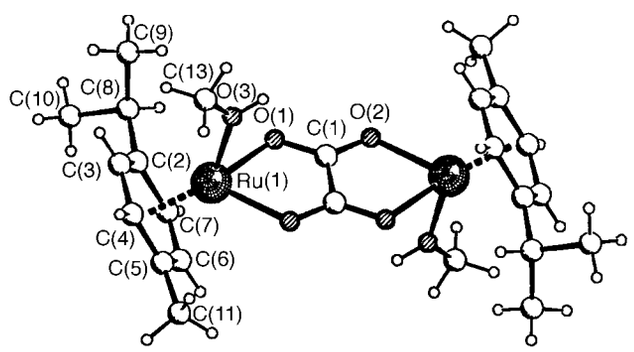


Fig. 3 View of the structure of $[Ru_2(\mu\text{-}\eta^4\text{-}C_2O_4)(MeOH)_2(\eta^6\text{-}p\text{-}Pr^i\text{-}C_6H_4Me)_2]^{2+}$ **5** (anions omitted for clarity)

The reaction of the methanol complex **5** with 4,4′-bipyridine gave the macrocyclic cation $[Ru_4(\mu\text{-}\eta^4\text{-}C_2O_4)_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-bipy})_2(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)_4]^{4+}$ **6** (Scheme 2). The IR spectrum exhibits only one ν_{CO} band at 1636 cm^{-1}, and the ^1H NMR spectrum indicates a symmetrical structure with 4,4′-bipyridine as a bridging ligand. The single-crystal X-ray analysis of the CF_3SO_3 salt reveals a macrocycle with alternating oxalato and 4,4′-bipyridine bridges between the ruthenium atoms as shown in Fig. 4. The complex possesses crystallographic C_2 symmetry, hence the two oxalato planes are parallel to one another. The two pyridine rings of each 4,4′-bipyridine ligand are not coplanar, being inclined to one another by an angle of 19.5(7)°. The dihedral angles between the two rings of bipyridine and the oxalato planes are 86.3(4) [a^d] and 83.0(3)° [a^c], respectively (Table 3). The macrocyclic arrangement of **6** is responsible for the distortion of the $(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)Ru(\mu\text{-}\eta^4\text{-}C_2O_4)Ru(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)$ units with respect to complex **5**. In **6** the two Ru–O bonds on the same side of the oxalato ligand are inequivalent [Ru(1)–O(4) 2.098(9), Ru(1)–O(3) 2.134(9); Ru(2)–O(1) 2.141(9), Ru(2)–O(2) 2.101(9) Å]. Other important bond lengths, angles and dihedral angles are summarized in Table 3. The poor quality of the crystal and the problems of disorder of

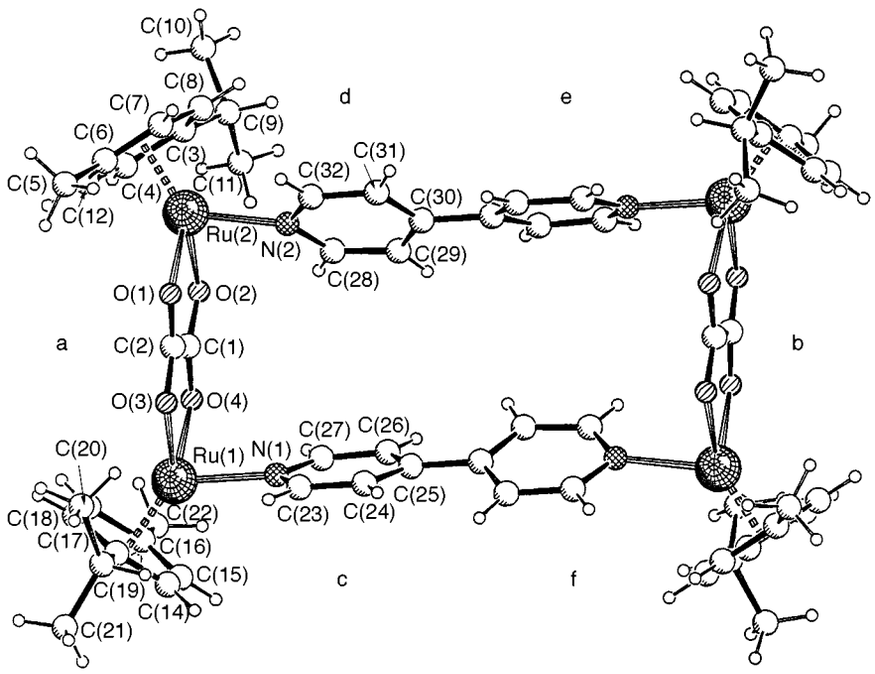


Fig. 4 View of the structure of $[Ru_4(\mu\text{-}\eta^4\text{-}C_2O_4)_2(\mu\text{-}\eta^1:\eta^1\text{-bipy})_2(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)_4]^{4+}$ **6** (anions omitted for clarity)

Table 3 Selected bond lengths (Å) angles (°) and dihedral angles* (°) for compound **6**

Ru(1)–O(3)	2.134(9)	Ru(1)–O(4)	2.098(9)
Ru(2)–O(1)	2.141(9)	Ru(2)–O(2)	2.101(9)
Ru(1)–N(1)	2.117(10)	Ru(2)–N(2)	2.136(10)
C(1)–O(2)	1.251(15)	C(2)–O(1)	1.245(15)
C(1)–O(4)	1.248(15)	C(2)–O(3)	1.271(16)
C(1)–C(2)	1.544(18)	N(1)–C(23)	1.340(19)
N(1)–C(27)	1.322(19)	N(2)–C(28)	1.352(18)
N(2)–C(32)	1.322(18)	Ru · · · Ru	5.532(9)
Ru · · · Ru (bipy bridged)	11.315(10)	(oxalato bridged)	
O(4)–Ru(1)–N(1)	84.7(4)	O(4)–Ru(1)–O(3)	78.1(3)
N(1)–Ru(1)–O(3)	83.9(4)	O(2)–Ru(2)–N(2)	87.6(4)
O(2)–Ru(2)–O(1)	77.8(3)	N(2)–Ru(2)–O(1)	84.6(4)
O(4)–C(1)–O(2)	126.8(13)	O(4)–C(1)–C(2)	117.1(14)
O(2)–C(1)–C(2)	115.9(14)	O(1)–C(2)–O(3)	126.6(13)
O(1)–C(2)–C(1)	117.5(14)	O(3)–C(2)–C(1)	115.9(13)
C(27)–N(1)–C(23)	118.0(12)	C(27)–N(1)–Ru(1)	121.6(10)
C(23)–N(1)–Ru(1)	120.3(10)	C(32)–N(2)–C(28)	116.3(12)
C(32)–N(2)–Ru(2)	121.7(10)	C(28)–N(2)–Ru(2)	122.6(11)
a^d(f^b)	86.3(4)	a^c(b^e)	83.0(4)
c^d(e^f)	46.3(5)	c^f(d^e)	19.5(7)
d^f	65.5(4)	c^e	26.9(4)

* See Fig. 4 for a–f.

the anion in **6** give rise to considerable errors in the bond lengths and angles.

In an attempt to replace the chloride ligands in **1** by azido ligands the complex was treated with sodium azide in a chloroform–methanol solution. However, in this case the bridging oxalato ligand was displaced, giving rise to the known complex $[\{Ru(\mu\text{-}\eta^1\text{-}N_3)Cl(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)\}_2]$ **7** (Scheme 2). This compound had already been synthesized and structurally characterized by Wright and co-workers[22] from the reaction of $[\{RuCl_2(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)\}_2]$ with $SiMe_3N_3$.

Experimental

All synthetic operations were performed in a nitrogen atmosphere using standard Schlenk techniques. Organic solvents were dried over appropriate drying agents, then distilled and kept under inert gas before use. The starting material $[\{RuCl_2(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)\}_2]$ was prepared according to the literature method.[19] All other reagents were commercially available and used as received.

The NMR spectra were recorded on Varian Gemini 200 and Bruker AMX 400 instruments with $SiMe_4$ as internal standard in organic solvents and sodium 4,4-dimethyl-4-silapentane-1-sulfonate as internal standard in D_2O. Chemical shifts for ^{31}P resonances were referred to 85% H_3PO_4. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer FTIR 1720 X spectrometer. Microanalytical data were obtained from the Mikroelementar-analytisches Laboratorium der ETH Zürich, and mass spectra (FAB) from Professor Titus A. Jenny, University of Fribourg.

Preparation

$[Ru_2(\mu\text{-}\eta^4\text{-}C_2O_4)Cl_2(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)_2]$ 1. To a solution of $[\{RuCl_2(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)\}_2]$ (306 mg, 0.5 mmol) in $CHCl_3$–MeOH (1:1, 30 cm^3) was added $(NH_4)_2C_2O_4\cdot H_2O$ (71 mg, 0.5 mmol). The mixture was refluxed for about 6 h, then the solvent was removed. The residue was taken up in CH_2Cl_2 and the resulting slurry filtered to remove the salts. The filtrate was evaporated to dryness *in vacuo* to give compound **1** as an orange powder. Yield 280 mg (89%). Crystals suitable for X-ray analysis were obtained by slow evaporation of a $CHCl_3$ solution (Found: C, 42.15; H, 4.43. $C_{22}H_{28}Cl_2O_4Ru_2$ requires C, 41.97; H, 4.48%). IR (cm^{-1}): ν(CO) 1614vs. ^1H NMR ($CDCl_3$): δ 5.569 (2 H, d, $J = 6.4$, C_6H_4), 5.336 (2 H, d, $J = 6.4$ Hz, C_6H_4), 2.883 [1 H, m, $CH(CH_3)_2$], 2.229 (3 H, s, CH_3), 1.333 [3 H, s, $CH(CH_3)_2$] and 1.298 [3 H, s, $CH(CH_3)_2$]. ^{13}C NMR ($CDCl_3$): δ 171.2 (CO), 99.8, 95.5, 80.4, 78.4 (C_6H_4), 31.1 [$CH(CH_3)_2$], 22.4 [$CH(CH_3)_2$] and 18.5 (CH_3). FAB mass spectrum: *m/z* (%) (18, M^+), (50, $[M - Cl]^+$) and (60, $[M - C_2O_4]^+$).

$[Ru(\eta^2\text{-}C_2O_4)(NH_3)(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)]$ 2. To a suspension of $[\{RuCl_2(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)\}_2]$ (122 mg, 0.2 mmol) in water (15 cm^3) was added Ag_2SO_4 (125 mg, 0.4 mmol). The mixture was stirred at room temperature for 3 h, then filtered. The salt $(NH_4)_2C_2O_4\cdot H_2O$ (57 mg, 0.4 mmol) was added to the filtrate, then the pH was adjusted to 7–8 and temperature raised to 70 °C for 1–2 h. The solvent was evaporated to dryness and addition of CH_2Cl_2 gave a slurry which was filtered to remove

the salts. The filtrate was evaporated *in vacuo* to give compound **2** as a yellow powder. Yield 120 mg (84%). Recrystallization from methanol–diethyl ether afforded yellow crystals (Found: C, 39.80; H, 5.13; N, 4.11. $C_{12}H_{17}NO_4Ru\cdot H_2O$ requires C, 40.22; H, 5.30; N, 3.91%). IR (cm^{-1}): ν(CO) 1665vs, 1701(br) s; ν(NH) and ν(OH) 3177–3300w. ^1H NMR (CD_3OD): δ 5.725 (2 H, d, $J = 6.2$, C_6H_4), 5.478 (2 H, d, $J = 6.2$ Hz, C_6H_4), 2.848 [1 H, m, $CH(CH_3)_2$], 2.214 (3 H, s, CH_3), 1.351 [3 H, s, $CH(CH_3)_2$] and 1.317 [3 H, s, $CH(CH_3)_2$]. ^{13}C NMR (CD_3OD); δ 167.9 (CO), 101.6, 97.5, 83.1, 80.5 (C_6H_4), 32.3 [$CH(CH_3)_2$], 22.9 [$CH(CH_3)_2$] and 18.2 (CH_3). FAB mass spectrum: *m/z* (%) (10, $[M - H_2O]^+$), (12, $[M - H_2O - NH_3]^+$), (70, $[M - H_2O - C_2O_4]^+$) and (35, $[M - H_2O - NH_3 - C_2O_4]^+$).

$[Ru_2(\mu\text{-}\eta^4\text{-}C_2O_4)(PPh_3)_2(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)_2][O_3SCF_3]_2$ 3. To a solution of compound **1** (63 mg, 0.1 mmol) in $CHCl_3$–MeOH (1 : 1, 20 cm^3) were added solid PPh_3 (52.8 mg, 0.2 mmol) and $Na[O_3SCF_3]$ (42 mg, 0.24 mmol). The mixture was stirred at 40 °C for 36 h. Then the solvent was drawn off, and the orange residue taken up in CH_2Cl_2. The slurry was centrifuged to remove the insoluble materials. The resulting solution was then treated with ether in order to precipitate the product. The supernatant was discarded and the yellow powder was washed with ether and then dried *in vacuo*. Yield 110 mg (80%) (Found: C, 52.41; H, 4.35. $C_{60}H_{58}F_6O_{10}P_2Ru_2S_2$ requires C, 52.17; H, 4.23%). IR (cm^{-1}): ν(CO) 1626vs. ^1H NMR ($CDCl_3$): δ 7.883–7.301 (30 H, m, PPh_3), 5.200 (2 H, d, $J = 6.0$, C_6H_4), 4.992 (2 H, d, $J = 6.0$ Hz, C_6H_4), 2.854 [1 H, m, $CH(CH_3)_2$], 1.872 (3 H, s, CH_3), 1.121 [3 H, s, $CH(CH_3)_2$] and 1.086 [3 H, s, $CH(CH_3)_2$]. ^{31}P NMR ($CDCl_3$): δ 32.1. FAB mass spectrum: *m/z* (%) {100, $[Ru(PPh_3)(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)]^+$} and {80, $[Ru(PPh_3)]^+$}.

$[Ru(\eta^2\text{-}C_2O_4)(PPh_3)(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)]$ 4. Solid PPh_3 (52.8 mg, 0.2 mmol) was added to a solution of compound **2** in $CHCl_3$–MeOH (1 : 1, 20 cm^3). The mixture was stirred at 40 °C for 30 h, and then concentrated to a smaller volume (about 2 cm^3). Ether was added to precipitate the product. The yellow powder was isolated by decanting and washed with ether, then dried *in vacuo*. Yield 95 mg (81%). Crystals suitable for the X-ray analysis were grown by slow diffusion of hexane into a $CHCl_3$ solution of **4** (Found: C, 52.52; H, 4.26. $C_{30}H_{29}O_4PRu\cdot CHCl_3$ requires C, 52.75; H, 4.25%). IR (cm^{-1}): ν(CO) 1694vs and 1672vs. ^1H NMR ($CDCl_3$): δ 7.537–7.343 (15 H, m, PPh_3), 5.324 (2 H, d, $J = 5.8$, C_6H_4), 5.091 (2 H, d, $J = 5.8$ Hz, C_6H_4), 2.531 [1 H, m, $CH(CH_3)_2$], 1.908 (3 H, s, CH_3), 1.159 [3 H, s, $CH(CH_3)_2$] and 1.124 [3 H, s, $CH(CH_3)_2$]. ^{31}P NMR ($CDCl_3$): δ 30.4. FAB mass spectrum: *m/z* (%) (33, M^+), (100, $[M - C_2O_4]^+$), {87, $[M - (\eta^6\text{-}p\text{-}Pr^iC_6H_4Me) - C_2O_4]^+$} and (30, $[M - PPh_3 - C_2O_4]^+$).

$[Ru_2(\mu\text{-}\eta^4\text{-}C_2O_4)(MeOH)_2(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)_2][O_3SCF_3]_2$ 5. Solid $Ag[O_3SCF_3]$ (102.8 mg, 0.40 mmol) was added to a solution of compound **1** (126 mg, 0.2 mmol) in methanol (20 cm^3). The mixture was stirred at room temperature for 2 h, then filtered. The filtrate was evaporated to dryness to give **5** as a yellow solid. Yield 184 mg (100%). Recrystallization from methanol–ether gave well shaped orange crystals (Found: C, 33.79; H, 3.85. $C_{26}H_{36}O_{12}F_6Ru_2S_2$ requires C, 33.91; H, 3.94%). IR (cm^{-1}): ν(CO) 1631vs. ^1H NMR (CD_3OD): δ 5.978 (2 H, d, $J = 6.2$, C_6H_4), 5.772 (2 H, d, $J = 6.2$ Hz, C_6H_4), 2.888 [1 H, m, $CH(CH_3)_2$], 2.271 (3 H, s, CH_3), 1.399 [3 H, s, $CH(CH_3)_2$] and 1.366 [3 H, s, $CH(CH_3)_2$]. FAB mass spectrum: *m/z* (%) (100, $[M - 2MeOH - O_3SCF_3]^+$) and (8, $[M - 2MeOH - 2O_3SCF_3]^+$).

$[Ru_4(\mu\text{-}\eta^4\text{-}C_2O_4)_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-bipy})_2(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)_4][O_3SCF_3]_4$ 6. Solid 4,4′-bipyridine (31.2 mg, 0.2 mmol) was added to a solution of compound **5** (184 mg, 0.2 mmol) in methanol (20 cm^3). The mixture was stirred at room temperature for 24 h, then reduced to dryness, yielding **6** as an orange-red solid (203 mg, 100%). Suitable crystals for X-ray analysis were grown by slow diffusion of ether into an acetonitrile solution (Found: C, 40.05; H, 3.41; N, 3.02. $C_{68}H_{72}F_{12}N_4O_{20}Ru_4S_4$ requires C, 40.32; H, 3.58; N, 2.77%). IR (cm^{-1}): ν(CO) 1636vs. ^1H NMR [$(CD_3)_2CO$]: δ 8.286 (4 H, d, $J = 6.6$, 4,4′-bipy), 7.900 (4 H, d, $J = 6.6$, 4,4′-bipy), 6.094 (2 H, d, $J = 6.6$, C_6H_4), 5.932 (2 H, d, $J = 6.6$ Hz, C_6H_4), 2.910 [1 H, m, $CH(CH_3)_2$], 2.234 (3 H, s, CH_3), 1.377 [3 H, s, $CH(CH_3)_2$] and 1.342 [3 H, s, $CH(CH_3)_2$]. FAB mass spectrum: *m/z* (%) (12, $[\frac{1}{2}M - O_3SCF_3]^+$), (100, $[\frac{1}{2}M - bipy - O_3SCF_3]^+$) and (8, $[\frac{1}{2}M - bipy - 2O_3SCF_3]^+$).

$[\{Ru(\mu\text{-}\eta^1\text{-}N_3)Cl(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)\}_2]$ 7. To a solution of compound **1** (63 mg, 0.1 mmol) in $CHCl_3$–MeOH (1 : 1, 20 cm^3) was added solid NaN_3 (13 mg, 0.2 mmol). The mixture was stirred at room temperature for 14 h, then evaporated to dryness. The orange residue was treated with CH_2Cl_2 to give a slurry which was filtered. The resulting filtrate was concentrated to a smaller volume (5 cm^3), then methanol and ether were added for crystallization. Yield 43 mg (70%). ν(NN) 2059s cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.333 (2 H, d, $J = 6.2$, C_6H_4), 5.247 (2 H, d, $J = 6.2$ Hz, C_6H_4), 2.907 [1 H, m, $CH(CH_3)_2$], 2.258 (3 H, s, CH_3), 1.291 [3 H, s, $CH(CH_3)_2$] and 1.269 [3 H, s, $CH(CH_3)_2$].

Crystallography

Orange crystals of compounds **1a**, **1b** and **4**–**6** were glued on the top of a glass fibre and mounted on a Stoe-Siemens AED2 four-circle diffractometer. Intensity data were measured using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Compounds **1a**, **4** and **6** were measured at room temperature while data for **1b** and **5** were collected at −50 °C. The ω–2θ scan technique was used to a maximum 2θ value of 51.0°. The cell parameters were determined from a least-squares treatment of the setting angles of 20 reflections with $12.5 < \theta < 18.4°$ (**1a**), 20 with $12.5 < \theta < 20.0°$ (**1b**), 22 with $12.5 < \theta < 17.2°$ (**4**), 22 with $14.0 < \theta < 19.2°$ (**5**) and 18 with $14.0 < \theta < 17.2°$ (**6**). For each compound the intensities of two representative reflections were measured every 60 min. During data collection the intensity of the standards decreased by less than 1% for all the compounds. Table 4 provides summaries of the crystal data, data collection and refinement parameters. No absorption corrections were applied, as the μ(Mo-Kα) values were all less than 2.0 mm^{-1}. For **6** the crystals were very irregular in shape and no suitable ψ scans were available.

The structures were solved by direct methods using the program SHELXS 86[23] and refined by full-matrix least squares on F^2 with SHELXL 93.[24] Hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL 93 default parameters. Crystals of compounds **5** and **6** could only be obtained using $CF_3SO_3^-$ as counter ion. In the case of **6** only poor-quality crystals with a large mosaic spread could be obtained. In these the counter ions $CF_3SO_3^-$ were highly disordered. Three partially occupied positions were found (occupancy 0.50 and 2 × 0.25) and it was necessary to apply constraints. A DFIX instruction was used to improve the C–F, C–S and S–O distances.The isopropyl substituent of the *p*-cymene ligand was also disordered in such a manner that one methyl group occupied two positions with an occupancy of 0.5. These problems, together with the poor quality of the crystal and the lack of absorption correction, are probably responsible for the high *R* factors and the considerable errors in bond lengths and angles for complex **6**.

The figures were drawn with SCHAKAL.[25]

CCDC reference number 186/730.

Acknowledgements

We thank the Swiss National Science Foundation for financial support and the Johnson Matthey Research Centre for a generous loan of ruthenium chloride hydrate.

Table 4 Crystallographic data, data collection and refinement parameters for compounds **1a**, **1b** and **4**–**6**

	1a	**1b**	**4**	**5**	**6**
Formula	$C_{22}H_{28}Cl_2O_4Ru_2$	$C_{22}H_{28}Cl_2O_4Ru_2$	$C_{30}H_{29}O_4PRu$	$C_{26}H_{36}F_6O_{12}Ru_2S_2$	$C_{68}H_{72}F_{12}N_4O_{20}Ru_4S_4$
M	629.48	629.48	585.57	920.8	2027.83
Crystal size/mm	0.46 × 0.27 × 0.15	0.68 × 0.30 × 0.27	0.61 × 0.23 × 0.23	0.30 × 0.30 × 0.15	0.61 × 0.38 × 0.11
T/K	293(2)	223(2)	293(2)	223(2)	293(2)
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	*Pbca*	$P2_1/c$	$P2_1/a$	$I2/a$
a, *b*, *c*/Å	7.571(1), 8.998(1), 16.528(2)	10.486(1), 11.822(1), 18.961(2)	8.705(1), 15.388(2), 19.727(3)	11.066(1), 13.374(2), 11.441(1)	20.728(2), 14.606(5), 29.663(5)
β/°	95.52(1)		90.16(1)	95.94(1)	109.84(1)
U/Å^3	1120.7(2)	2350.5(4)	2642.5(6)	1684.2(4)	8448(3)
Z	2	4	4	2	4
μ(Mo-Kα)/mm^{-1}	1.163	1.538	0.688	1.112	0.893
D_c/g cm^{-3}	1.865	1.779	1.472	1.816	1.594
F(000)	628	1256	1200	924	4072
θ Scan range/°	2.48–25.49	2.15–25.48	2.06–25.52	2.15–25.51	2.03–25.51
No. reflections measured	2083	2186	4931	3139	7868
No. independent reflections	2083	2186	4931	3139	7868
No. observed reflections	1700	1936	3695	2527	4182
Goodness of fit on F^2	1.185	1.221	1.212	1.192	1.163
Final *R*1, *wR*2 indices					
$[I > 2\sigma(I)]$	0.0407, 0.0954	0.0292, 0.0714	0.0546, 0.0850	0.0543, 0.1270	0.1088, 0.2065
(all data)	0.0520, 0.1108	0.0359, 0.0779	0.0862, 0.1071	0.0737, 0.1533	0.2010, 0.2619
$\Delta\rho_{max}$, $\Delta\rho_{min}$/e Å^{-3}	1.444, −1.385	0.453, −0.549	0.418, −0.350	0.861, −0.535	1.0861, −0.535

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Received 2*nd July* 1997; *Paper* 7/04658H