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Synthesis and reactivity of non-polymeric tetracarboxylatochlorodiruthenium(II,III) complexes. Crystal structure of $[Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4(OPPh_3)]$‡

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New non-polymeric diruthenium(II,III) carboxylates of the type $[Ru_2Cl(\mu\text{-}O_2CR)_4]$ (R = CHEt$_2$ **1**, CHMeEt **2** or CHMePh **3**) were obtained by reaction of HO$_2$CR with $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ in methanol–water. The mixed-ligand complex $[Ru_2Cl(\mu\text{-}O_2CMe)_2(\mu\text{-}O_2CCMe_3)_2]$ **4** has also been prepared. The reactivity of these complexes and of the previously described $[Ru_2Cl(\mu\text{-}O_2CR)_4]$ (R = CMe$_3$ **5** or CHMe$_2$ **6**) has been studied and compared with those found for polymeric $[Ru_2Cl(\mu\text{-}O_2CR)_4]$ (R = alkyl or aryl). The interaction of AgSCN with $[Ru_2Cl(\mu\text{-}O_2CR)_4]$ or $[Ru_2Cl(\mu\text{-}O_2CMe)_2(\mu\text{-}O_2CCMe_3)_2]$ leads to $[Ru_2(\mu\text{-}O_2CR)_4(SCN)]$ (R = CHEt$_2$ **7**, CHMePh **8** or CMe$_3$ **9**) and $[Ru_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O_2CCMe_3)_2(SCN)]$ **10** respectively. The first derivatives of the type $[Ru_2X(\mu\text{-}O_2CR)_4(OPPh_3)]$ (X = Cl; R = CHEt$_2$ **11**, CHMeEt **12**, CHMePh **13**, CMe$_3$ **14** or CHMe$_2$ **15**; X = SCN; R = CHEt$_2$ **17**, CHMePh **18** or CMe$_3$ **19**) and $[Ru_2Cl(\mu\text{-}O_2CMe)_2(\mu\text{-}O_2CCMe_3)_2(OPPh_3)]$ **16** containing two different axial ligands have been obtained. Cationic compounds of the type $[Ru_2(\mu\text{-}O_2CR)_4(thf)_2]BF_4$ (R = CMe$_3$ **20** or CHMe$_2$ **21**; thf = tetrahydrofuran), $[Ru_2(\mu\text{-}O_2CCHMe_2)_4(OPPh_3)_2]BF_4$ **22** or $[Ru_2(\mu\text{-}O_2CCHMe_2)_4(OPPh_3)(thf)]BF_4$ **23** were also prepared. The crystal structure of **15** has been determined by X-ray crystallography. It has two ruthenium atoms linked by four bridging isobutyrate ligands with the axial positions being occupied by one chlorine atom and one OPPh$_3$ molecule.

For several years[1–8] it has been considered that the structure of all $Ru_2Cl(\mu\text{-}O_2CR)_4$ (R = alkyl or aryl) compounds consists of $[Ru_2(\mu\text{-}O_2CR)_4]^+$ units linked into infinite chains by bridging chloride ions. However, we have recently reported[9,10] the first non-polymeric compounds of this type which form discrete dinuclear molecules in solution and the solid state. The non-polymeric nature of $[Ru_2Cl(\mu\text{-}O_2CC_4H_4N)_4(thf)]\cdot thf\cdot H_2O$ (thf = tetrahydrofuran) has been related to the presence of NH groups in the carboxylate ligands and the formation of several hydrogen bonds.[9] However, in the cases[10] of $[Ru_2Cl(\mu\text{-}O_2CCMe_3)_4(H_2O)]$ and $[Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4(thf)]$ the non-polymeric nature cannot be attributed to the presence of NH groups or pendant substituents in the ligands which can block one of the axial positions of the Ru_2^{5+} unit, because the volume of the *tert*-butyl and isopropyl groups of the bridging ligands does not affect the axial positions of the dimetallic unit. Thus, in the last two cases no special reason has been found for the formation of isolated dinuclear molecules.

In an effort to explore the influence of the carboxylate ligands in the polymeric/non-polymeric nature of the $Ru_2Cl(\mu\text{-}O_2CR)_4$ compounds, we have now studied the reactions of $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ with carboxylic acids HO$_2$CR (R = CHEt$_2$, CHMeEt or CHMePh) which lead to new non-polymeric compounds of the type $[Ru_2Cl(\mu\text{-}O_2CR)_4]$. The reactivity of these compounds and of those previously described[10] $[Ru_2Cl(\mu\text{-}O_2CR)_4]$ (R = CMe$_3$ or CHMe$_2$) has been investigated to explore the chemical behaviour of such species and to establish the differences from the polymeric compounds. The first diruthenium(II,III) carboxylate compounds with two different axial ligands $[Ru_2X(\mu\text{-}O_2CR)_4L]$ (X = Cl or SCN; L = OPPh$_3$) have been isolated.

Results and Discussion

The reactions carried out are summarized in Scheme 1. The reaction of $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ with alkyl carboxylic acids HO$_2$CR (molar ratio Ru$_2$: L = 1 : 6; R = CHEt$_2$, CHMeEt or CHMePh) in methanol–water (1 : 1) leads to total substitution of the acetate ligands with formation of $[Ru_2Cl(\mu\text{-}O_2CR)_4(H_2O)]$. The mixed-ligand complex $[Ru_2Cl(\mu\text{-}O_2CMe)_2(\mu\text{-}O_2CCMe_3)_2(H_2O)]$ was obtained using a molar ratio Ru$_2$: L = 1 : 2. The corresponding unsolvated $[Ru_2Cl(\mu\text{-}O_2CR)_4]$ (R = CHEt$_2$ **1**, CHMeEt **2** or CHMePh **3**) and $[Ru_2Cl(\mu\text{-}O_2CMe)_2(\mu\text{-}O_2CCMe_3)_2]$ **4** were obtained when $[Ru_2Cl(\mu\text{-}O_2CR)_4(H_2O)]$ are pumped to vacuum. These compounds are soluble in polar organic solvents such as methanol, thf, acetone and dichloromethane, giving the corresponding solvated species. Conductivity measurements in methanol, thf or CH$_2$Cl$_2$ solutions indicate that they are non-electrolytes,[11] showing no dissociation of the Ru–Cl bond and the presence of discrete dimeric molecules. The solubility and conductivity data and the reactivity patterns described below suggest that these complexes have a non-polymeric structure, similar to those observed in the case of pyrrole-2-carboxylato, trimethylacetato and isobutyrato derivatives.[9–10]

The reaction of $[Ru_2Cl(\mu\text{-}O_2CR)_4]$ with AgSCN was carried out to introduce the SCN$^-$ ligand which has a stronger tendency to act as a bridge than does chloride, in order to determine whether, also under these conditions, non-polymeric compounds are also formed. When the products of these reactions were pumped to vacuum unsolvated $[Ru_2(\mu\text{-}O_2CR)_4(SCN)]$ (R = CHEt$_2$ **7**, CHMePh **8** or CMe$_3$ **9**) and $[Ru_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O_2CCMe_3)_2(SCN)]$ **10** were obtained. Analogously to the starting compounds, these complexes are non-electrolytes in methanol or acetone solution and are soluble in polar organic solvents, suggesting a non-polymeric structure in contrast to the behaviour of $[Ru_2(\mu\text{-}O_2CMe)_4(SCN)]$ which is very insoluble

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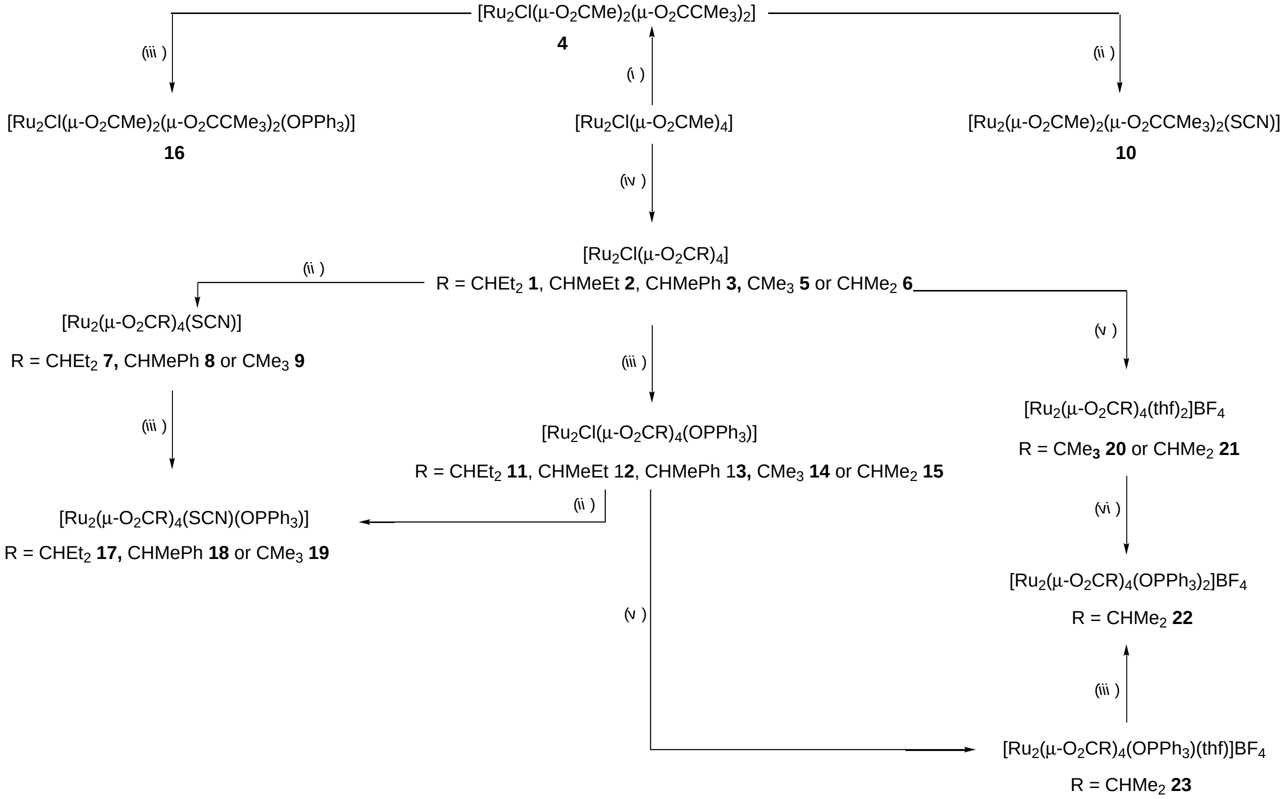
‡ *Non-SI unit employed*: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.



Scheme 1 Synthetic routes to the complexes. (*i*) $2HO_2CR$, MeOH–water; (*ii*) AgSCN, thf; (*iii*) $OPPh_3$, acetone; (*iv*) $6HO_2CR$, MeOH–water; (*v*) $AgBF_4$, thf; (*vi*) $2OPPh_3$, thf

in all solvents. The last compound has previously been prepared by reaction of $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ and KSCN and due to its insolubility a polymeric structure was proposed.[12] The IR spectra of **7**–**10**, in thf solution, in which the solvate $[Ru_2(\mu\text{-}O_2CR)_4(SCN)(thf)]$ is present, show the CN stretching vibration in the range 2057–2059 cm^{-1} in accordance with the SCN group being bonded only through the sulfur atom. However, the spectra of the unsolvated complexes, as KBr discs, show this ν(CN) band shifted to 2106–2094 cm^{-1}, typical of an S-bonded SCN group which also has some σ-CN interaction. Thus, in the unsolvated derivatives, the SCN ligand of each $[Ru_2(\mu\text{-}O_2CR)_4(SCN)]$ molecule probably has a σ-CN interaction with the vacant axial position of another $[Ru_2(\mu\text{-}O_2CR)_4(SCN)]$ molecule giving chains. However, this interaction is weak and is easily broken by donor and non-donor solvent molecules, such as MeOH, acetone and dichloromethane, giving solvated discrete molecules $[Ru_2(\mu\text{-}O_2CR)_4(SCN)(solv)]$ (solv = solvent). This behaviour contrasts with that observed[12] in $[Ru_2(\mu\text{-}O_2CMe)_4(SCN)]$. These results indicate that also in these cases the solvated compounds have a non-polymeric structure. In accordance with these observations, the CN stretching vibrations in $[Ru_2(\mu\text{-}O_2CR)_4(SCN)(OPPh_3)]$ are in the same range in KBr discs (2059–2066 cm^{-1}) and in thf solutions (2059–2061 cm^{-1}).

The non-polymeric nature of these compounds and the conductivity data suggest the possibility to obtain diruthenium compounds having two different axial ligands. Thus, by reaction of $[Ru_2Cl(\mu\text{-}O_2CR)_4]$ or $[Ru_2Cl(\mu\text{-}O_2CR)_4(solv)]$ with $OPPh_3$ in thf, monoadducts of the type $[Ru_2Cl(\mu\text{-}O_2CR)_4(OPPh_3)]$ (R = $CHEt_2$ **11**, CHMeEt **12**, CHMePh **13**, CMe_3 **14** or $CHMe_2$ **15**) have been obtained. The compound $[Ru_2Cl(\mu\text{-}O_2CMe)_2(\mu\text{-}O_2CCMe_3)_2(OPPh_3)]$ **16** has been prepared by the same procedure. Similarly the reactions of $[Ru_2(\mu\text{-}O_2CR)_4(SCN)]$ with $OPPh_3$ lead to the formation of $[Ru_2(\mu\text{-}O_2CR)_4(SCN)(OPPh_3)]$ (R = $CHEt_2$ **17**, CHMePh **18** or CMe_3 **19**); these compounds were also obtained by reaction of $[Ru_2Cl(\mu\text{-}O_2CR)_4(OPPh_3)]$ with AgSCN. Their isolation confirms the molecular nature of the starting material. In addition, the formation of these monoadducts contrasts with the behaviour observed for the polymeric $[Ru_2Cl(\mu\text{-}O_2CR)_4]$ which when soluble in polar solvents lead only to bis adducts[4] such as $[Ru_2(\mu\text{-}O_2CMe)_4(H_2O)_2]BF_4$.

On the other hand, bis adducts of the type $[Ru_2(\mu\text{-}O_2CR)_4(thf)_2]BF_4$ are also accessible by reaction of $[Ru_2Cl(\mu\text{-}O_2CR)_4]$ with $AgBF_4$ in thf, similarly to the reactions with polymeric carboxylates.[13–15] Thus, for example, the reactions of **5** and **6** with $AgBF_4$ lead to $[Ru_2(\mu\text{-}O_2CR)_4(thf)_2]BF_4$ (R = CMe_3 **20** or $CHMe_2$ **21**). Compounds of the type $[Ru_2(\mu\text{-}O_2CR)_4(OPPh_3)_2]BF_4$ were easily obtained by substitution of thf ligands by $OPPh_3$. Thus, the reaction of **21** with $OPPh_3$ leads to $[Ru_2(\mu\text{-}O_2CCHMe_2)_4(OPPh_3)_2]BF_4$ **22**.

Unsymmetrical adducts of the type $[Ru_2(\mu\text{-}O_2CCR)_4(OPPh_3)(thf)]BF_4$ were formed, starting from $[Ru_2Cl(\mu\text{-}O_2CR)_4(OPPh_3)]$. Thus, for instance, the reaction of **15** with $AgBF_4$ in thf leads to $[Ru_2(\mu\text{-}O_2CCHMe_2)_4(OPPh_3)(thf)]BF_4$ **23**. The thf ligand in these complexes, similarly to those observed in the bis(thf) adducts, is lost very easily giving $[Ru_2(\mu\text{-}O_2CR)_4(OPPh_3)]BF_4$. That in **23** can be also substituted by $OPPh_3$ giving the bis adduct **22**.

The magnetic susceptibilities of all compounds were measured in the range 70–300 K, showing that they obey the Curie–Weiss law. In all cases the magnetic moment at room temperature (3.30–4.60 μ_B) is in accordance with the presence of three unpaired electrons per dimer. Such magnetic moments are consistent with a ground state having $S = \frac{3}{2}$, which has been proposed for all previously described diruthenium(II,III) compounds.[16–18] There are no appreciable differences in the magnetic moments and in the magnetic behaviour between these compounds and the polymeric derivatives in the measured temperature range.

Electronic spectra of the complexes in methanol solution show two absorption bands. The visible band near 430 nm is assignable to a $\pi(Ru\text{–}O, Ru_2) \longrightarrow \pi^*(Ru_2)$ transition, as proposed by Norman *et al.*[19] and Miskowsky and Gray.[20]

Table 1 Selected bond lengths (Å) and angles (°) for $[Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4(OPPh_3)]$

Ru(1)–Ru(2)	2.279(1)	O(2)–C(1)	1.27(2)
Ru(1)–Cl	2.490(4)	O(6)–C(1)	1.25(2)
Ru(1)–O(2)	2.030(8)	O(3)–C(2)	1.26(2)
Ru(1)–O(3)	2.022(8)	O(7)–C(2)	1.27(2)
Ru(1)–O(4)	2.036(7)	O(4)–C(3)	1.27(1)
Ru(1)–O(5)	2.029(7)	O(8)–C(3)	1.27(1)
Ru(2)–O(1)	2.249(9)	O(5)–C(4)	1.27(1)
Ru(2)–O(6)	2.004(8)	O(9)–C(4)	1.27(2)
Ru(2)–O(7)	2.027(8)	P–C(17)	1.80(1)
Ru(2)–O(8)	2.001(8)	P–C(18)	1.77(1)
Ru(2)–O(9)	2.016(9)	P–C(19)	1.76(1)
O(1)–P	1.48(1)		
Ru(1)–Ru(2)–O(1)	175.5(2)	Ru(2)–Ru(1)–O(3)	88.9(2)
Ru(1)–Ru(2)–O(6)	89.73(3)	Ru(2)–Ru(1)–O(4)	88.7(2)
Ru(1)–Ru(2)–O(7)	89.7(2)	Ru(2)–Ru(1)–O(5)	88.9(2)
Ru(1)–Ru(2)–O(8)	89.7(2)	O(1)–Ru(2)–O(6)	92.2(3)
Ru(1)–Ru(2)–O(9)	89.8(3)	O(1)–Ru(2)–O(7)	94.4(3)
Cl–Ru(1)–O(2)	91.3(3)	O(1)–Ru(2)–O(8)	88.5(3)
Cl–Ru(1)–O(3)	92.0(2)	O(1)–Ru(2)–O(9)	86.0(3)
Cl–Ru(1)–O(4)	91.9(2)	O(6)–Ru(2)–O(7)	89.2(4)
Cl–Ru(1)–O(5)	90.3(2)	O(6)–Ru(2)–O(8)	178.2(4)
O(2)–Ru(1)–O(3)	88.7(3)	O(6)–Ru(2)–O(9)	91.64(4)
O(2)–Ru(1)–O(4)	176.5(3)	O(7)–Ru(2)–O(8)	89.1(3)
O(2)–Ru(1)–O(5)	91.8(3)	O(7)–Ru(2)–O(9)	179.1(3)
O(3)–Ru(1)–O(4)	89.7(3)	O(8)–Ru(2)–O(9)	90.0(4)
O(3)–Ru(1)–O(5)	177.7(3)	Ru(2)–O(1)–P	150.0(5)
O(4)–Ru(1)–O(5)	89.6(3)	O(1)–P–Cl(17)	109.2(6)
Ru(2)–Ru(1)–Cl	179.0(1)	O(1)–P–C(18)	112.5(5)
Ru(2)–Ru(1)–O(2)	88.1(2)	O(1)–P–C(19)	111.3(6)

This transition appears at a similar wavelength for all compounds, and is not sensitive to change of the carboxylate ligand. The absorption near 280 nm is assignable to a π(axial ligand) $\longrightarrow$ π*(Ru_2) transition. This axial ligand-to-metal charge transfer could be sensitive to change of axial ligand according to Miskowsky and Gray.[20] However, we have not observed any significant shifts on varying the nature of the axial ligands. The electronic spectra in thf or CH_2Cl_2 solution are very similar to those observed in methanol solution. The most striking difference is the splitting into two maxima of the band in the UV region. Similar splitting has been observed previously for other diruthenium(II,III) compounds.[21]

The FAB mass spectra of $[Ru_2(\mu\text{-}O_2CR)_4X]$ (X = Cl or SCN) show molecular or protonated molecular peaks in all cases, although the base peak corresponds always to the fragment $[Ru_2(\mu\text{-}O_2CR)_4]^+$. However, peaks corresponding to two dimer units of the type $[Ru_2(\mu\text{-}O_2CR)_4XRu_2(\mu\text{-}O_2CR)_4]^+$ are also observed. On the other hand, the spectra of $[Ru_2(\mu\text{-}O_2CR)_4X(OPPh_3)]$ do not show the molecular ion, but peaks corresponding to $[Ru_2(\mu\text{-}O_2CR)_4(OPPh_3)]^+$ and $[Ru_2(\mu\text{-}O_2CR)_4]^+$ are observed. Similarly to the above-mentioned compounds, peaks corresponding to fragments $[Ru_2(\mu\text{-}O_2CR)_4XRu_2(\mu\text{-}O_2CR)_4]^+$ are detected.

The association of fragments is not unusual in FAB mass spectra and in many cases it is not easy to determine whether these fragments are present in the solid or are formed in the fragmentation processes. In our case the crystal structures[10] of $[Ru_2Cl(\mu\text{-}O_2CR)_4(solv)]$ (solv = H_2O, R = CMe_3; solv = thf, R = $CHMe_2$) show that these compounds give discrete molecules in the solid state, but, for the unsolvated derivatives, the formation of chains through Cl or SCN groups cannot be ruled out. However, in $[Ru_2(\mu\text{-}O_2CR)_4X(OPPh_3)]$ (X = Cl or SCN) the formation of chains is not possible and therefore the association of fragments occurs upon ionization or fragmentation. A complete study of the FAB mass spectra of these compounds will be published elsewhere.

The X-ray analysis of complex **15** shows that the crystal consists of discrete dinuclear molecules $[Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4(OPPh_3)]$ separated by normal van der Waals distances. The molecular structure is shown in Fig. 1 and selected bond distances and angles are given in Table 1. The dinuclear unit has two ruthenium atoms linked by four bridging isobutyrate ligands, with one chlorine atom and one triphenylphosphine oxide in the axial positions. The co-ordination polyhedra of the two metal atoms are distorted with respect to regular octahedral arrangements. The bond distances and angles in the $[Ru_2(\mu\text{-}O_2CCHMe_2)_4]^+$ unit are similar to those observed in related compounds.[1–10] The Ru–Ru distance of 2.279(1) Å falls within the typical range for diruthenium complexes.[1–10] A shortening of the Ru–Cl bond [2.490(4) Å] is observed in comparison to polymeric complexes containing Ru_2^{5+} units. Similar Ru–Cl distances are exhibited by the non-polymeric[9,10] $[Ru_2Cl(\mu\text{-}O_2CC_4H_4N)_4(thf)]\cdot thf\cdot H_2O$ [2.523(3) Å] and $[Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4(thf)]$ [2.445(6) Å]. However, the Ru–O_{axial} distance [2.249(9) Å] is analogous to those observed[23,24] in $[Ru_2(\mu\text{-}O_2CMe)_4(OPPh_3)_2]^+$ [2.227(4) Å] and $[Ru_2(\mu\text{-}O_2CC_4H_3S)_4(OPPh_3)_2]^+$ [2.216(7) Å], but shorter than that[10] in $[Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4(thf)]$ [2.37(2) Å]. The stronger donor character of the $OPPh_3$ ligand, with respect to thf, must be responsible for this shortening. Analogously to $[Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4(thf)]$ the low values of the torsion angles (0.43–1.07°) about the metal–metal bond show the absence of steric forces that would produce a twist in the molecule.

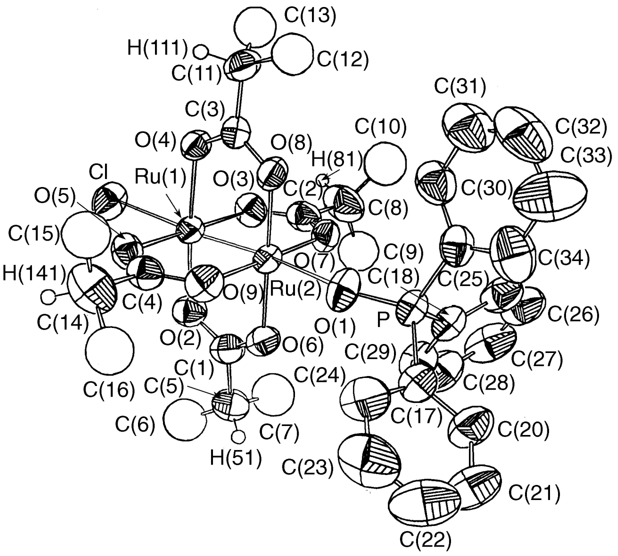


Fig. 1 An ORTEP[22] view of $[Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4(OPPh_3)]$ showing the atom-numbering scheme. The methyl and phenyl hydrogen atoms are omitted for clarity

Conclusion

We have synthesized and characterized new non-polymeric $[Ru_2(\mu\text{-}O_2CR)_4X]$ (X = Cl or SCN) compounds. The factors which determine the non-polymeric nature of these remain unclear but we believe that they are related to the presence of a branched chain in the carboxylate ligand. These branched chains interact with solvent molecules increasing the solubility of the $[Ru_2Cl(\mu\text{-}O_2CR)_4]$ species which crystallize as discrete molecules. The results obtained show definitively that there are many non-polymeric tetracarboxylatodiruthenium(II,III) compounds and that the widespread belief that all these must be polymeric is inaccurate. The non-polymeric nature has permitted us to obtain the first diruthenium(II,III) carboxylates with two different axial ligands.

Experimental

All reactions were carried out in an inert atmosphere, using standard Schlenk techniques. Ruthenium trichloride and carboxylic acids were obtained from commercial sources. Solvents were used without previous purification. The complex [Ru₂Cl(μ-

$O_2CMe)_4]$ was prepared by the literature procedure.[25] The IR spectra were recorded, as KBr discs or thf solutions, on Perkin-Elmer 1330 or Nicolet Magna-IR 550 spectrophotometers. Molar conductivities were measured with a Philips PW 9526 digital conductivity meter using a Philips PW 9512/60 conductivity measuring cell. Elemental analyses for C, H and N were performed by the Microanalytical Service of the Complutense University of Madrid. Electronic spectra in the region 190–800 nm were recorded on a Hewlett-Packard Vectra spectrophotometer. Magnetic susceptibility measurements were made in the range 70–300 K using a fully automatic DSM 8 magneto-susceptometer, based on the Faraday method. The FAB mass spectra were recorded on a VG AutoSpec spectrometer.

Syntheses

$[Ru_2Cl(\mu\text{-}O_2CR)_4]$ (R = $CHEt_2$ 1, CHMeEt 2 or CHMePh 3). To a solution of $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ (0.3 g, 0.63 mmol) in methanol–water (1:1, 40 cm^3) was added an excess of HO_2CR (3.78 mmol). The reaction mixture was heated to reflux for 4 h, giving a red-brown solution. This was evaporated to dryness under vacuum giving a red-brown solid which was redissolved in a fresh methanol–water mixture and treated again with HO_2CR (3.78 mmol) to ensure complete substitution of acetate ligands. The solution was evaporated and the solid washed twice with light petroleum (b.p. 40–60 °C), dissolved in thf and cooled overnight to −18 °C gave a red solid. This solid was filtered off and dried in vacuum.

$[Ru_2Cl(\mu\text{-}O_2CCHEt_2)_4]$ **1** (0.34 g, 77%) (Found: C, 41.0; H, 6.1. $C_{24}H_{24}ClO_8Ru_2$ requires C, 41.3; H, 6.35%): $\tilde{\nu}_{max}/cm^{-1}$ (KBr disc) 2995s, 2950m, 2900m (CH) and 1490–1400vs (CO_2). μ_{eff} (room temperature, r.t.) = 3.84 μ_B. λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) (thf) 290 (2366), 334 (4533) and 458 (1508). FAB mass spectrum: *m*/*z* 700, $[Ru_2Cl(\mu\text{-}O_2CCHEt_2)_4 + H]^+$ (2.5); 664, $[Ru_2(\mu\text{-}O_2CCHEt_2)_4]^+$ (100); and 1362 $[Ru_2(\mu\text{-}O_2CCHEt_2)_4ClRu_2(\mu\text{-}O_2CHEt_2)_4]^+$ (1.2%).

$[Ru_2Cl(\mu\text{-}O_2CCHMeEt)_4]$ **2** (0.32 g, 80%) (Found: C, 37.2; H, 5.4. $C_{20}H_{36}ClO_8Ru_2$ requires C, 37.4; H, 5.65%): $\tilde{\nu}_{max}/cm^{-1}$ (KBr disc) 2980s, 2940m, 2890m (CH) and 1505–1405vs (CO_2). μ_{eff} (r.t.) = 3.72 μ_B.

$[Ru_2Cl(\mu\text{-}O_2CCHMePh)_4]$ **3** (0.44 g, 83%) (Found: C, 51.5; H, 4.4. $C_{36}H_{36}ClO_8Ru_2$ requires C, 51.8; H, 4.35%): $\tilde{\nu}_{max}/cm^{-1}$ (KBr disc) 3080w, 3040w (CH), 2980m, 2940m (CH), 1500–1400s (CO_2). μ_{eff} (r.t.) = 3.30 μ_B. λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) (thf) 290 (3843), 334 (4529) and 462 (1613). FAB mass spectrum: *m*/*z* 835, $[Ru_2Cl(\mu\text{-}O_2CCHMePh)_4]^+$ (1.6); 800, $[Ru_2(\mu\text{-}O_2CCHMePh)_4]^+$ (100); and 1634, $[Ru_2(\mu\text{-}O_2CHMePh)_4ClRu_2(\mu\text{-}O_2CCHMePh)_4]^+$ (1.2%).

$[Ru_2Cl(\mu\text{-}O_2CMe)_2(\mu\text{-}O_2CCMe_3)_2]$ 4. This complex was prepared as described above using a molar ratio $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$: HO_2CR 1:2 and a reaction time of 7 h (0.26 g, 74%) (Found: C, 29.9; H, 4.0. $C_{14}H_{24}ClO_8Ru_2$ requires C, 30.1; H, 4.3%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr disc) 2970m, 2920w, 2860w (CH) and 1490–1350s (CO_2). μ_{eff} = 3.62 μ_B. λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) (thf) 290 (4041), 332 (4740) and 460 (1789).

$[Ru_2Cl(\mu\text{-}O_2CCMe_3)_4]$ 5 and $[Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4]$ 6. These complexes were prepared as previously described.[10]

$[Ru_2Cl(\mu\text{-}O_2CCMe_3)_4]$ **5**: λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) (thf) 288 (3430), 334 (4539) and 460 (1687); (MeOH) 278 (2163) and 428 (740); (CH_2Cl_2) 276 (3988), 312 (5041) and 456 (1282). FAB mass spectrum: *m*/*z* 643, $[Ru_2Cl(\mu\text{-}O_2CCMe_3)_4]^+$ (2.5); 608, $[Ru_2(\mu\text{-}O_2CCMe_3)_4 + H]^+$ (100); and 1249, $[Ru_2(\mu\text{-}O_2CCMe_3)_4ClRu_2(\mu\text{-}O_2CCMe_3)_4]^+$ (11.9%).

$[Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4]$ **6**: λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) (thf) 292 (3102), 332 (4740) and 458 (1497).

$[Ru_2(\mu\text{-}O_2CR)_4(SCN)]$ (R = $CHEt_2$ 7, CHMePh 8 or CMe_3 9). The complex $[Ru_2Cl(\mu\text{-}O_2CR)_4]$ (0.30 mmol) was dissolved in thf (20 cm^3) and AgSCN (50 mg, 0.30 mmol) added. The mixture was stirred for 24 h in the dark giving a deep red solution and a white precipitate of AgCl. It was filtered over Celite, concentrated under vacuum to 10 cm^3 and layered with light petroleum (b.p. 40–60 °C), giving a red solid, which was filtered off and dried under vacuum.

$[Ru_2(\mu\text{-}O_2CCHEt_2)_4(SCN)]$ **7** (0.17 g, 78%) (Found: C, 41.9; H, 6.15; N, 1.8. $C_{25}H_{44}NO_8Ru_2S$ requires C, 41.7; H, 6.15; N, 1.9%): $\tilde{\nu}_{max}/cm^{-1}$ (KBr disc) 2995s, 2950m, 2900m (CH), 2100s (SCN) and 1490–1405s (CO_2); (thf solution) 2058s (SCN). μ_{eff} = 4.07 μ_B. λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) (MeOH) 278 (2276) and 436 (598). FAB mass spectrum: *m*/*z* 722, $[Ru_2(\mu\text{-}O_2CCHEt_2)_4(SCN)]^+$ (0.8); 664, $[Ru_2(\mu\text{-}O_2CCHEt_2)_4]^+$ (100); and 1384, $[Ru_2(\mu\text{-}O_2CCHEt_2)_4(SCN)Ru_2(\mu\text{-}O_2CCHEt_2)_4]^+$ (1.9%).

$[Ru_2(\mu\text{-}O_2CCHMePh)_4(SCN)]$ **8** (0.17 g, 65%) (Found: C, 52.2; H, 4.4; N, 1.7. $C_{37}H_{36}NO_8Ru_2S$ requires C, 51.9; H, 4.2; N, 1.6%): $\tilde{\nu}_{max}/cm^{-1}$ (KBr disc) 3080w, 3040w, 2980m, 2940m (CH), 2094s (SCN) and 1500–1405vs (CO_2); (thf solution) 2057s (SCN). μ_{eff} = 4.05 μ_B. λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) (thf) 292 (4293), 418 (1501) and 500 (4283).

$[Ru_2(\mu\text{-}O_2CCMe_3)_4(SCN)]$ **9** (0.13 g, 63%) (Found: C, 37.4; H, 5.1; N, 1.9. $C_{21}H_{36}NO_8Ru_2S$ requires C, 37.95; H, 5.5; N, 2.1%): $\tilde{\nu}_{max}/cm^{-1}$ (KBr disc) 2980m, 2940w, 2880w (CH), 2105s (SCN) and 1500–1400s (CO_2); (thf solution) 2059s (SCN). μ_{eff} = 3.89 μ_B. λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) (thf) 290 (3992), 412 (1568) and 492 (4466); (MeOH) 280 (2648) and 434 (974); (CH_2Cl_2) 274 (7142), 394 (2472) and 464 (3511). FAB mass spectrum: *m*/*z* 666, $[Ru_2(\mu\text{-}O_2CCMe_3)_4(SCN)]^+$ (0.01); and 608, $[Ru_2(\mu\text{-}O_2CCMe_3)_4 + H]^+$ (100%).

$[Ru_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O_2CCMe_3)_2(SCN)]$ 10. This complex was obtained by the method described above for **7**–**9** using **4** as starting material. Yield 0.13 g, 77% (Found: C, 30.7; H, 4.0; N, 2.2. $C_{15}H_{24}NO_8Ru_2S$ requires C, 31.0; H, 4.2; N, 2.4%); $\tilde{\nu}_{max}/cm^{-1}$ (KBr disc) 2970m, 2920w, 2860w (CH), 2106s (SCN) and 1500–1390vs (CO_2); (thf solution) 2057m (SCN). μ_{eff} = 3.89 μ_B. λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) (thf) 292 (3808), 408 (1624) and 490 (4786). FAB mass spectrum: *m*/*z* 523, $[Ru_2(\mu\text{-}O_2CCMe_3)_2(\mu\text{-}O_2CMe)_2]^+$ (60.2); and 1105, $[Ru_2(\mu\text{-}O_2CCMe_3)_2(\mu\text{-}O_2CMe)_2(SCN)Ru_2(\mu\text{-}O_2CCMe_3)_2(\mu\text{-}O_2CMe)_2 + H]^+$ (3.1%).

$[Ru_2Cl(\mu\text{-}O_2CR)_4(OPPh_3)]$ (R = $CHEt_2$ 11, CHMeEt 12, CHMePh 13, CMe_3 14 or $CHMe_2$ 15). To a solution of $[Ru_2Cl(\mu\text{-}O_2CR)_4]$ (0.30 mmol) in acetone (20 cm^3) was added $OPPh_3$ (90 mg, 0.30 mmol). The reaction mixture was stirred for 24 h giving a dark brown solution. The solvent was removed under vacuum giving a brown solid which was washed twice with light petroleum (b.p. 40–60 °C), dissolved in thf and layered with light petroleum. The red microcrystalline solid was filtered off and dried in a stream of nitrogen.

$[Ru_2Cl(\mu\text{-}O_2CCHEt_2)_4(OPPh_3)]$ **11** (0.20 g, 67%) (Found: C, 51.15; H, 5.7. $C_{42}H_{59}ClO_9PRu_2$ requires C, 51.7; H, 6.1%): $\tilde{\nu}_{max}/cm^{-1}$ (KBr disc) 3055w, 2965s, 2935s, 2875m (CH), 1510–1395vs (CO_2) and 1152s (O=P). μ_{eff} = 4.19 μ_B. λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) (thf) 280 (2070), 334 (4086) and 462 (1330).

$[Ru_2Cl(\mu\text{-}O_2CCHMeEt)_4(OPPh_3)]$ **12** (0.21 g, 76%) (Found: C, 49.2; H, 5.3. $C_{38}H_{51}ClO_9PRu_2$ requires C, 49.6; H, 5.6%): $\tilde{\nu}_{max}/cm^{-1}$ (KBr disc) 3055w, 2970s, 2940s, 2880m (CH), 1500–1395vs (CO_2) and 1150s (O=P). μ_{eff} = 4.17 μ_B.

$[Ru_2Cl(\mu\text{-}O_2CCHMePh)_4(OPPh_3)]$ **13** (0.21 g, 63%) (Found: C, 58.6; H, 4.6. $C_{54}H_{51}ClO_9PRu_2$ requires C, 58.3; H, 4.6%): $\tilde{\nu}_{max}/cm^{-1}$ (KBr disc) 3075w, 3040w, 2980s, 2940m (CH), 1490–1380vs (CO_2) and 1150s (O=P). μ_{eff} = 3.29 μ_B. λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) (thf) 284 (3412), 336 (4306) and 464 (1460).

$[Ru_2Cl(\mu\text{-}O_2CCMe_3)_4(OPPh_3)]$ **14** (0.19 g, 70%) (Found: C, 49.4; H, 5.4. $C_{38}H_{51}ClO_9PRu_2$ requires C, 49.6; H, 5.6%): $\tilde{\nu}_{max}/cm^{-1}$ (KBr disc) 3050w, 2980m, 2940w, 2870w (CH), 1495–1400vs (CO_2) and 1145s (O=P). μ_{eff} = 4.00 μ_B. λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) (thf) 290 (3538), 332 (5649) and 460 (1973); (MeOH) 282 (2589) and 428 (1006); (CH_2Cl_2) 272 (7720), 312

(7649) and 456 (1906). FAB mass spectrum: m/z 643, $[\mathrm{Ru_2Cl(\mu\text{-}O_2CCMe_3)_4}]^+$ (2.1); 607, $[\mathrm{Ru_2(\mu\text{-}O_2CCMe_3)_4}]^+$ (100); 886, $[\mathrm{Ru_2(\mu\text{-}O_2CCMe_3)_4(OPPh_3)}]^+$ (0.2); and 1250, $[\mathrm{Ru_2(\mu\text{-}O_2CCMe_3)_4ClRu_2(\mu\text{-}O_2CCMe_3)_4 + H}]^+$ (0.6%).

$[\mathrm{Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4(OPPh_3)}]$ 15. Dark red crystals of this compound were grown by the layering of a dichloromethane solution with light petroleum (b.p. 40–60 °C). Yield 0.20 g, 77% (Found: C, 46.9; H, 4.8. $\mathrm{C_{34}H_{43}ClO_9PRu_2}$ requires C, 47.2; H, 5.0%); $\tilde{\nu}_{max}/\mathrm{cm^{-1}}$ (KBr disc) 3060w, 2975m, 2935w, 2875w (CH), 1500–1400vs ($\mathrm{CO_2}$) and 1164s (O=P). $\mu_{eff} = 4.60\ \mu_B$. λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (thf) 284 (2615), 334 (3670) and 456 (1863). FAB mass spectrum: m/z 551, $[\mathrm{Ru_2(\mu\text{-}O_2CCHMe_2)_4}]^+$ (100); and 830, $[\mathrm{Ru_2(\mu\text{-}O_2CCHMe_2)_4(OPPh_3)}]^+$ (2.9%).

$[\mathrm{Ru_2Cl(\mu\text{-}O_2CMe)_2(\mu\text{-}O_2CCMe_3)_2(OPPh_3)}]$ 16. This complex was obtained by the method described for **11**–**15** using **4** as starting material. Yield 0.17 g, 69% (Found: C, 45.3; H, 4.6. $\mathrm{C_{32}H_{39}ClO_9PRu_2}$ requires C, 46.0; H, 4.7%); $\tilde{\nu}_{max}/\mathrm{cm^{-1}}$ (KBr disc) 3070w, 2990w, 2950w, 2880w (CH), 1500–1400vs ($\mathrm{CO_2}$) and 1155m (O=P). $\mu_{eff} = 3.61\ \mu_B$. λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (thf) 288 (2546), 334 (3748) and 460 (1597).

$[\mathrm{Ru_2(\mu\text{-}O_2CR)_4(SCN)(OPPh_3)}]$ (R = CHEt$_2$ 17, CHMePh 18 or CMe$_3$ 19). These complexes were prepared by two procedures: (*a*) starting from $[\mathrm{Ru_2Cl(\mu\text{-}O_2CR)_4(OPPh_3)}]$ with AgSCN using a procedure identical to that describved above for the synthesis of **7**–**9**; (*b*) starting from $[\mathrm{Ru_2(\mu\text{-}O_2CR)_4(SCN)}]$ and $\mathrm{OPPh_3}$ using a procedure identical to that described for **11**–**15**. The yields obtained by both methods were similar (64–79%).

$[\mathrm{Ru_2(\mu\text{-}O_2CHEt_2)_4(SCN)(OPPh_3)}]$ **17** (Found: C, 52.0; H, 6.0; N, 0.9. $\mathrm{C_{43}H_{54}NO_9PRu_2S}$ requires C, 51.7; H, 5.95; N, 1.1%): $\tilde{\nu}_{max}/\mathrm{cm^{-1}}$ (KBr disc) 3060w, 2965s, 2935s, 2875m (CH), 2062s (SCN), 1490–1385vs ($\mathrm{CO_2}$) and 1163s (O=P); (thf solution) 2061s (SCN). $\mu_{eff} = 3.98\ \mu_B$. λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (thf) 290 (4341), 330 (3023) and 490 (3375).

$[\mathrm{Ru_2(\mu\text{-}O_2CHMePh)_4(SCN)(OPPh_3)}]$ **18** (Found: C, 58.8; H, 5.0; N, 1.2. $\mathrm{C_{55}H_{51}NO_9PRu_2S}$ requires C, 58.2; H, 4.5; N, 1.2%): $\tilde{\nu}_{max}/\mathrm{cm^{-1}}$ (KBr disc) 3060w, 3025w, 2975m, 2935w, 2875w (CH), 2059s (SCN), 1495–1375vs ($\mathrm{CO_2}$) and 1150s (O=P); (thf solution) 2059s (SCN). $\mu_{eff} = 4.14\ \mu_B$.

$[\mathrm{Ru_2(\mu\text{-}O_2CCMe_3)_4(SCN)(OPPh_3)}]$ **19** (Found: C, 37.4; H, 5.0; N, 1.9. $\mathrm{C_{39}H_{51}NO_9PRu_2S}$ requires C, 37.95; H, 5.5; N, 2.1%): $\tilde{\nu}_{max}/\mathrm{cm^{-1}}$ (KBr disc) 3065w, 2980s, 2940m, 2890w (CH), 2066s (SCN), 1500–1400vs ($\mathrm{CO_2}$) and 1149s (O=P); (thf solution) 2061s (SCN). $\mu_{eff} = 4.21\ \mu_B$. λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (thf) 292 (2684), 418 (1325) and 490 (3784); (MeOH) 280 (2598) and 432 (1106); ($\mathrm{CH_2Cl_2}$) 274 (9107), 386 (3095) and 462 (4310). FAB mass spectrum: m/z 1272, $[\mathrm{Ru_2(\mu\text{-}O_2CCMe_3)_4(SCN)Ru_2(\mu\text{-}O_2CCMe_3)_4}]^+$ (9.8); 886, $[\mathrm{Ru_2(\mu\text{-}O_2CCMe_3)_4(OPPh_3)}]^+$ (19.3); and 607, $[\mathrm{Ru_2(\mu\text{-}O_2CCMe_3)_4}]^+$ (100%).

$[\mathrm{Ru_2(\mu\text{-}O_2CR)_4(thf)_2}]\mathrm{BF_4}$ (R = CMe$_3$ 20 or CHMe$_2$ 21). To a solution of $[\mathrm{Ru_2Cl(\mu\text{-}O_2CR)_4}]$ (0.30 mmol) in thf (20 cm^3) was added $\mathrm{AgBF_4}$ (60 mg, 0.30 mmol). The mixture was stirred for 24 h in the dark giving a white precipitate of AgCl. This was filtered off over Celite and the red-brown solution concentrated under vacuum then layered with light petroleum (b.p. 40–60 °C) to give dark brown solid. This was filtered off and dried in a stream of nitrogen.

$[\mathrm{Ru_2(\mu\text{-}O_2CCMe_3)_4(thf)_2}]\mathrm{BF_4}$ **20** (0.18 g, 70%) (Found: C, 38.9; H, 5.5. $\mathrm{C_{28}H_{52}BF_4O_{10}Ru_2}$ requires C, 40.15; H, 6.3%): $\tilde{\nu}_{max}/\mathrm{cm^{-1}}$ (KBr disc) 2990m, 2950w, 2875w (CH), 1500–1405vs ($\mathrm{CO_2}$) and 1110–1030s ($\mathrm{BF_4}$). $\mu_{eff} = 4.12\ \mu_B$. λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (thf) 288 (3567) and 432 (1210).

$[\mathrm{Ru_2(\mu\text{-}O_2CCHMe_2)_4(thf)_2}]\mathrm{BF_4}$ **21** (0.15 g, 64%) (Found: C, 34.9; H, 4.9. $\mathrm{C_{24}H_{44}BF_4O_{10}Ru_2}$ requires C, 36.9; H, 5.7%): $\tilde{\nu}_{max}/\mathrm{cm^{-1}}$ (KBr disc) 2975m, 2935w, 2885w (CH), 1500–1400vs ($\mathrm{CO_2}$) and 1150–1070s (BF). $\mu_{eff} = 4.30\ \mu_B$.

Table 2 Crystallographic data for $[\mathrm{Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4(OPPh_3)}]$

Formula	$\mathrm{C_{34}H_{43}ClO_9PRu_2}$
M	864.3
Space group	$P2_1/n$ (no. 14)
a/Å	17.160(2)
b/Å	15.958(2)
c/Å	14.076(2)
β/°	108.34(1)
Z	4
U/Å^3	3658.7(8)
D_c/g cm^{-3}	1.57
F(000)	1756
μ(Mo-Kα)/cm^{-1}	9.76
2θ Range/°	1–56
Unique data	8787
Observed reflections [$I > 2\sigma(I)$]	4516
Absorption correction range	0.97–1.04
Number of refined parameters	376
R [a]	0.062
R' [b]	0.071

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

$[\mathrm{Ru_2(\mu\text{-}O_2CHMe_2)_4(OPPh_3)_2}]\mathrm{BF_4}$ 22. A solution of complex **21** (230 mg, 0.30 mmol) in thf (20 cm^3) was treated with $\mathrm{OPPh_3}$ (170 mg, 0.60 mmol). The mixture was stirred for 24 h and dried under vacuum. The resulting red solid was washed twice with light petroleum (b.p. 40–60 °C), dissolved in $\mathrm{CH_2Cl_2}$ and layered with light petroleum, giving **22** which was filtered off and dried under vacuum (0.23 g, 65%) (Found: C, 50.9; H, 4.8. $\mathrm{C_{52}H_{58}BF_4O_{10}P_2Ru_2}$ requires C, 50.2; H, 4.9%); $\tilde{\nu}_{max}/\mathrm{cm^{-1}}$ (KBr disc) 3060w, 2975m, 2935w, 2885w (CH), 1495–1400vs ($\mathrm{CO_2}$), 1130–1030s ($\mathrm{BF_4}$) and 1150s (O=P). $\mu_{eff} = 4.46\ \mu_B$. λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 290 (3121), 332 (3099) and 456 (1491).

$[\mathrm{Ru_2(\mu\text{-}O_2CCHMe_2)_4(OPPh_3)(thf)}]\mathrm{BF_4}$ 23. The reaction of complex **15** (260 mg, 0.30 mmol) and $\mathrm{AgBF_4}$ (60 mg, 0.30 mmol) in thf was caried out under identical conditions to those used for the preparation of **20** and **21**. Yield 0.21 g, 70% (Found: C, 45.9; H, 4.8. $\mathrm{C_{38}H_{51}BF_4O_{10}PRu_2}$ requires C, 46.2; H, 5.2%); $\tilde{\nu}_{max}/\mathrm{cm^{-1}}$ (KBr disc) 3060w, 2975m, 2935w, 2885w (CH), 1500–1400vs ($\mathrm{CO_2}$), 1130–1030s (BF) and 1150s (O=P). $\mu_{eff} = 4.17\ \mu_B$.

Crystallography

A summary of the fundamental crystal data for complex **15** is given in Table 2. A reddish crystal of prismatic shape and dimensions 0.25 × 0.25 × 0.30 mm was mounted on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å). The cell dimensions were refined by least squares fitting the 2θ values of the 25 accurately centred reflections within a range of 12–28°. Data were collected at 295 K using the ω–2θ scan technique to a maximum 2θ = 56° from (−22, 0, 0) to (22, 21, 18) to yield 8787 unique reflections, of which 4516 were considered observed [$I > 2\sigma(I)$]. The stability of the crystal was monitored every 100 reflections using three standard reflections; no significant decay of their intensities was observed. Raw data were corrected for Lorentz-polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Ru, Cl and P were taken from ref. 26. The structure was solved by Patterson and Fourier methods. An empirical absorption correction[27] was applied at the end of the isotropic refinements. The hydrogen atoms were included with fixed isotropic contributions at their calculated positions determined by the molecular geometry. A final refinement was undertaken with anisotropic thermal parameters for the non-hydrogen atoms, except for those carbon atoms belonging to terminal $\mathrm{CH_3}$ groups which were refined using isotropic thermal parameters. Since no trend in ΔF *vs.* F_o or sin θ/λ was observed no special weighting scheme has been applied, *i.e.* unit weights were used. The final difference synthesis showed no significant electron density. Most calculations were carried out with the X-RAY 80 system.[28]

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/352.

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