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THE PREPARATION AND STRUCTURE OF THE TETRANUCLEAR RUTHENIUM CLUSTER $[Ru_4(CO)_{10}(\mu_2\text{-}Cl)_2(\mu_3\text{-}OEt)_2]$

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Summary

The tetranuclear ruthenium cluster $[Ru_4(CO)_{10}Cl_2(OEt)_2]$ has been prepared in low yield by the reaction of $[Ru_3(CO)_{12}]$ with $[N(PPh_3)_2]Cl$ in refluxing EtOH, followed by oxidation with either $[NO][BF_4]$ or $Ag[ClO_4]$. A single-crystal X-ray analysis of the complex shows that the four metal atoms adopt a planar geometry with one ruthenium bonded by two μ_2-Cl ligands and two μ_3-OEt ligands to a trinuclear fragment. This complex crystallises in the monoclinic space group $I2/c$, with a 14.458(3), b 22.073(6), c 15.302(4) Å, β 99.54(2)°, $Z = 8$; 3113 observed data with $F > 3\sigma(F)$ were refined by blocked full-matrix least squares to $R = 0.031$, $R_w = 0.034$.

Introduction

We have previously reported the synthesis of a number of compounds of the type $[Ru_4(CO)_{10}Cl_x(OH)_y(OR)_z]$ (R = Me, Et; $x + y + z = 4$) as minor products of the carbonylation of $RuCl_3 \cdot 3H_2O$ in the appropriate alcohol [1]. At that time, on the preliminary evidence available, we suggested that these compounds could be derived from the cubane structure anticipated for the corresponding dodecarbonyl species $[Ru_4(CO)_{12}Cl_x(OH)_y(OR)_z]$. We now report that a further member of this series of compounds, viz. $[Ru_4(CO)_{10}Cl_2(OEt)_2]$, has been prepared, albeit in small yields, from the reaction of $[Ru_3(CO)_{12}]$ with $[N(PPh_3)_2]Cl$ in EtOH followed by oxidation with either $[NO]^+$ or Ag^+. In this case sufficient material was obtained to permit complete characterisation and structure determination by single-crystal X-ray analysis. Contrary to our previous opinion we have found that this molecule is not of the cubane type but may be described as the combination of a Ru_3 triangulo-species with a monomeric Ru unit via two μ_2-Cl and two μ_3-OEt bridges.

The nitrosyl cation $[NO]^+$ may react with mononuclear metal carbonyl complexes in two possible ways, to give either a nitrosyl derivative or an oxidation product [2]. Similar behaviour has been observed in cluster systems. The reaction of

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$[NO]^+$ with cluster anions is a well-known route to cluster nitrosyls [3–6]. However, the reaction of $[H_4Ru_4(CO)_{12}]$ with $[NO]^+$ gives the cationic complex $[H_4Ru_4(CO)_{12}]^+$, the nitrosyl cation acting as an oxidising agent [7]. Whether or not $[NO]^+$ acts as a ligand or as an oxidising agent can depend on the solvent employed. The reaction of $[NO]^+$ with the cluster anion $[H_3Os_4(CO)_{12}]^-$ in dichloromethane or tetrahydrofuran gives the nitrosyl compound $[H_3Os_4(CO)_{12}(NO)]$ [4]. However, if the reaction is carried out in acetonitrile, oxidation occurs and cationic cluster $[H_3Os_4(CO)_{12}(MeCN)_2]^+$ is formed [7,8]. Controlled potential elctrolysis of $[H_3Os_4(CO)_{12}]^-$ also gives this cation, in quantitative yield. A mechanism involving the formation of a nitrosyl intermediate has been proposed to account for the oxidation of some mononuclear metal carbonyl complexes by $[NO]^+$ [2]. However, no evidence has been found to support the presence of a nitrosyl intermediate in cluster systems.

In this paper we report that when reacted with the products of refluxing $[Ru_3(CO)_{12}]$ with $[N(PPh_3)_2]Cl$ in EtOH, $[NO]^+$ can act as an oxidising agent, forming among its products the new cluster species $[Ru_4(CO)_{10}Cl_2(OEt)_2]$.

Results and discussion

Triosmium dodecarbonyl $[Os_3(CO)_{12}]$ reacts with $[N(PPh_3)_2]Cl$ in refluxing tetrahydrofuran to yield the cluster anion $[ClOs_4(CO)_{13}]^-$, while in refluxing ethanol $[H_3Os_4(CO)_{12}]^-$ is formed [10]. Similarly, $[Ru_3(CO)_{12}]$ reacts with $[N(PPh_3)_2]Cl$ in refluxing tetrahedrofuran to give the anion $[ClRu_4(CO)_{13}]^-$ [11]. We have found that, in contrast to the osmium system, $[ClRu_4(CO)_{13}]^-$ is also formed as the major product from the reaction of $[Ru_3(CO)_{12}]$ with $[N(PPh_3)_2]Cl$ in ethanol. The complex is a 62-electron system, adopting a butterfly metal geometry with the chloride ligand bridging the 'wingtips', and was identified on the basis of a comparison of its infrared spectrum with that of $[ClRu_4(CO)_{13}]^-$ in ref. 11 (Table 1).

In an attempt to produce nitrosyl-containing products, we reacted the crude product mixture obtained from the reaction of $[Ru_3(CO)_{12}]$ with $[N(PPh_3)_2]Cl$ in ethanol with $[NO][BF_4]$ in dichloromethane. A number of low yield products were obtained, none of which appeared to arise from direct addition of $[NO]^+$ to $[ClRu_4(CO)_{13}]^-$. They, therefore, most probably arise from the reaction of $[NO]^+$ with impurities in the reaction mixture, or decomposition products from the $[ClRu_4(CO)_{13}]^-$. Products identified include $[H_4Ru_4(CO)_{12}]$, $[Ru_3(CO)_{12}]$ and $[H_2Ru_4(CO)_{13}]$, and the nitrogen-containing clusters $[HRu_4N(CO)_{12}]$ and $[HRu_3(CO)_{10}(NO)]$, all in less than 8% yield. Also isolated, in low yield, was the tetranuclear cluster $[Ru_4(CO)_{10}Cl_2(OEt)_2]$.

The formulation of this cluster was established by mass spectroscopy, which showed a molecular ion at $m/z = 858$ (^{104}Ru), and confirmed by microanalysis. The IR spectrum shows a highly unusual pattern for a tetranuclear system, indicating an unusual molecular geometry. The ^1H NMR shows a quartet centred at δ 4.92 ppm and a triplet centred at δ 1.85 ppm, of relative intensity 2/3, thus indicating the presence of one or more identical ethoxide groups. These data are summarised in Table 1.

In order to establish the overall molecular structure of the complex a single-crystal X-ray analysis was undertaken. The molecular structure is shown in Fig. 1 while

TABLE 1

SPECTROSCOPIC AND MICROANALYTICAL DATA

Compound	IR (ν_{max}(C=O) (cm^{-1}))	Mass spectra [M^+, m/z, ^{104}Ru]	^{1}H NMR (δ(ppm))	Reference
$[N(PPh_3)_2]$-$[ClRu_4(CO)_{13}]$	2030s, 2006vs, 1975m(br), 1965m(br), 1838w [a]			11
$[Ru_4(CO)_{10}$-$Cl_2(OEt)_2]$ [e]	2098m, 2070s, 2033m, 2026vs, 2016vs, 2009m, 1999w, 1953m [b]	858	4.92 (q, 2H) [d] 1.85 (t, 3H, J(HH) 8 Hz)	
$[Ru_4(CO)_{10}$-$Cl_2(OMe)_2]$	2103m, 2078s, 2036m(sh), 2032vs, 2022vs, 2002w, 1958s [c]	818	4.73 (s) [d]	1
$[Ru_4(CO)_{10}$-$Cl(OMe)_3]$	2094m, 2058s, 2029m(sh), 2024vs, 2012vs, 2006w(sh), 1994m, 1951w(sh), 1964m [c]	814		1
$[Ru_4(CO)_{10}Cl_2$-$(OH)(OMe)]$	2094w, 2069s, 2023vs, 2016vs, 1950m [c]	804		1
$[Ru_4(CO)_{10}Cl_2(OH)_2]$	2093w, 2073s, 2070s, 2027s(sh), 2023vs, 2015s(sh), 2011vs, 1956m, 1951m [c]	790		1
$[Ru_4(CO)_{10}$-$Cl(OH)(OMe)_2]$	2090m, 2058m(sh), 2055s, 2024s(sh), 2019vs, 2010s, 1990m, 1943m [c]	800		1

[a] In tetrahydrofuran. [b] In cyclohexane. [c] In n-heptane. [d] In $CDCl_3$. [e] Analysis. Found: C, 19.67; H, 1.17; Cl, 8.41. Calc: C, 19.86; H, 1.18; Cl, 8.51%.

bond parameters are listed in Table 2. The metal arrangement in the cluster may be described either as two triangles sharing a common elongated edge or as a rhomboid. The four metal atoms are essentially coplanar with a maximum deviation of 0.03 Å for Ru(4). The two unshared edges of the metal triangle defined by Ru(1), Ru(2) and Ru(3) are asymmetrically bridged by chlorine atoms which lie in the plane of the metals. This triangle is capped on either side by the oxygen atoms of the two ethoxy groups; these O atoms lie 1.22 Å above and below the plane. Each of the atoms Ru(1), Ru(2) and Ru(3) is also bonded to two terminal carbonyl groups while Ru(4) is bonded to four terminal carbonyls, two in equatorial and two in axial sites.

In terms of simple electron counting rules, if the bridging Cl atoms act as three electron donors, and the capping ethoxy groups acts as five electron donors, the complex as a whole is a 68-electron system which is consistent with the presence of only two two-centre two-electron metal–metal bonds. The Ru–Ru distances within the complex are in keeping with this assignment. The unsupported Ru(1)–Ru(4) and Ru(2)–Ru(4) distances (average 2.756(6) Å are ca. 0.1 Å shorter than the value observed in $[Ru_3(CO)_{12}]$ [12] (average 2.854(4) Å) but within the range expected for Ru–Ru "single" bonds. The third edge [Ru(1)–Ru(2)] of triangle defined by Ru(1), Ru(2) and Ru(4) is ca. 0.31 Å longer than the other two edges, and is similar in length to the elongated bond of 3.039(1) Å in the quinolinal complex $[Ru_3(CO)_8(C_9H_6NO)_2]$ [13] where the formal bond order is considered to be zero.

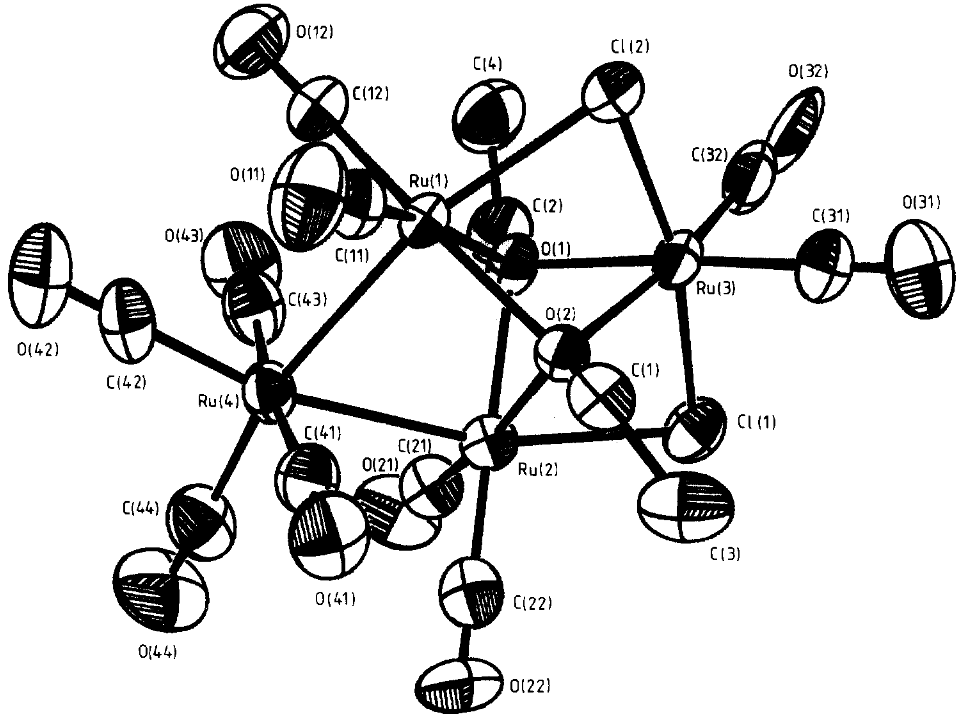

Fig. 1. The molecular structure of $[Ru_4(CO)_{10}(\mu_2\text{-}Cl)_2(\mu_3\text{-}OEt)_2]$ showing the atom numbering scheme adopted.

TABLE 2

SELECTED BOND PARAMETERS FOR $[Ru_4(CO)_{10}(\mu_2\text{-}Cl)_2(\mu_3\text{-}OEt)_2]$

Atomic separations (Å)			
Ru(2)–Ru(1)	3.072(1)	Ru(3)–Ru(2)	3.130(1)
Ru(3)–Ru(1)	3.113(1)	Ru(4)–Ru(2)	2.761(1)
Ru(4)–Ru(1)	2.750(1)	Cl(1)–Ru(2)	2.576(2)
Cl(2)–Ru(1)	2.560(2)	O(1)–Ru(2)	2.188(4)
O(1)–Ru(1)	2.193(4)	O(2)–Ru(2)	2.197(3)
O(2)–Ru(1)	2.181(4)	C(21)–Ru(2)	1.826(7)
C(11)–Ru(1)	1.827(7)	C(22)–Ru(2)	1.851(8)
C(12)–Ru(1)	1.837(7)	Cl(1)–Ru(3)	2.367(2)
C(41)–Ru(4)	1.962(8)	Cl(2)–Ru(3)	2.367(2)
C(42)–Ru(4)	1.942(7)	O(1)–Ru(3)	2.131(4)
C(43)–Ru(4)	1.948(8)	O(2)–Ru(3)	2.131(4)
C(44)–Ru(4)	1.946(8)	C(31)–Ru(3)	1.857(7)
		C(32)–Ru(3)	1.859(8)
Bond angles (°)			
Ru(3)–Ru(1)–Ru(2)	60.8(1)	Ru(3)–Ru(2)–Ru(1)	60.3(1)
Ru(4)–Ru(1)–Ru(2)	56.3(1)	Ru(4)–Ru(2)–Ru(1)	56.0(1)
Ru(4)–Ru(1)–Ru(3)	117.0(1)	Ru(4)–Ru(2)–Ru(3)	116.2(1)
Ru(2)–Ru(4)–Ru(1)	67.7(1)	Ru(2)–Ru(3)–Ru(1)	59.0(1)
Ru(3)–Cl(1)–Ru(2)	78.4(1)	Ru(3)–Cl(2)–Ru(1)	78.3(1)
Ru(2)–O(1)–Ru(1)	89.1(2)	Ru(2)–O(2)–Ru(1)	89.1(1)
Ru(3)–O(1)–Ru(1)	92.1(1)	Ru(3)–O(2)–Ru(1)	92.4(1)
Ru(3)–O(1)–Ru(2)	92.9(2)	Ru(3)–O(2)–Ru(2)	92.6(1)

The metal–metal separations for the chloride-bridged Ru(1)–Ru(3) and Ru(2)–Ru(3) edges are even longer (average 3.122(9) Å). It is probable that there is little direct Ru–Ru interaction along these edges and that the bonding interaction is via the chlorine and ethoxy bridges. The Ru–Cl distances show some asymmetry, with the bonds to Ru(3) being ca. 0.20 Å shorter than to either Ru(1) or Ru(2). The observed Ru–Cl distances lie at the extreme ends of the range of Ru–Cl bond lengths (2.42–2.49 Å) observed in a number of other chloro-bridged Ru clusters [11,14,15]. The Ru–Cl–Ru angles are consistent with values observed in polynuclear bridged structures where there is no direct metal–metal interaction [16]. The capping of the Ru(1)Ru(2)Ru(3) triangle by the oxygen atoms of the two ethoxy groups is also somewhat asymmetric; the average Ru–O distance for Ru(1) and Ru(2) of 2.190(6) Å is ca. 0.06 Å longer than the Ru(3)–O distances. There are no previous examples of capping μ_3-OEt groups in the structural chemistry of ruthenium clusters but in the complex $[Ru_3(\mu_3\text{-}O)(CO)_6(Ph_2AsCH_2AsPh_2)_2]$ [17], where an O atom caps the Ru_3 triangle the Ru–O distances lie in the range 2.06(1)–2.11(1) Å. The bond parameters within the ethoxy groups do not deviate significantly from the expected values. All ten carbonyl groups are terminally bound and the Ru–C–O angles do not deviate significantly from linearity. The average Ru–C(carbonyl) distance of 1.949(8) Å for the carbonyl groups bonded to Ru(4) is somewhat longer than the average distance of 1.843(9) Å for the carbonyls bonded to the other Ru atoms. However, no significant differences are observed in Ru–C(carbonyl) bond lengths between the axial and equatorial carbonyls bound to Ru(4).

Although this cluster is new, compounds with a similar molecular formula have previously been isolated. The carbonylation of hydrated ruthenium trichloride in methanol, using zinc as a halogen acceptor, is a commonly used method of preparing $[Ru_3(CO)_{12}]$ [18]. Eady [1] has investigated this reaction in detail, and has shown that the major by-products are $[H_4Ru_4(CO)_{12}]$ and $[H_2Ru_4(CO)_{13}]$. However, a number of compounds of general formula $[Ru_4(CO)_{10}Cl_x(OH)_y(OR)_z]$ (R = Me, Et and $x + y + z = 4$) were isolated in low yield. Five analogues were characterised spectroscopically, and the data reproduced in Table 1. Preparation of $[Ru_3(CO)_{12}]$ using ethanol rather than methanol as the solvent yielded the compounds $[Ru_4(CO)_{10}Cl_2(OH)(OEt)]$, $[Ru_4(CO)_{10}Cl_2(OH)_2]$ and $[Ru_4(CO)_{10}Cl(OH)(OEt)_2]$, in even lower yields, identified by mass spectroscopy. Comparison of IR data for these compounds with those for $[Ru_4(CO)_{10}Cl_2(OEt)_2]$ shows a close similarity, especially for the compound $[Ru_4(CO)_{10}Cl_2(OMe)_2]$. It is, therefore, most likely that the compounds possess a similar structure. In cases with three alkoxy ligands, following the formalism adopted above, one must presumably act as a 3-electron donor when replacing the chloride.

A compound of relevance to this system is the cluster anion $[Ru_4(CO)_8(\mu\text{-}CO)_2(\mu_2\text{-}Cl)_4]^{2-}$ [16]. This is formed as one of the products in the reaction of $[Co(CO)_4]^-$ with $RuCl_3$ in tetrahydrofuran. It is a 66-electron system, in which the four ruthenium atoms form a distorted tetrahedron with metal–metal separations greater than 3 Å. Two chloride ligands and one carbonyl ligand alternately bridge all the ruthenium atoms. This leads to a formal bond order of 0.5 between the metals. Comparing this with $[Ru_4(CO)_{10}Cl_2(OEt)_2]$, it is interesting to note that by considering the ethoxide groups as 3-electron rather than 5-electron donors, a nominal bond order of 0.66 results between Ru(1)–Ru(2), Ru(1)–Ru(3) and Ru(2)–Ru(3), compatable with the long metal–metal distances observed.

The route by which $[Ru_4(CO)_{10}Cl_2(OEt)_2]$ is formed in the reaction of $[NO]^+$ with the products of the reaction between $[Ru_3(CO)_{12}]$ and $[N(PPh_3)_2]Cl$ in refluxing ethanol is somewhat obscure. However, it has been noted above that the nitrosyl cation is capable of acting as an oxidising agent. As no neutral species are present before the addition of $[NO][BF_4]$, it is possible that the $[NO]^+$ oxidises an anionic precursor to form the observed product. To test this possibility, we have reacted the mixture obtained from $[Ru_3(CO)_{12}]$ and $[N(PPh_3)_2]Cl$ in ethanol with excess $Ag[ClO_4]$ in dichloromethane. Small amounts of $[Ru_3(CO)_{12}]$ and $[H_2Ru_4(CO)_{13}]$ were obtained, together with the expected yield of $[Ru_4(CO)_{10}Cl_2(OEt)_2]$, identified by IR and mass spectroscopy. It therefore appears possible that the reaction of $[Ru_3(CO)_{12}]$ with $[N(PPh_3)_2]Cl$ in ethanol produces the anion "$[Ru_4(CO)_{10}Cl_2(OEt)_2]^{2-}$" in low yields, which can then be oxidised by $[NO]^+$ or Ag^+ to the neutral species.

Experimental

Reaction of $[Ru_3(CO)_{12}]$ with $[N(PPh_3)_2]Cl$ in ethanol, followed by reaction with $[NO][BF_4]$

The cluster $[Ru_3(CO)_{12}]$ (300 mg, 0.469 mmol) and the salt $[N(PPh_3)_2]Cl$ (287 mg, 0.500 mmol) were dissolved in 25 ml of ethanol and refluxed (78°C) for 2 h. The solution changed colour from deep orange to very deep red, and the starting material was consumed. The solution was dried, extracted with Et_2O, dried and dissolved in 25 ml of dichloromethane. No neutral species were present and infrared spectroscopy showed the major product to be $[ClRu_4(CO)_{13}]^-$. To this solution $[NO][BF_4]$ (28 mg, 0.239 mmol) was added as a solid, and the solution stirred at room temperature for 18 h. The solution was now orange in colour, and was evaporated to dryness and the products separated using a silica column with 1/1 acetone/hexane as eluant. A broad yellow band was recovered, which was further separated by thin layer chromatography using cyclohexane as eluant. The products were extracted with dichloromethane and identified as: $R_f = 0.55$, $[Ru_3(CO)_{12}]$; $R_f = 0.50$, $[HRu_4N(CO)_{12}]$ (14.7 mg, yield 5.5%); $R_f = 0.45$, $[HRu_3(CO)_{10}(NO)]$ (24 mg, yield 8%); $R_f = 0.40$, $[H_2Ru_4(CO)_{13}]$; $R_f = 0.35$, $[Ru_4(CO)_{10}Cl_2(OEt)_2]$ (14.2 mg, yield 5% (more typically 1% or less)). A baseline was also observed.

Reaction of $[Ru_3(CO)_{12}]$ with $[N(PPh_3)_2]Cl$ in ethanol, followed by reaction with $Ag[ClO_4]$

The cluster $[Ru_3(CO)_{12}]$ (107 mg, 0.167 mmol) and the salt $[N(PPh_3)_2]Cl$ (95 mg, 0.167 mmol) were dissolved in 20 ml of ethanol and refluxed (78°C) for 0.75 h. The starting material had been consumed, so the solution was evaporated to dryness and redissolved in 20 ml of dichloromethane. A large excess of $Ag[ClO_4]$ was added, and the reagents stirred at room temperature for 0.5 h. The solution changed colour from deep red to green-ochre with a heavy ochre precipitate, so it was filtered and evaporated to dryness. The products were separated by thin layer chromatography using cyclohexane as eluant, and extracted with dichloromethane. Four compounds were obtained in low yield and identified as: $R_f = 0.60$, $[H_4Ru_4(CO)_{12}]$ with $[Ru_3(CO)_{12}]$; $R_f = 0.40$, $[H_2Ru_4(CO)_{13}]$; $R_f = 0.35$, $[Ru_4(CO)_{10}Cl_2(OEt)_2]$.

Crystal structure determination of $[Ru_4(CO)_{10}Cl_2(OEt)_2]$

Suitable single crystals were obtained as red blocks from an octane/CH_2Cl_2 solution at −20°C. A crystal with dimensions ca. 0.41 × 0.33 × 0.31 mm was

TABLE 3

ATOMIC COORDINATES ($\times 10^4$)

Atom	x	y	z
Ru(1)	3293(1)	1212(1)	5749(1)
Ru(2)	1909(1)	1468(1)	4039(1)
Ru(3)	2657(1)	2539(1)	5300(1)
Ru(4)	2508(1)	323(1)	4600(1)
Cl(1)	1559(1)	2613(1)	3972(1)
Cl(2)	3763(1)	2218(1)	6529(1)
O(1)	1960(3)	1702(2)	5435(3)
O(2)	3279(2)	1835(2)	4640(2)
C(11)	4447(5)	861(3)	5809(4)
O(11)	5157(4)	634(2)	5824(1)
C(12)	3175(5)	729(3)	6702(4)
O(12)	3106(4)	418(2)	7283(3)
C(21)	727(5)	1160(3)	3732(5)
O(21)	−14(4)	965(3)	3543(4)
C(22)	2046(4)	1280(3)	2888(5)
O(22)	2154(4)	1163(2)	2191(3)
C(31)	3342(5)	3221(3)	5094(5)
O(31)	3739(4)	3646(2)	4976(4)
C(32)	2003(6)	3046(3)	5951(5)
O(32)	1610(5)	3365(3)	6332(4)
C(41)	3507(5)	485(3)	3907(4)
O(41)	4054(4)	567(2)	3489(4)
C(42)	3172(5)	−355(3)	5224(5)
O(42)	3538(4)	−753(2)	5601(4)
C(43)	1527(5)	270(3)	5330(5)
O(43)	964(4)	214(3)	5738(4)
C(44)	1745(5)	−125(3)	3648(5)
O(44)	1275(5)	−397(3)	3139(4)
C(1)	4120(4)	1951(3)	4267(4)
C(2)	1081(5)	1697(3)	5790(5)
C(3)	3920(5)	2312(4)	3425(5)
C(4)	1254(7)	1700(4)	6757(5)

mounted on a glass fibre with epoxy resin, and space group and approximate cell parameters determined via Weissenberg (Cu-K_α radiation) photography.

Crystal data. $C_{14}H_{10}Cl_2O_{12}Ru_4$, $M = 845.4$, Monoclinic, a 14.458(3), b 22.073(6), c 15.302(4) Å, β 99.54(2)°, U 4816(2) Å^3 (by least-squares refinement for 15 automatically centred reflections in the range $20 < 2\theta < 25°$), space group $I2/c$ (non-standard setting of $C2/c$; No. 15), D_m not measured, $Z = 8$, D_c 2.33 g cm^{-3}, $F(000) = 3424$, Monochromatic Mo-K_α radiation, λ 0.71069 Å, μ(Mo-K_α) 26.61 cm^{-1}.

Data collection and processing [11]. Syntex P2$_1$ diffractometer, 96 step ω–2θ scan mode with a scan range of from 1° below K_{α_1} to 1° above K_{α_2}, scan speed 2.5–29.3°/min, graphite-monochromated Mo-K_α radiation; 3876 reflections measured ($5.0 < 2\theta < 50.0°$, $+h$, $+k$, $\pm l$), [3201 unique, merging $R = 0.019$ after absorption correction based on a pseudo-ellipsoid model using 382 azimuthal scan data from nine independent reflections (maximum and minimum transmission 0.972–0.757)], giving 3113 with $|F| > 3\sigma(F)$. Two check reflections were monitored periodically throughout data collection and showed no significant variation.

Sructure analysis and refinement. Centrosymmetric direct methods (Ru atoms) followed by Fourier difference techniques. Blocked full-matrix least-squares with all non-hydrogen atoms anisotropic. Methyl and methylenic H atoms placed in idealised positions and allowed to ride 1.08 Å from the relevant C atom during refinement; the methyls were treated as rigid groups. Each type of H was assigned a common isotropic temperature factor. The weighting scheme $w = 1.0973/[\sigma^2(F) + 0.001|F|^2]$ gave satisfactory agreement analysis. Final R and R' values are 0.031 and 0.034. Complex neutral atom scattering factors were employed [20], and all computations were performed on an IBM 3081 computer at the University of Cambridge using SHELX [21]. The final atomic fractional coordinates are listed in Table 3 .

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* Details of thermal parameters, H-atom coordinates, complete bond lengths and angles, and structure factors may be obtained from the authors.