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The Synthesis and Characterization of an Homologous Series of Cyclopentadienyl Diruthenium Alkanediyl Complexes $[CpRu(CO)_2]_2[\mu\text{-}(CH_2)_n]$ (where $n = 5-10$): the Crystal Structure of $[CpRu(CO)_2]_2[\mu\text{-}(CH_2)_5]$

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Abstract

The new alkanediyl compounds $[CpRu(CO)_2]_2$-$[\mu\text{-}(CH_2)_n]$ (n = 5–10; Cp = η^5-C_5H_5) have been synthesized by the reaction of $Na[CpRu(CO)_2]$ with $I(CH_2)_nI$ in tetrahydrofuran. The compounds have been fully characterized by methods including IR, ^1H NMR, ^{13}C NMR and mass spectroscopy. These data are compared with those obtained for the corresponding di-iron compounds. The molecular structure of the compound $[CpRu(CO)_2]_2[\mu\text{-}(CH_2)_5]$ has been determined by X-ray crystallography. The complex crystallizes in the $P\bar{1}$ space group with a = 7.792(1), b = 10.691(3) and c = 12.316(2) Å, α = 106.76(2), β = 95.58(1) and γ = 90.94(2)°. The structure was solved and refined to R = 0.037. The structure shows that the two $CpRu(CO)_2$ groups are connected by the zigzag pentamethylene chain with the average Ru–C(alkyl) 2.172(9) Å.

Introduction

Compounds containing a hydrocarbon ligand bridging two metals hold a pivotal position in the development of dinuclear organometallic chemistry and are of considerable current interest [1, 2]. This, in part, is due to the possible involvement of such species in important catalytic reactions, including the Fischer–Tropsch reaction. Alkanediyl or polymethylene bridged compounds of the type $L_mM(CH_2)_nML_m$ are specific examples of dinuclear hydrocarbyl bridged compounds [3, 4].

Hydrocarbyl complexes of ruthenium are of particular interest [5–7] partly because ruthenium is known to be an active Fischer–Tropsch catalyst [8] and also because it could provide a more economical alternative to rhodium based catalyst systems [9]. Ruthenium and its compounds have thus been the recent subjects of both theoretical [10] and practical [11–13] catalytic investigations. Two of these studies [12, 13] involve intermediates where an alkanediyl group bridges two active ruthenium sites on a catalyst surface.

We now report on our studies of the synthesis, properties and structure of some new compounds of the series $[CpRu(CO)_2]_2[\mu\text{-}(CH_2)_n]$ (where n = 5–10).

Experimental

All reactions were routinely carried out in Schlenk apparatus under an atmosphere of nitrogen. THF was distilled over sodium/benzophenone under a nitrogen atmosphere before use. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions (unless otherwise stated) using either a Varian VXR 200 or Bruker WH 90 NMR spectrometer. Chemical shifts are reported relative to tetramethylsilane (δ 0.00 ppm) as an external (VXR 200) or internal (WH 90) reference standard. Infrared spectra were recorded on a Perkin-Elmer 983 spectrophotometer in solution cells using NaCl windows. Mass spectra were recorded on a VG Micromass 16F spectrometer operating at 70 eV with an accelerating voltage of 4 kV. Melting point ranges were determined on a Kofler hotstage microscope (Reichert Thermovar) and are uncorrected. Microanalyses were performed in the microanalytical laboratory of the University of Cape Town. Di-iodoalkanes were obtained from Aldrich Chemical Corporation or Ega Chemie and were used without further purification. The compound $[CpRu(CO)_2]_2$ was prepared by the method of Doherty and Knox [14]. The sodium salt of the anion $[CpRu(CO)_2]^-$ was prepared by stirring a THF solution of the dimer with a *c.* 1% sodium amalgam for 2–8 h at room temperature.

Preparation of the Compounds $[CpRu(CO)_2]_2$-$[\mu\text{-}(CH_2)_n]$ *(where* n = 5–10 (1–6))

The compounds 1–6 were all prepared by the same general synthetic route. $I(CH_2)_nI$ (1.05 mmol) in THF (1 cm^3) was added dropwise over 5 min to a stirred solution of $Na[CpRu(CO)_2]$ (2.29 mmol) in THF (10 cm^3). The red–brown mixture was stirred

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for 1.25 h in the dark at room temperature and then the solvent was removed under reduced pressure. The dark brown residue was extracted with hexane (c. 5 X 30 cm^3) and the extractions filtered and concentrated to give an orange solution. This solution was chromatographed on a Florisil column (c. 6 cm high by 3 cm diameter). A colourless band was eluted initially with hexane. Removal of the solvent under reduced pressure yielded the cream coloured crystals of $[CpRu(CO)_2]_2[\mu\text{-}(CH_2)_n]$ which were recrystallized from hexane at −78 °C. Yields and microanalytical data are reported in Table 1; melting point and IR data in Table 2. In addition to the products **1**–**6**, small quantities of $[CpRu(CO)_2I]$ (c. 5%) and $[CpRu(CO)_2]_2$ (c. 10%) were eluted from the chromatography columns using hexane/ether eluants in the ratio of (80:20) and (50:50) respectively. These products were identified by their infrared spectra in the ν(CO) region.

Crystal and Intensity Data

Single crystals of compound **1**, suitable for X-ray studies, were obtained by slow crystallization of the compound from a dilute hexane solution at 0 °C.

A suitable single crystal was selected and irradiated with Mo Kα (λ = 0.7107 Å) radiation using an Enraf-Nonius CAD4 diffractometer. Cell parameters were obtained by least-squares analysis of the setting angles of 24 reflections in the range $16 \leqslant \theta \leqslant 17°$. During the data collection, intensities of three standard reference reflections were monitored every hour and recentring checked every hundred measured reflections. Intensities were corrected for Lorentz polarization effects and for absorption [15].

The structure was solved by location of the two Ru atoms in a Patterson map. All remaining non-hydrogen atoms were located in subsequent difference Fouriers. In the final refinements, all non-hydrogen atoms were treated anisotropically. The methylene hydrogens were placed in calculated positions with a single isotropic temperature factor. The maximum parameter shift/e.s.d. was less than 0.005. In the difference map, computed after the final cycle of refinements maximum residual electron density was 0.33 e Å^{-3}. Complex neutral atom scattering factors for the non-hydrogen atoms were taken from Cromer and Mann [16] and from Stewart *et al.* [17] for hydrogen atoms, with dispersion corrections from Cromer and Libermann [18]. Structure solution and refinement were carried out using SHELX-76 [19], molecular parameters obtained from PARST [20] and drawings obtained with PLUTO [21]. All computations were carried out on a SPERRY 1100 computer.

Further details of the data collection, structure solution and refinement are given in Table 3.

TABLE 1. Yields and microanalysis for $[CpRu(CO)_2]_2[\mu\text{-}(CH_2)_n]$, n = 5–10 (1–6)

Compound number	n	Yield^a (%)	Analysis^b (%)	
			C	H
1	5	61(39)	44.40(44.35)	4.10(3.93)
2	6	60(30)	45.50(45.44)	4.30(4.20)
3	7	55(18)	46.50(46.48)	4.50(4.47)
4	8	75(44)	47.50(47.47)	4.70(4.72)
5	9	64(32)	48.20(48.41)	5.00(4.96)
6	10	66(24)	49.30(49.30)	5.20(5.18)

^{a}Yields after recrystallisation in parentheses. ^{b}Calculated values in parentheses.

TABLE 2. Melting points and IR data for the compounds $[CpRu(CO)_2]_2[\mu\text{-}(CH_2)_n]$, n = 5–10 (1–6)

Compound number	n	Melting point range (°C)	ν(CO) (cm^{-1})^a	
1	5	77–84	2018vs	1959vs
2	6	106–109	2019vs	1959vs
3	7	65–70	2019vs	1959vs
4	8	73–77	2019vs	1959vs
5	9	34–37	2019vs	1959vs
6	10	45–51	2019vs	1959vs

^{a}Hexane solution, vs = very strong.

TABLE 3. Crystal data, experimental details of data collection and structure refinement for $[CpRu(CO)_2]_2[\mu\text{-}(CH_2)_5]$ (1)

Molecular formula	$C_{19}H_{20}O_4Ru_2$
M_r/(g mol^{-1})	514.51
Space group	$P\bar{1}$
a (Å)	7.792(1)
b (Å)	10.691(3)
c (Å)	12.316(2)
α (°)	106.76(2)
β (°)	95.58(1)
γ (°)	90.94(2)
V (Å^3)	976.7(4)
D_c for Z = 2 (g cm^{-3})	1.75
F(000)	508
μ (Mo Kα) (cm^{-1})	15.36
Dimensions of crystal (mm)	0.28 × 0.28 × 0.30
Crystal decay (%)	0.4
Scan mode	ω–2θ
Scan width (°ω)	(1.00 + 0.35 tan θ)
Aperture width (mm)	(1.20 + 1.05 tan θ)
θ range (°)	1–25
% Transmission on absorption correction min./max./average	91/100/97
Total no. reflections collected	3278
No. reflections observed, N (with I rel > $2\sigma I$ rel)	3092
No. parameters, NP	227
$R = \Sigma\lvert\Delta\rvert/\Sigma\lvert F_o\rvert$	0.037
$S = (\Sigma\lvert\Delta\rvert^2/N - NP)^{1/2}$	1.71

Results and Discussion

The diruthenium alkanediyl compounds of the series $[CpRu(CO)_2]_2[\mu\text{-}(CH_2)_n]$ where n = 1–3 [22] and n = 4 [23] have been reported previously. We wished to prepare other members of this series and, in particular, to attempt to identify any differences in chemistry on increasing the length of the hydrocarbon chain between the two ruthenium atoms [24]. Compounds **1**–**6** were prepared by the reaction of the anion $[CpRu(CO)_2]^-$ with the appropriate di-iodoalkane.

$$2Na[CpRu(CO)_2] + I(CH_2)_nI \longrightarrow [CpRu(CO)_2]_2[\mu\text{-}(CH_2)_n] + 2NaI \quad (1)$$

with $n = 5$ (**1**), 6 (**2**), 7 (**3**), 8 (**4**), 5 (**9**), 6 (**10**).

The new compounds were all isolated as air stable, cream coloured crystalline compounds in generally good yields (55–75%) and characterized by microanalytical data (see Table 1). The melting points (m.p.) of compounds **1**–**6** decrease with increasing hydrocarbon chain length (Table 2) and also, the compounds with even n have generally higher m.p.s than those with n odd. Similar trends have been observed for the analogous di-iron alkanediyl compounds [25, 26].

Solutions of compounds **1**–**6** in hydrocarbon solvents decompose within a few hours in air but under nitrogen, solutions of the compounds exhibit unusually high stability even at elevated temperature (*c.* 140 °C) for prolonged periods (several days). The infrared spectra of the compounds show two strong ν(CO) bands (see Table 2) at 2019 and 1959 cm^{-1}, which are at higher frequency than the analogous di-iron complexes (2008 and 1954 cm^{-1}) [25, 26]. The ^1H NMR spectra of compounds **1**–**6** (Table 4) show a singlet at δ 5.2 for the ten protons of both Cp rings. The protons of the polymethylene chain give rise to three complex signals at *c.* δ 1.67 (4H), δ 1.53 (4H) and δ 1.27 {(2n-8)H} which do not differ significantly with changes in chain length (Table 4).

The $^{13}C\{^1H\}$ NMR spectra of the compounds $[CpRu(CO)_2]_2[\mu\text{-}(CH_2)_n]$ (n = 4–10) were recorded in $CDCl_3$ solution and the results are presented in Table 5. The signals due to the carbonyl ligands (δ 202.5) and the Cp carbon atoms (δ 88.5) agreed well with those previously reported for $[CpRu(CO)_2]_2[\mu\text{-}(CH_2)_n]$ (n = 3 or 4) [23]. No shift in these signals is observed on increasing the alkanediyl chain length. In contrast to the previous report [23], we assign the slightly broadened and less intense ^{13}C signal at δ −3.3 to C_α and that at δ 45.2 to C_β. Confidence in this assignment was gained by comparison with the $^{13}C\{^1H\}$ NMR spectra of $[CpRu(CO)(PR_3)]_2[\mu\text{-}C(O)(CH_2)_nC(O)]$, where the signal at δ −3.2, observed for $[CpRu(CO)_2]_2]\mu\text{-}(CH_2)_n]$, is replaced by a new signal at *c.* δ 65 due to the

TABLE 4. ^1H NMR data for the compounds $[CpRu(CO)_2]_2[\mu\text{-}(CH_2)_n]$, n = 4–10, in $CDCl_3$

Compound number	n	C_5H_5	δ (ppm)		
			Ru–CH_2	β-CH_2–	–CH_2–
	4	5.23(s, 10H)	1.68(m, 4H)	1.55(m, 4H)	
1	5	5.22(s, 10H)	1.66(m, 4H)	1.53(m, 4H)	1.28(m, 2H)
2	6	5.22(s, 10H)	1.67(m, 4H)	1.53(m, 4H)	1.28(m, 4H)
3	7	5.23(s, 10H)	1.67(m, 4H)	1.53(m, 4H)	1.27(bs, 6H)
4	8	5.22(s, 10H)	1.67(m, 4H)	1.53(m, 4H)	1.27(bs, 8H)
5	9	5.22(s, 10H)	1.67(m, 4H)	1.54(m, 4H)	1.27(bs, 10H)
6	10	5.23(s, 10H)	1.67(m, 4H)	1.53(m, 4H)	1.26(bs, 12H)

s = singlet, m = multiplet, bs = broad singlet.

TABLE 5. $^{13}C\ \{^1H\}$ NMR data for the compounds $[CpRu(CO)_2]_2[\mu\text{-}(CH_2)_n]$, n = 4–10, in $CDCl_3$

Compound number	n	δ (ppm)						
		CO	C_5H_5	α-CH_2	β-CH_2	γ-CH_2	δ-CH_2	ϵ-CH_2
	4	202.5	88.6	−3.3	45.2			
1	5	202.5	88.5	−3.0	39.7	40.1		
2	6	202.5	88.6	−3.2	34.4	39.9		
3	7	202.5	88.6	−3.2	34.9	39.9	29.1	
4	8	202.5	88.5	−3.2	34.9	39.8	29.4	
5	9	202.5	88.5	−3.2	34.9	39.9	29.4	29.8
6	10	202.5	88.5	−3.2	34.9	39.9	29.4	29.8

deshielded methylene carbon in Ru—C(O)—CH_2 [24]. Similarly, we assign the high field ^{13}C signals to C_α in compounds **1**–**6**; the lower field signals in the range δ 29 to 40 then are easily assigned to C_β, C_γ, C_δ etc. on the basis of peak intensities in the series (Table 5). The chemical shifts of C_β in $[CpRu(CO)_2]_2[\mu\text{-}(CH_2)_n]$ show the largest variation: from δ 49.1 for the compound where $n = 3$ to δ 34.4 where $n = 6$, with little variation thereafter. This may be due to steric crowding in the short chain alkanediyl complexes but could also be due to some agostic interaction of the hydrogens on C_β. To test for an agostic interaction, $^1J(^{13}C-^1H)$ was measured (see Table 6) for the compounds where $n = 4$ or 5. These were found to be within the range expected for sp^3-hybridized C—H bonds and did not suggest an agostic interaction [27]. Furthermore, no high field proton signal could be observed down to δ −20 for the same compounds.

The mass spectra for compounds **1**–**6** were recorded and showed parent molecular ions in all cases except for **1** (see Table 7). Two major fragmentation pathways can be identified: the first involves loss of one CO followed by elimination of an entire CpRu$(CO)_2$ group to form $[CpRu(CO)(C_nH_{2n})]^+$, which fragments further; the second, less significant pathway, involves loss of CO from the molecular ion followed by elimination of the whole alkanediyl group. Unlike the mass spectra of the di-iron analogue [26], the stepwise loss of CO from the molecular ion is not important for the di-ruthenium compounds.

TABLE 6. $^1J(^{13}C-^1H)$ data for the compounds $[CpRu(CO)_2]_2[\mu\text{-}(CH_2)_n]$, $n = 4, 5$

n	C–H(C_5H_5[a])	^1J ($^{13}C-^1H$) Hz		
		C_α–H[b]	C_β–H[b]	C_γ–H[b]
4	177.8(d) 6.8(q)	133.8	127.0	–
5	177.9(d) 6.8(q)	134.6	130.4	125.3

[a]Signal occurs as a doublet of quintets; values represent the coupling constants of the doublet (d) and quintet (q) respectively. [b]Signals occur as triplets.

Description of the Structure of $[CpRu(CO)_2]_2$-$[\mu\text{-}(CH_2)_5]$ (1)

Suitable crystals of **1** for the X-ray crystal structure determination were obtained by slow crystallization from hexane solution at 0 °C. The crystals chosen for X-ray studies were prisms; some plates were also observed which may be the compound in a different conformation, although this was not established. The compound crystallizes in space group $P\bar{1}$. Other details concerning the crystal, data collection and structure refinement for **1** may be found in Table 3. Fractional atomic coordinates and anisotropic temperature factors are reported in Table 8, selected bond lengths in Table 9 and bond angles in Table 10. The molecular structure of **1** and the atomic labelling scheme are shown in Fig. 1. This confirms that the two $CpRu(CO)_2$ groups are bonded to the terminal carbon atoms of a zigzag pentamethylene chain. Surprisingly, the two Cp rings lie on the same side of the Ru_1—Ru_2 axis in a gauche (or *cis*) orientation (see Fig. 2). This contrasts with structures of the compounds $[CpRu(CO)_2]_2[\mu\text{-}(CH_2)]$ [22] and with $[CpFe(CO_2)]_2[\mu\text{-}(CH_2)_n]$ (n = 3 or 4) [28] where the Cp

TABLE 7. Peak intensities and assignments of common peaks in the mass spectra of 1–6

Ion[a]	*m/e*	Relative peak intensity (%)[b]					
		1	2	3	4	5	6
$[M]^+$			5	2	2	2	3
$[M - CO]^+$		1	6	6	6	6	11
$[M - CO - C_nH_{2n}]^+$	418	3	5	5	3	4	6
$[M - 2CO - C_nH_{2n}]^+$	390	6	19	24	23	16	24
$[M - 3CO - C_nH_{2n}]^+$	362	3	6	5	5	4	6
$[M - 4CO - C_nH_{2n}]^+$	334	9	16	7	9	6	25
$[CpRu(CO)_3]^+$	251	22	52	21	23	20	21
$[CpRu(CO)_2]^+$	223	77	98	64	63	61	79
$[CpRu(CO)]^+$	195	52	63	55	55	56	70
$[Cp_2Ru]^+$	232	45	18	16	13	14	15
$[CpRu]^+$	167	100	100	100	100	100	100
$[CpRu(CO)_3(C_nH_{2n})]^+$		29	80	37	35	23	25
$[C_3H_3Ru]^+$	141	14	14	13	15	15	14
$[Ru]^+$	102	3	3	4	3	3	5
$[C_nH_{2n}]^+$	2		2	2	2	10	

[a]M is the molecular ion $Cp_2Ru_2(CO)_4(C_nH_{2n})$. [b]Percentage of the base peak *m/e* 167 in the low resolution mass spectra.

TABLE 8. Fractional atomic coordinates ($\times 10^4$) and thermal parameters ($Å^2 \times 10^3$) with e.s.d.s in parentheses for compound $[CpRu(CO)_2]_2[\mu\text{-}(CH_2)_5]$

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
Ru(1)	−452(1)	9244(1)	2824(0)	38(0)
Ru(2)	5741(1)	6001(1)	−2872(0)	39(0)
C(1)	1052(11)	9543(8)	1510(7)	53(3)
C(2)	1863(10)	8325(8)	856(7)	52(3)
C(3)	2862(10)	8561(8)	−97(7)	52(3)
C(4)	3612(10)	7318(7)	−835(6)	49(3)
C(5)	4693(10)	7638(7)	−1680(7)	49(3)
C(11)	−2370(12)	7968(11)	1435(9)	75(4)
C(12)	−1536(12)	7170(9)	2017(10)	75(5)
C(13)	−1941(13)	7556(10)	3154(10)	78(5)
C(14)	−3022(12)	8581(11)	3310(9)	73(4)
C(15)	−3317(11)	8857(10)	2248(11)	83(5)
C(111)	1659(10)	9167(7)	3643(7)	47(3)
O(111)	2952(8)	9111(6)	4131(6)	71(3)
C(112)	−391(10)	11060(8)	3465(8)	55(3)
O(112)	−394(10)	12148(6)	3872(7)	95(4)
C(21)	8382(14)	5812(13)	−2038(17)	122(9)
C(22)	7175(14)	5357(11)	−1436(8)	75(4)
C(23)	6413(15)	4270(12)	−2227(15)	97(6)
C(24)	7072(25)	4090(13)	−3244(14)	125(8)
C(25)	8232(19)	4961(22)	−3148(13)	125(8)
C(211)	3495(10)	5500(7)	−3561(7)	48(3)
O(211)	2146(7)	5168(6)	−3980(6)	73(3)
C(212)	5913(11)	7145(8)	−3777(7)	57(3)
O(212)	6002(10)	7832(7)	−4301(6)	92(3)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Anisotropic thermal parameters[a]						
Ru(1)	35(0)	40(0)	39(0)	11(0)	9(0)	2(0)
Ru(2)	36(0)	38(0)	43(0)	11(0)	10(0)	3(0)
C(1)	61(5)	61(5)	50(5)	28(4	27(4)	20(4)
C(2)	53(5)	55(5)	52(5)	18(4)	22(4)	8(4)
C(3)	56(5)	58(5)	48(5)	21(4)	22(4)	20(4)
C(4)	50(4)	51(4)	48(5)	15(4)	20(4)	6(4)
C(5)	60(5)	39(4)	51(5)	12(3)	24(4)	8(3)
C(11)	60(6)	93(8)	61(6)	7(5)	−4(5)	−26(5)
C(12)	58(6)	46(5)	105(9)	0(5)	7(6)	−10(4)
C(13)	68(6)	79(7)	99(8)	52(6)	−10(6)	−36(6)
C(14)	50(5)	93(7)	67(6)	6(5)	21(5)	−26(5)
C(15)	34(5)	66(6)	137(11)	21(7)	−18(5)	−6(4)
C(111)	45(4)	43(4)	51(5)	12(4)	5(4)	0(3)
O(111)	50(4)	73(4)	81(5)	14(3)	−10(3)	7(3)
C(112)	44(4)	51(5)	72(6)	16(4)	16(4)	5(4)
O(112)	98(6)	41(4)	138(7)	9(4)	24(5)	10(4)
C(21)	49(6)	94(9)	229(18)	83(11)	−62(9)	−18(6)
C(22)	80(7)	90(7)	56(6)	25(5)	0(5)	35(6)
C(23)	75(7)	68(7)	162(13)	71(9)	−31(8)	0(6)
C(24)	142(14)	78(9)	110(12)	−21(8)	−56(11)	70(9)
C(25)	77(9)	225(21)	84(10)	50(12)	31(8)	91(11)
C(211)	46(4)	44(4)	60(5)	21(4)	8(4)	4(3)
O(211)	43(3)	77(4)	96(5)	27(4)	−6(3)	−8(3)
C(212)	58(5)	59(5)	56(5)	16(4)	17(4)	−2(4)
O(212)	114(6)	95(5)	89(5)	60(5)	20(4)	−11(4)

[a] Anisotropic atoms have thermal parameters ($Å^2 \times 10^3$) of the form: $\exp(-2\pi^2(U_{11}h^2(a^*)^2 + \ldots + 2U_{12}hk(a^*)(b^*) + \ldots)$.

TABLE 9. Bond lengths (Å) with e.s.d.s in parentheses for compound $[\mathrm{CpRu(CO)_2}]_2[\mu\text{-}(\mathrm{CH_2})_5]$

Ru(1)–C(1)	2.180(9)	C(2)–C(3)	1.546(13)
Ru(1)–C(11)	2.260(9)	C(3)–C(4)	1.538(10)
Ru(1)–C(12)	2.263(9)	C(4)–C(5)	1.509(12)
Ru(1)–C(13)	2.283(12)	C(11)–C(12)	1.395(17)
Ru(1)–C(14)	2.301(11)	C(11)–C(15)	1.439(14)
Ru(1)–C(15)	2.269(9)	C(12)–C(13)	1.411(17)
Ru(1)–C(111)	1.861(8)	C(13)–C(14)	1.373(15)
Ru(1)–C(112)	1.871(8)	C(14)–C(15)	1.419(19)
Ru(2)–C(5)	2.164(7)	C(111)–O(111)	1.133(10)
Ru(2)–C(21)	2.247(13)	C(112)–O(112)	1.126(10)
Ru(2)–C(22)	2.279(11)	C(21)–C(22)	1.414(21)
Ru(2)–C(23)	2.264(16)	C(21)–C(25)	1.400(23)
Ru(2)–C(24)	2.255(15)	C(22)–C(23)	1.365(15)
Ru(2)–C(25)	2.258(17)	C(23)–C(24)	1.364(26)
Ru(2)–C(211)	1.868(7)	C(24)–C(25)	1.259(26)
Ru(2)–C(212)	1.889(10)	C(211)–O(211)	1.130(9)
C(1)–C(2)	1.503(11)	C(212)–O(212)	1.113(13)
Ru(1)–X^a	1.935(8)		
Ru(2)–Y^a	1.942(8)		

^{a}X and Y represent the centroids of the Cp rings C(11)–C(15) and C(21)–C(25) respectively.

TABLE 10. Bond angles (°) with e.s.d.s in parentheses for compound $[\mathrm{CpRu(CO)_2}]_2[\mu\text{-}(\mathrm{CH_2})_5]$

C(111)–Ru(1)–C(112)	90.2(4)
C(15)–Ru(1)–C(112)	99.9(4)
C(15)–Ru(1)–C(111)	157.9(4)
C(14)–Ru(1)–C(112)	102.8(4)
C(14)–Ru(1)–C(111)	122.4(4)
C(14)–Ru(1)–C(15)	36.2(3)
C(13)–Ru(1)–C(112)	133.2(4)
C(13)–Ru(1)–C(111)	99.8(4)
C(13)–Ru(1)–C(15)	59.1(4)
C(13)–Ru(1)–C(14)	34.9(4)
C(12)–Ru(1)–C(112)	159.7(4)
C(12)–Ru(1)–C(111)	107.8(4)
C(12)–Ru(1)–C(15)	59.9(4)
C(12)–Ru(1)–C(14)	59.8(4)
C(12)–Ru(1)–C(13)	36.2(4)
C(11)–Ru(1)–C(112)	128.5(4)
C(11)–Ru(1)–C(111)	140.9(4)
C(11)–Ru(1)–C(15)	37.0(4)
C(11)–Ru(1)–C(14)	61.2(4)
C(11)–Ru(1)–C(13)	60.2(4)
C(11)–Ru(1)–C(12)	35.9(4)
C(1)–Ru(1)–C(112)	88.4(4)
C(1)–Ru(1)–C(111)	86.1(3)
C(1)–Ru(1)–C(15)	113.6(4)
C(1)–Ru(1)–C(14)	148.7(3)
C(1)–Ru(1)–C(13)	137.4(4)
C(1)–Ru(1)–C(12)	101.8(4)
C(1)–Ru(1)–C(11)	88.9(4)
C(211)–Ru(2)–C(212)	89.3(4)
C(25)–Ru(2)–C(212)	100.6(5)
C(25)–Ru(2)–C(211)	130.7(5)
C(24)–Ru(2)–C(212)	121.8(5)
C(24)–Ru(2)–C(211)	102.9(5)
C(24)–Ru(2)–C(25)	32.4(6)
C(23)–Ru(2)–C(212)	156.2(4)
C(23)–Ru(2)–C(211)	100.9(4)
C(23)–Ru(2)–C(25)	56.6(6)
C(23)–Ru(2)–C(24)	35.1(5)
C(22)–Ru(2)–C(212)	142.9(4)
C(22)–Ru(2)–C(211)	127.6(4)
C(22)–Ru(2)–C(25)	59.9(5)
C(22)–Ru(2)–C(24)	59.3(5)
C(22)–Ru(2)–C(23)	35.0(5)
C(21)–Ru(2)–C(212)	108.9(5)
C(21)–Ru(2)–C(211)	158.2(5)
C(21)–Ru(2)–C(25)	36.2(6)
C(21)–Ru(2)–C(24)	57.6(6)
C(21)–Ru(2)–C(23)	57.8(5)
C(21)–Ru(2)–C(22)	36.4(5)
C(5)–Ru(2)–C(212)	85.2(4)
C(5)–Ru(2)–C(211)	88.2(3)
C(5)–Ru(2)–C(25)	140.4(4)
C(5)–Ru(2)–C(24)	150.4(5)
C(5)–Ru(2)–C(23)	116.3(5)
C(5)–Ru(2)–C(22)	92.2(3)
C(5)–Ru(2)–C(21)	104.7(5)
Ru(1)–C(1)–C(2)	113.5(6)
C(1)–C(2)–C(3)	112.1(7)
C(2)–C(3)–C(4)	113.7(7)
C(3)–C(4)–C(5)	110.9(6)
Ru(2)–C(5)–C(4)	116.5(5)
Ru(1)–C(11)–C(15)	71.8(6)
Ru(1)–C(11)–C(12)	72.1(6)
C(12)–C(11)–C(15)	106.0(10)
Ru(1)–C(12)–C(11)	71.9(7)
C(11)–C(12)–C(13)	108.7(9)
Ru(1)–C(12)–C(13)	72.7(6)
Ru(1)–C(13)–C(12)	71.1(6)
C(12)–C(13)–C(14)	109.7(10)
Ru(1)–C(13)–C(14)	73.3(7)
Ru(1)–C(14)–C(13)	71.8(6)
C(13)–C(14)–C(15)	107.0(10)
Ru(1)–C(14)–C(15)	70.7(5)
C(11)–C(15)–C(14)	108.6(9)
Ru(1)–C(15)–C(14)	73.2(5)
Ru(1)–C(15)–C(11)	71.1(5)
Ru(1)–C(111)–O(111)	179.2(8)
Ru(1)–C(112)–O(112)	177.8(8)
Ru(2)–C(21)–C(25)	72.3(8)
Ru(2)–C(21)–C(22)	73.0(7)
C(22)–C(21)–C(25)	107.3(12)
Ru(2)–C(22)–C(21)	70.6(8)
C(21)–C(22)–C(23)	103.3(12)
Ru(2)–C(22)–C(23)	71.9(8)
Ru(2)–C(23)–C(22)	73.1(8)
C(22)–C(23)–C(24)	110.5(13)
Ru(2)–C(23)–C(24)	72.1(9)
Ru(2)–C(24)–C(23)	72.8(9)
C(23)–C(24)–C(25)	109.6(15)
Ru(2)–C(24)–C(25)	73.9(13)
C(21)–C(25)–C(24)	109.3(14)
Ru(2)–C(25)–C(24)	73.7(12)
Ru(2)–C(25)–C(21)	71.5(8)

(continued)

TABLE 10. *(continued)*

Ru(2)–C(211)–O(211)	178.4(7)
Ru(2)–C(212)–O(212)	179.0(8)
C(1)–Ru(1)–X	121.0
C(111)–Ru(1)–X	129.6
C(112)–Ru(1)–X	128.3
C(5)–Ru(2)–Y	123.5
C(211)–Ru(2)–Y	127.3
C(212)–Ru(2)–Y	129.8

[a] X and Y represent the centroids of the Cp rings C(11)–C(15) and C(21)–C(25) respectively.

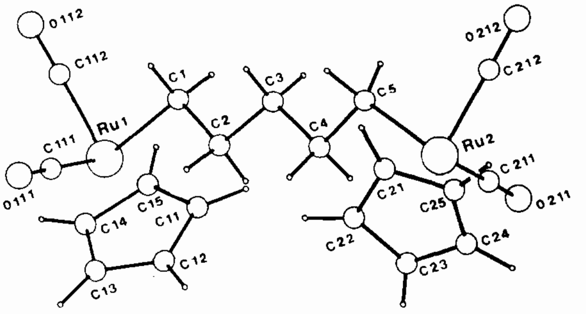


Fig. 1. The molecular structure of compound 1 showing the atomic numbering scheme.

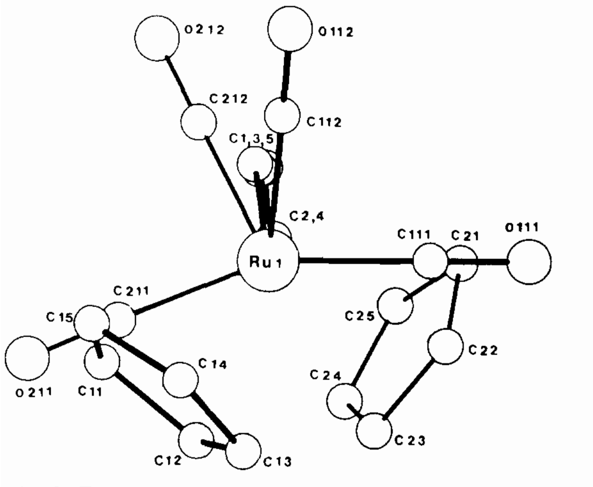
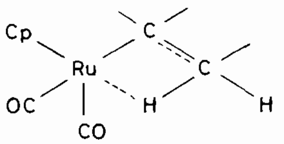


Fig. 2. The molecular structure of 1 viewed down the Ru_1, Ru_2 direction.

rings lie on opposite sides of the metal–metal axis. The position of the Cp rings, whether *cis* or *trans* to one another, may be a function of the length of the polymethylene chain between the two metals. In compound 1 the two metals are further apart than in the other structures and this may allow the Cp rings to adopt the *cis* orientation. It may be that another conformation of 1 exists with *trans* disposition of the Cp rings. The structure of 1, in fact is the first to be reported for an alkanediyl complex with more than four CH_2 groups between the two metals, for complexes with or without a metal–metal bond [3, 4]. As expected, both Cp rings are planar with the dihedral angle between their least-squares planes 79.5(4)°. The average Ru–C (alkyl) bond distance of 2.172(9) Å is close to that found in the μ-methylene complex $[CpRu(CO)_2]_2[\mu\text{-}(CH_2)]$ of 2.18 Å [22]. The Ru_1–Ru_2 distance of 8.81 Å confirms that the two ruthenium atoms in 1 are not bonded; this compares with the non-bonded Ru–Ru distance of 3.8 Å in $[CpRu(CO)_2]_2[\mu\text{-}(CH_2)]$ [22]. The large Ru–C–Ru bond angle of 123° in this μ-methylene complex suggests a large amount of steric crowding around the μ-CH_2 group which may explain the greater reactivity of this complex with, for example, CO which inserts readily into Ru–C (alkyl) [22] when compared to either $[CpRu(CO)_2R]$ or $[CpRu(CO)_2]_2[\mu\text{-}(CH_2)_n]$.

The CO–Ru–CH_2 and CO–Ru–CO bond angles are close to 90° (see Table 10). In addition, the bond angle between the centroid of the Cp ligand, Ru and any other ligand is in the range 121.0–129.8°. This is consistent with an octahedral arrangement of ligands around the metal where the Cp ligand occupies three coordination sites. Similar features have been reported previously in complexes of the type [CpFe(CO)(L)R] demonstrating that such complexes are better viewed as octahedral rather than tetrahedral [29]. The slightly larger Ru–C_1–C_2, Ru_2–C_5–C_4 bond angles of 113.5(15) and 116.5(5)° compared to the C_1–C_2–C_3, C_3–C_4–C_5 bond angles of 112.1(7) and 110.9(6)°, respectively, may be a result of the interactions of the protons on C_2 and C_4 with the Cp rings which lie in close proximity to the β-CH_2 groups.

An interesting feature of the structure of 1 is the shorter C_1–C_2, C_4–C_5 bond distances of 1.50(1), 1.51(1) Å respectively in comparison to the C_2–C_3, C_3–C_4 distance of 1.55(1), 1.54(1) Å respectively in the alkyl chain. Similar shortening was not observed in the di-iron compounds $[CpFe(CO)_2]_2[\mu\text{-}(CH_2)_n]$ (n = 3 or 4) [28]. For compound 1, the data may suggest that there is some C=C double bond character in C_1–C_2 and C_4–C_5, this could be accompanied by the β-hydrogens of the alkanediyl chain interacting with the Ru atoms as shown.



No evidence, however, was obtained for this agostic type of interaction in the ^{13}C or ^{1}H NMR spectra of compound 1, although the Ru–C_α (alkyl) bond distance of 2.17 Å in 1 is very similar to that found in $[CpRu(CO)_2]_2[\mu\text{-}(CH_2)]$, which is long for Ru–C single bond distance [22].

Conclusions

The new diruthenium alkanediyl complexes reported in this paper complete the series of [CpRu-$(CO)_2]_2[\mu$-$(CH_2)_n]$ compounds for all values of n from 1–10. The new compounds have been fully characterized by spectroscopic methods and the structure of the compound where $n = 5$ has been determined by X-ray crystallography. In a subsequent paper, we will describe the reactivity of these diruthenium alkanediyl compounds and compare the reactivities with both the di-iron alkanediyl analogues and with mononuclear ruthenium compounds of the type $[CpRu(CO)_2R]$.

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