A re-investigation of the reaction of [RuCl₂(CO)₃]₂ with C₅H₅(Me₃Si) X-ray structure determination of [Ru(CO)₃(η-C₅H₅)][fac-RuCl₃(CO)₃]

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Abstract

The reaction of [RuCl₂(CO)₃]₂ with C₅H₅(SiMe₃) has been re-investigated. In our hands, in refluxing tetrahydrofuran, the reaction gives consistently [Ru(CO)₃(η-C₅H₅)][fac-RuCl₃(CO)₃], 1, and [RuCl(CO)₂(η-C₅H₅)], 2, in 68% and 12% yield respectively. The reaction of CO with commercially available hydrated OsCl₃ gives [OsCl₂(CO)₃]₂ in 44% yield. The crystal structure of [Ru(CO)₃(η-C₅H₅)][fac-RuCl₃(CO)₃] is reported; superlattice symmetry is observed.

Keywords: Ruthenium anion; Carbonyl; Silicon; Cyclopentadienyl; Starting material; Superlattice symmetry; Ruthenium cation

1. Introduction

The route to [RuCl(CO)₂(η-C₅H₅)] from the reaction of [RuCl₂(CO)₃]₂ with C₅H₅(SiMe₃) [1] appears attractive if access to the binary metal carbonyl or high pressure autoclaves is limited by availability or cost, having the advantage of economy of steps and efficacy. However, a re-investigation of the reaction has shown consistently that its utility is limited, with lower than expected yield of [RuCl(CO)₂(η-C₅H₅)] and a high yield of a previously unreported by-product, [Ru(CO)₃-(η-C₅H₅)][fac-RuCl₃(CO)₃]. A single crystal X-ray study of the latter is reported.

2. Experimental

2.1. General procedures

The reactions were conducted under an atmosphere of high purity argon using standard Schlenk techniques and tetrahydrofuran (thf) dried over potassium metal.

[RuCl₂(CO)₃]₂ was prepared using the published procedure [1] from RuCl₃ · xH₂O purchased from Johnson-Matthey and dried under high vacuum (ca. 0.1 mmHg) at ca. 45°C. NMR spectra were measured on Bruker WP80 and AM300 spectrometers operating at 80 and 75.47 MHz for ¹H and ¹³C respectively.

2.2. Reaction of [RuCl₂(CO)₃]₂ and C₅H₅(SiMe₃)

C₅H₅(SiMe₃) (0.25 ml, 1.8 mmol) was added to a solution of [RuCl₂(CO)₃]₂ (250 mg, 0.488 mmol) in thf (50 ml) and refluxed (26 h). Concentration of the reaction mixture followed by cooling yielded colourless crystals of [Ru(CO)₃(η-C₅H₅)][fac-RuCl₃(CO)₃], 1, (180 mg, 0.33 mmol, 68%) m.p. 166–168°C. Anal. Calc. for C₁₁H₅Cl₃O₆Ru₂: C, 24.38; H, 0.93; M, 544; M⁺, 251; M⁻, 293. Found: C, 24.34; H, 0.92%. FAB MS(CH₂Cl₂, NOBA) 251, [M⁺], 37. IR(thf), ν(CO) 2051s, 2071s, 2075s, 2125s, 2133vs cm⁻¹; ¹H NMR, δ(d₆-acetone) 7.96 (s, C₅H₅); ¹³C NMR, δ(d₆-acetone) 92.7 (s, C₅H₅), 187.9 (s, CO), 189.7 (s, CO). The supernatant was reduced to dryness in vacuo with the residue taken up in CH₂Cl₂ (ca. 0.4 ml) and applied to an alumina column (2 cm × 10 cm). Elution with CH₂Cl₂ produced a single yellow band. The eluate was reduced to an oil and petroleum ether added to yield

yellow crystals of $RuCl(CO)_2(\eta$-$C_5H_5)$ (31 mg, 0.120 mmol, 12%).

2.3. Variata

2.3.1. Reaction of [RuCl₂(CO)₃]₂, HCl and C₅H₅-(SiMe₃)

In a manner similar to 2.1 above, $C_5H_5(SiMe_3)$ (0.55 ml, 3.96 mmol) and $[RuCl_2(CO)_3]_2$ (500 mg, 0.976 mmol) with one drop of conc. HCl added, in thf (10 ml) for 20 h gave $[Ru(CO)_3(\eta$-$C_5H_5)][RuCl_3(CO)_3]$ (383 mg, 0.707 mmol, 72%).

2.3.2. Reaction of [RuCl₂(CO)₃]₂ and C₅H₅(SiMe₃)

In a manner similar to 2.1 above, $C_5H_5(SiMe_3)$ (0.25 ml, 1.8 mmol) and $[Ru(CO)_3Cl_2]_2$ (250 mg, 0.488 mmol), in thf (50 ml) for 20 h, with an argon purge, gave **1** (60 mg, 0.11 mmol, 23%) and **2** (41 mg, 0.078 mmol, 16%).

2.3.3. Reaction of [Ru(CO)₃(η-C₅H₅)][RuCl₃(CO)₃] with C₅H₅(SiMe₃)

In a manner similar to 2.1 above, $C_5H_5(SiMe_3)$ (0.085 ml, 0.612 mmol) and **1** (100 mg, 0.185 mmol), in thf (20 ml) for 20 h recovered **1** (32 mg, 32%) and gave **2** (11 mg, 0.043 mmol, 11%).

The application of an argon purge to this reaction resulted in similar results.

2.4. Preparation of [OsCl₂(CO)₃]₂

The reported method [1] with hydrated $OsCl_3$ (1400 mg, 4.72 mmol) in place of OsO_4, with the passage of CO gave $[OsCl_2(CO)_3]_2$ (708 mg, 1.03 mmol).

Table 1
Summary of X-ray diffraction data for $[Ru(CO)_3(\eta$-$C_5H_5)][fac$-$RuCl_3(CO)_3]$, **1**

Source of crystals	crystal from thf
Colour	colourless
Habit	thin plate
Specimen size	0.28×0.50×0.16
Formula	$C_{11}H_5Cl_3O_6Ru_2$
Molecular weight	541.7
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 14)
a (Å)	16.493(3)
b (Å)	8.8182(8)
c (Å)	23.978(4)
β (deg)	106.13(1)
V (Å³)	3350
Z	8
ρ(calcd) (g cm⁻³)	2.48
$F(000)$ (e)	2064
Temperature (K)	298
Radiation (monochromatic)	Mo Kα, $\lambda = 0.7107_3$ Å
Diffractometer	CAD4
Scan type	2θ–θ
μ (cm⁻¹)	23.0
A° (min, max)	1.40, 1.91
$2\theta_{max}$ (deg)	60
No. of independent reflections	9738
No. observed reflections	5236 ($I > 3\sigma(I)$)
R	0.032
R_w	0.031

2.5. Structure determination

Colourless crystals of **1**, from thf, took the form of thin plates and some trouble was taken over obtaining a specimen of optimum form and diffraction characteris-
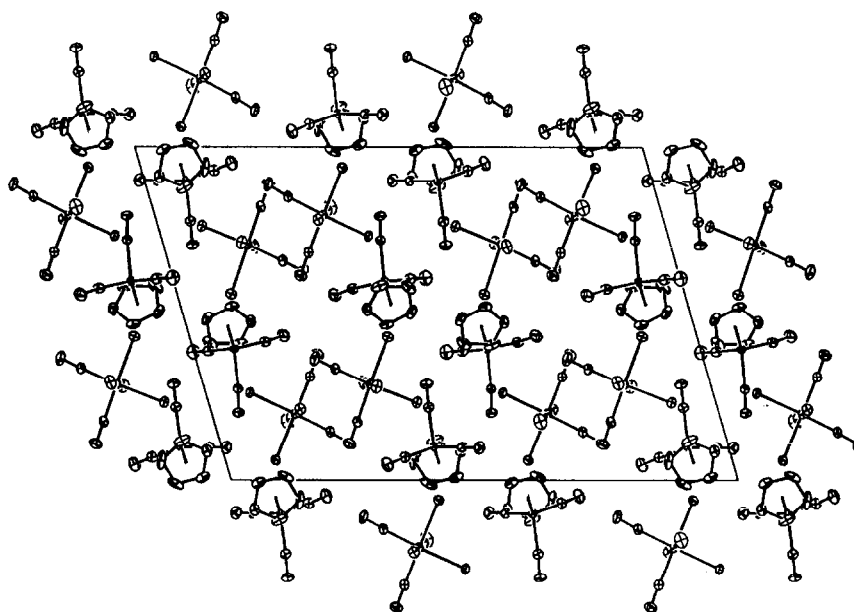

Fig. 1. Unit cell contents projected down *b* axis. 20% thermal ellipsoids are shown for the non-hydrogen atoms.

tics for the measured data in view of the associated superlattice difficulties. A unique room temperature diffractometer data set was measured yielding 9738 independent reflections, 5236 of which, with $I > 3\sigma(I)$, were considered 'observed' and used in the full-matrix least squares refinement after Gaussian absorption correction. Hydrogen atoms were included in idealised positions. Conventional residuals R and R_w on $|F|$ at convergence were 0.032 and 0.031; statistical reflection weights derivative of $\sigma^2(I) = \sigma^2(I_{\mathrm{diff}}) + 0.0004\sigma^4$ (I_{diff}) being employed. Computation used the XTAL 3.4 suite of programs [2], implemented by Hall. Further pertinent details of data collection, solution and refine-

ment are contained in Tables 1 and 2, and Figs. 1 and 2. Data deposited with the Cambridge Crystallographic Data Centre comprises thermal and hydrogen parameters, full molecular non-hydrogen geometries.

3. Results and discussion

3.1. Synthesis and properties

The ionic complex $[Ru(CO)_3(\eta\text{-}C_5H_5)][\mathit{fac}\text{-}RuCl_3\text{-}(CO)_3]$, **1**, is obtained in approximately 68% yield from the reported reaction, along with $[RuCl(CO)_2(\eta\text{-}C_5H_5)]$

Table 2

Non-hydrogen positional and isotropic displacement parameters for **1**

Atom	x	y	z	U_{eq} (Å²)
Ru(1)	0.89901(2)	0.19828(4)	0.57968(2)	0.0355(1)
C(101)	0.9919(4)	0.3450(6)	0.5536(4)	0.070(3)
C(102)	0.9116(4)	0.4025(6)	0.5307(3)	0.060(2)
C(103)	0.8799(4)	0.4465(6)	0.5744(4)	0.080(3)
C(104)	0.9403(7)	0.4119(8)	0.6263(3)	0.098(4)
C(105)	1.0110(4)	0.3492(7)	0.6111(4)	0.087(3)
C(11)	0.9003(3)	0.0434(6)	0.5248(2)	0.050(2)
O(11)	0.9014(2)	−0.0449(4)	0.4914(2)	0.072(2)
C(12)	0.7786(3)	0.1667(5)	0.5671(2)	0.048(2)
O(12)	0.7073(2)	0.1556(4)	0.5580(2)	0.064(2)
C(13)	0.9308(3)	0.0559(6)	0.6426(2)	0.053(2)
O(13)	0.9527(3)	−0.0210(5)	0.6806(2)	0.083(2)
Ru(3)	0.70844(3)	0.72727(4)	0.66807(2)	0.0381(2)
Cl(31)	0.76349(9)	0.7716(1)	0.58731(6)	0.0535(5)
Cl(32)	0.56348(9)	0.7347(2)	0.60678(7)	0.0695(6)
Cl(33)	0.7151(1)	0.4566(1)	0.65681(7)	0.0641(6)
C(31)	0.8222(4)	0.7147(6)	0.7149(2)	0.053(2)
O(31)	0.8898(3)	0.7011(5)	0.7432(2)	0.084(2)
C(32)	0.7043(3)	0.9387(6)	0.6755(2)	0.048(2)
O(32)	0.7032(3)	1.0667(4)	0.6792(2)	0.072(2)
C(33)	0.6605(3)	0.6917(6)	0.7284(2)	0.052(2)
O(33)	0.6301(3)	0.6685(5)	0.7635(2)	0.086(2)
Ru(2)	0.60014(2)	0.69216(4)	0.41799(2)	0.0386(1)
C(201)	0.5186(4)	0.8762(7)	0.3688(3)	0.068(3)
C(202)	0.4726(4)	0.7954(7)	0.3982(3)	0.070(3)
C(203)	0.5104(5)	0.8157(8)	0.4543(3)	0.075(3)
C(204)	0.5835(5)	0.9034(8)	0.4623(3)	0.086(3)
C(205)	0.5871(4)	0.9427(7)	0.4064(4)	0.085(4)
C(21)	0.5795(3)	0.5605(7)	0.3525(3)	0.059(2)
O(21)	0.5610(3)	0.4900(5)	0.3124(2)	0.086(2)
C(22)	0.6074(3)	0.5255(6)	0.4694(3)	0.061(2)
O(22)	0.6103(3)	0.4307(5)	0.5008(2)	0.092(2)
C(23)	0.7224(3)	0.6856(6)	0.4339(2)	0.048(2)
O(23)	0.7946(2)	0.6889(5)	0.4466(2)	0.068(2)
Ru(4)	0.79748(3)	0.24583(4)	0.33403(2)	0.0377(1)
Cl(41)	0.73426(9)	0.2579(2)	0.41235(6)	0.0545(5)
Cl(42)	0.93972(8)	0.2679(2)	0.39916(6)	0.0551(5)
Cl(43)	0.78359(8)	0.5173(1)	0.32115(6)	0.0551(5)
C(41)	0.6847(3)	0.2268(5)	0.2838(2)	0.048(2)
O(41)	0.6172(3)	0.2138(5)	0.2555(2)	0.073(2)
C(42)	0.8110(3)	0.0356(6)	0.3453(2)	0.055(2)
O(42)	0.8205(3)	−0.0891(5)	0.3526(2)	0.091(2)
C(43)	0.8524(3)	0.2454(6)	0.2748(2)	0.052(2)
O(43)	0.8888(3)	0.2493(5)	0.2424(2)	0.086(2)

(a)

gk1 [CpRu(CO)₃]⁺[Ru(CO)ₓClₓ]⁻ cation 1

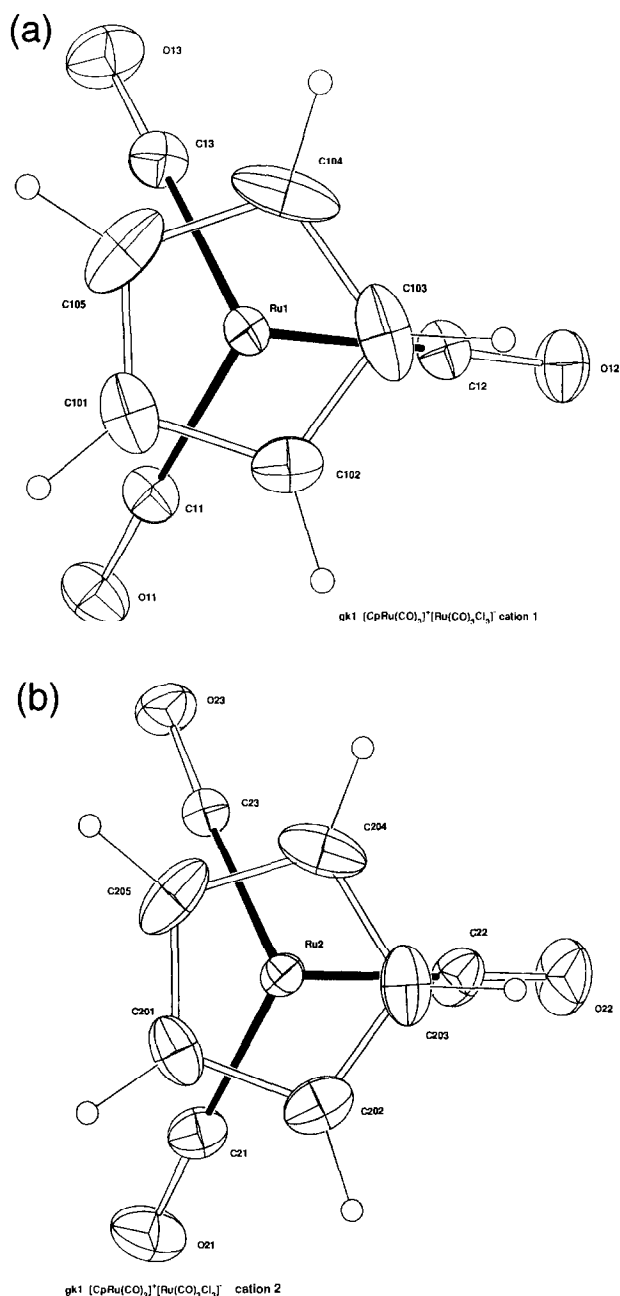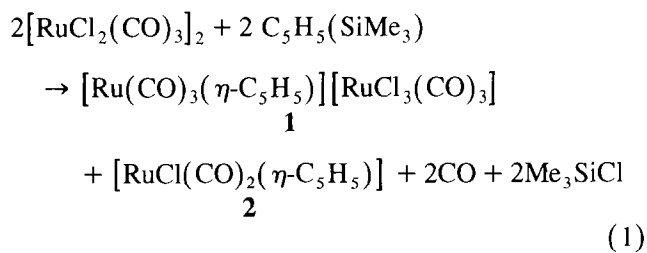**(b)**

gk1 [CpRu(CO)₃]⁺[Ru(CO)ₓClₓ]⁻ cation 2

Fig. 2. The two cations found in the asymmetric unit. (a) Cation 1; (b) Cation 2.

(12%), **2**, which was much smaller than the anticipated ca. 75%.

$$2[RuCl_2(CO)_3]_2 + 2\ C_5H_5(SiMe_3)$$

$$\rightarrow [Ru(CO)_3(\eta\text{-}C_5H_5)][RuCl_3(CO)_3]$$
$$\mathbf{1}$$

$$+ [RuCl(CO)_2(\eta\text{-}C_5H_5)]\ + 2CO + 2Me_3SiCl$$
$$\mathbf{2}$$

$$(1)$$

An initial white precipitate is formed when the reactants are allowed to stir while warming to reflux temperature. In one instance this precipitate was collected and shown to be **1** by infrared spectroscopy. The relative ratio of **1** and **2** was not affected greatly by then allowing the reaction to proceed for the prescribed time. Similarly, the use of freshly distilled $C_5H_5(SiMe_3)$ or a greater proportion of this ligand failed to give exclusively **2**. Considering the balanced equation (Eq. (1)), initial postulates involved liberation of CO which was then taken up to give the cationic species found in the reaction. However, purging the refluxing thf solution with a steady stream of argon failed to affect the course of the reaction significantly.

The anion as formulated in **1** is well known and accessible directly from refluxing solutions of hydrated $RuCl_3$, HCl and formic acid by the addition of CsCl[3] as $Cs[RuCl_3(CO)_3]$. Similarly, of the species formed on carbonylation of ethanolic solutions of hydrated $RuCl_3$ for prolonged periods, $H[RuCl_3(CO)_3]$ results in greater or lesser amounts as a function of the amount of HCl present [4]. Given that the starting material for this work is prepared by the reaction of hydrated $RuCl_3$, HCl and formic acid, the effect of adventitious HCl was investigated as a possible contaminant. The effect of adding HCl was to give exclusively the ionic species in 72% yield and none of the neutral species, **2**. However, starting material, $[RuCl_2(CO)_3]_2$, that was devoid of HCl was found to give the same distribution of products observed initially.

The chloride bridges in $[RuCl_2(CO)_3]_2$ are readily cleaved by thf forming complexes of the type $[RuCl_2(CO)_3(thf)]$ [5] and indeed the use of polar donating solvents is essential for the reaction to proceed [1]. The mechanism as suggested by this re-investigation of the reaction of $[RuCl_2(CO)_3]_2$ with $C_5H_5(SiMe_3)$ is depicted in Scheme 1.

Cleavage of the chloride bridges gives **A**. It is then possible for heterolytic cleavage of the Cl^- ligand in the polar medium of the reaction to occur giving species **B** and releasing Cl^- ion into solution which can then result in the formation of the anion from **A** or $[RuCl_2(CO)_3]_2$. Note that the Ru–Cl bond of $[RuCl(PPh_3)_2(C_5H_5)]$ is highly polarised and dissociates completely in methanol [6]. The diene can then react with either species, **A** or **B**; the latter is presumably favoured because of the more accessible metal centre with two lightly coordinated thf ligands, giving the neutral complex **2** and the cation, respectively. Presumably this whole process is an equilibrium that is driven in this manner by the precipitation of **1** from solution.

The fact that small amounts of **2** are obtained from the prolonged reaction of **1** with $C_5H_5(SiMe_3)$ suggests that the heterolytic cleavage of anion Ru–Cl bonds occurs on dissolution of **1** in thf.
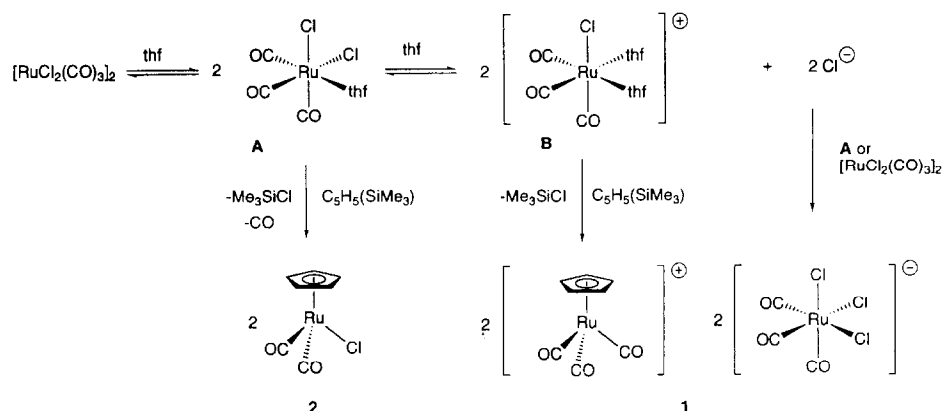
Scheme 1.

3.2. X-ray structure determination of [Ru(CO)$_3$(η-C$_5$H$_5$)][RuCl$_3$(CO)$_3$], 1

Colourless specimens of **1** were obtained from thf. Examination of the systematic absences revealed evidence of **B** superlattice symmetry in the monoclinic space group, $P2_1/c$. The results of the room temperature structure determination are consistent, in terms of stoichiometry and connectivity, with the description of the complex as the ionic aggregate, [Ru(CO)$_3$(η-C$_5$H$_5$)]$^+$[RuCl$_3$(CO)$_3$]$^-$, Figs. 1 and 2. A search of the Cambridge Structural Database revealed that the anion was indeed a known structure, but surprisingly the cation has yet to be reported [7]. Two pseudo-symmetrically related complete formula units comprise the asymmetric unit of the monoclinic unit cell. The moieties, Table 3, have a quasi-octahedral geometry with the cyclopentadienyl ligand, in the cation, occupying three coordination sites and the three carbonyl ligands taking the other sites. The overall effect is of a 'three legged piano stool'. The cyclopentadienyl geometry is comparable with that seen for other such complexes, those of

Table 3
Selected geometries for **1**
(a) Cation ruthenium environments [a]

Atoms	Distance (Å)	Atoms	Angle (deg)
Ru–C(00)	1.876(4), 1.882(4)	C(00)–Ru–C(1)	124.2(2), 121.8(2)
Ru–C(1)	1.900(5), 1.907(6)	C(00)–Ru–C(2)	122.9(1), 124.4(2)
Ru–C(2)	1.944(5), 1.900(6)	C(00)–Ru–C(3)	125.0(2), 126.1(2)
Ru–C(3)	1.920(5), 1.946(5)	C(1)–Ru–C(2)	89.8(2), 91.6(2)
Ru–C(0n) (range)	2.192–2.231(7)	C(1)–Ru–C(3)	91.2(2), 94.6(2)
C–O (range)	1.113–1.145(6)	C(2)–Ru–C(3)	94.1(2), 88.6(2)
		C(0n)–Ru–C(0n')	34.6–37.6(3)
		(ranges)	58.4–61.3(7)

[a] The two values in each entry are for the corresponding values about Ru(1, 2) respectively. C(00) is the cyclopentadienyl centroid.

(b) Anion ruthenium environments [b]

Atom	r	Cl(2)	Cl(3)	C(1)	C(2)	C(3)
Cl(1)	2.388(2)	92.12(6)	91.82(5)	87.4(2)	86.9(2)	177.3(2)
	2.390(2)	92.60(5)	90.55(5)	86.5(2)	89.5(2)	176.3(2)
Cl(2)	2.435(1)	—	91.54(5)	178.0(2)	88.6(1)	85.2(2)
	2.438(1)	—	92.47(5)	179.0(2)	86.1(2)	84.5(2)
Cl(3)	2.408(1)	—	—	86.6(2)	178.7(2)	87.9(2)
	2.416(1)	—	—	88.0(1)	178.6(1)	87.4(2)
C(1)	1.903(5)	—	—	—	93.3(2)	95.3(2)
	1.921(5)	—	—	—	93.4(2)	96.4(2)
C(2)	1.876(5)	—	—	—	—	93.4(2)
	1.878(5)	—	—	—	—	92.5(2)
C(3)	1.859(6)	—	—	—	—	—
	1.885(6)	—	—	—	—	—

[b] r is the metal to ligand atom distance (Å). Other entries in the matrix are the angles (deg) subtended at the metal by the relevant atoms at the head of the row and column. Values for Ru(4) lie below those for Ru(4). Ru–C–O range 175.7(5)–178.7(5)°.

the carbonyl ligands comparable with those found in mononuclear and polynuclear ruthenium compounds [8].

In two previous studies of the anion [9,10], as well as the present, the anions were found to essentially octahedral with a fac arrangement of ligands; previous metal ligand geometries are similar to those established in this study.

In one of these previous studies [10], viz. the structure determination of $[H_5O_2][RuCl_3(CO)_3][SbCl_3]$, there is distortion from the expected C_{3v} symmetry by virtue of Ru–Cl $\cdots$ Sb and Cl $\cdots$ HO interactions. In the present study there are several close contacts between cyclopentadienyl C–H and the anion Cl ligands. The most notable of these is an interaction lying within one formula unit of the asymmetric unit, this distance (2.7 Å) is not mimicked within the other formula unit.

Acknowledgements

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