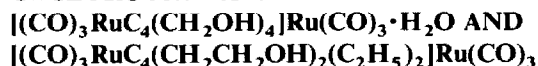


SYNTHESES AND STRUCTURAL STUDIES ON TWO CYCLORUTHENAPENTADIENYL COMPLEXES:



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Summary

Syntheses and single-crystal X-ray diffraction studies have been completed on two cycloruthenapentadienyl $(\text{CO})_6\text{Ru}_2\text{L}_2$ derivatives, with $\text{L} = \text{CH}_2\text{OHC} = \text{CCH}_2\text{OH}$ and $\text{C}_2\text{H}_5\text{C} = \text{CCH}_2\text{CH}_2\text{OH}$ respectively. Crystal data are as follows: for $[(\text{CO})_3\text{RuC}_4(\text{CH}_2\text{OH})_4]\text{Ru}(\text{CO})_3 \cdot \text{H}_2\text{O}$, $P2_1/c$, a 13.72(1), b 9.501(4), c 14.86(1) Å, β 101.10(6)°, $R_w = 0.052$ for 1911 reflections; for $[(\text{CO})_3\text{RuC}_4(\text{CH}_2\text{CH}_2\text{OH})_2(\text{C}_2\text{H}_5)_2]\text{Ru}(\text{CO})_3$, $P2_1/c$, a 9.191(3), b 16.732(4), c 14.903(3) Å, β 113.61(4)°, $R_w = 0.042$ for 2865 reflections. Both compounds are built up from binuclear units, each unit being regarded as a $\text{Ru}(\text{CO})_3$ fragment π -bonded to a cycloruthenapentadienyl ring. The molecular parameters are compared with those of known cyclometallapentadienyl complexes of transition metals. The presence of a semi-bridging CO group is discussed.

Introduction

The inhibition of corrosion of a metal surface by organic substances can be accounted for the building of a barrier between the metal surface and the corrosive solution. This barrier contains inhibitor molecules as revealed by radioactive measurements; those molecules are assumed to be attached to the metal surface by coordinative bonds, since most organic inhibitors are potential ligands.

The direct methods of surface structural determinations are at present unable to define fully and unambiguously this superficial complex. The study of the stereochemical action of organic inhibitors can be approached through X-ray diffraction, provided a crystal of a compound simulating a protected surface can be prepared. This might lead to the knowledge of the chemical bonds between the metal and the inhibitor, and of the stereochemistry of the whole system. Starting from metal carbonyl clusters, which can be considered to a first approximation as models for a

metallic surface since they contain metal–metal bonds, with metal in a low oxidation state, we previously reported the reaction of mercaptobenzothiazole and mercaptoethanoic acid on dodecacarbonyltriruthenium and the structure of two compounds [1]. We describe here the reaction of some acetylenic alcohols on the same cluster, acetylenic alcohols having been widely used for more than thirty years as corrosion inhibitors. The 2-butyne-1,4-diol and the 3-hexyn-1-ol react with $\text{Ru}_3(\text{CO})_{12}$ to give dimeric species of formula $\text{Ru}_2(\text{CO})_6\text{L}_2$ containing a cycloruthenapentadienyl ring. Several transition metal complexes containing such cyclometallapentadienyl ligand moieties are known. Typical compounds are binuclear complexes of iron [2,7], rhodium [8], osmium [9], tungsten [10], iridium [11] chromium [12] and the heterobinuclear tungsten-cobalt complex [13]. However although the occurrence of such ruthenium dimeric species was mentioned by Aime and Deeming [14], no crystallographic studies have been published for ruthenium derivatives.

Experimental section

Syntheses

Reaction of $\text{CH}_2\text{OHC}=\text{CCH}_2\text{OH}$ on $\text{Ru}_3(\text{CO})_{12}$. 2-Butyn-1,4-diol (0.4 g) in 15 ml ethanol is added to a solution of $\text{Ru}_3(\text{CO})_{12}$ (0.2 g) in 75 ml toluene at 60°C under dry nitrogen. After 4 h the solution is cooled to 20°C , then 15 ml of water is added, giving two phases. Pale yellow crystals of $\{(\text{CO})_3\text{RuC}_4(\text{CH}_2\text{OH})_4\}\text{Ru}(\text{CO})_3 \cdot \text{H}_2\text{O}$ (I), suitable for X-ray analysis, are obtained by keeping the toluene phase at -15°C for two weeks. The yield is about 1% based on the ruthenium carbonyl. The aqueous phase contains water, ethanol and excess butyne.

Reaction of $\text{C}_2\text{H}_5\text{C}=\text{CCH}_2\text{CH}_2\text{OH}$ on $\text{Ru}_3(\text{CO})_{12}$. A solution of $\text{Ru}_3(\text{CO})_{12}$ (0.5 g) and the 3-hexyn-1-ol (0.4 ml) in a mixture of 75 ml hexane and 15 ml ethanol was heated under reflux under N_2 for 24 h. After cooling, chromatography of the solution (TLC, SiO_2 ; eluent: light petroleum/acetalddehyde) gave $\{(\text{CO})_3\text{RuC}_4(\text{C}_2\text{H}_4\text{OH})_2(\text{C}_2\text{H}_5)_2\}\text{Ru}(\text{CO})_3$ (II) (ca. 0.090 g, 18%) as brown air stable crystals; two others products were separated as brown yellow powders but not characterized.

Infrared

Infrared spectra (KBr pellets) were recorded on Perkin–Elmer 597 spectrophotometer (Table 1).

X-ray study

After survey photography by the precession technique, a selected crystal of each compound was set up on a laboratory-made automatic three circle diffractometer. In each case, cell dimensions and orientation matrices were obtained by least square analysis from the setting angles of 9 reflections chosen from various regions of reciprocal space ($22^\circ < 2\theta < 34^\circ$). The scintillation counter was fitted with a pulse-height analyser tuned to accept 90% of the Mo-K_α peak. A take off angle of 3° was used.

Crystal data and data collection parameters are listed in Table 2. The intensities of two standard reflections 2 0 0, 0 1 1 for compound I and 0 10 0.5 5 0 for compound II, were measured every 100 reflections; no significant fluctuations were observed. If the counting rate exceeded $7000 \text{ counts sec}^{-1}$, counting loss was taken

TABLE 1
SPECTRAL DATA

Compound	$\nu(\text{CO})$ (cm^{-1})	$\nu(\text{Ru}-\text{C})$ (cm^{-1})	Reference
$\text{Ru}_2(\text{CO})_6 \text{C}_4(\text{CH}_2\text{OH})_4 \cdot \text{H}_2\text{O}$	2090s, 2060vs, 2015vs, 1990sh, 1970sh	560s, 540vs	this work
$\text{Ru}_2(\text{CO})_6 \text{C}_4(\text{CH}_2\text{CH}_2\text{OH})_2(\text{C}_2\text{H}_5)_2$	2080s, 2045vs, 2010vs, 1975vs	560s, 540vs	this work
$\text{Ru}_2(\text{CO})_6 \text{C}_4(\text{CH}_2\text{OH})_4$	2085m, 2054vs, 2009vs, 1994sh	-	[15]
$\text{Ru}_2(\text{CO})_6 \text{C}_4\text{H}_2 \text{C}(\text{CH}_3)_2\text{OH}_2$	2086m, 2054vs, 2015vs, 1992sh	-	[14]

into account. The data were corrected for Lorentz and polarisation effects. In view of the low absorption coefficients, no absorption corrections were applied. Each structure factor was assigned a standard deviation $\sigma = (FAI)/2I$ where I was the integrated intensity and ΔI the error. Reflections with $F < 3\sigma$ were considered as unobserved and excluded from calculations.

Computations were performed using standard programs [16] on the CII IRIS 80 computer. Scattering factors were taken from International Tables for X-ray Crys-

TABLE 2
EXPERIMENTAL DATA FOR THE X-RAY DIFFRACTION STUDIES

Compound	$[(\text{CO})_3\text{RuC}_4(\text{CH}_2\text{OH})_4]\cdot$ $\text{Ru}(\text{CO})_3 \cdot \text{H}_2\text{O}$ (I)	$[(\text{CO})_3\text{Ru}(\text{C}_4(\text{C}_2\text{H}_4\text{OH})_2(\text{C}_2\text{H}_5)_2)]\cdot$ $\text{Ru}(\text{CO})_3$ (II)
Cryst. system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a , (Å)	13.72(1)	9.191(3)
b , (Å)	9.501(4)	16.732(4)
c , (Å)	14.86(1)	14.903(3)
β , ($^\circ$)	101.10(6)	113.61(4)
V , (Å ³)	1901(3)	2100(1)
Z	4	4
Mol. wt.	560.1	566.1
ρ (calcd.), (g cm ⁻³)	1.96	1.79
μ (cm ⁻¹)	16.1	13.6
T , ($^\circ\text{C}$)	22	24
Diffractionmeter	Laboratory made automatic three circle diffractometer	
Radiation	Mo- K_α (λ 0.71069 Å)	
Monochromator	graphite monochromator set in front of the counter	
Reflections measd.	$+h, +k, \pm 1$	$+h, +k, \pm 1$
2θ range, ($^\circ$)	3.0–50.0	3.0–50.0
Scan type	coupled $\theta(\text{cryst})-2\theta(\text{counter})$	
Scan speed, deg min ⁻¹	1.5	1.5
Scan range, deg	$1.0 + 0.345 \tan\theta$	$1.10 + 0.345 \tan\theta$
bkgd	stationary-crystal, stationary counter at beginning and end of scan, each for one-fourth of the time taken for the scan	
Reflections coll'd	3348 independent	3700 independent

TABLE 3

FRACTIONAL ATOMIC COORDINATES OF COMPOUNDS I AND II (with e.s.d.'s in parentheses)

Atom	x/a	y/b	z/c
[(CO) ₃ RuC ₄ (CH ₂ OH) ₄]Ru(CO) ₃ ·H ₂ O (I)			
Ru(1)	0.21329(8)	0.3314(1)	0.44624(8)
Ru(2)	0.18924(8)	0.6181(1)	0.44270(8)
C(1)	0.2765(9)	0.476(2)	0.3712(9)
C(2)	0.3448(9)	0.577(1)	0.4209(8)
C(3)	0.3464(9)	0.575(1)	0.517(1)
C(4)	0.2814(9)	0.473(1)	0.5449(8)
C(5)	0.266(1)	0.468(2)	0.2645(9)
C(6)	0.273(1)	0.468(2)	0.6447(9)
C(7)	0.411(1)	0.669(2)	0.376(1)
C(8)	0.415(1)	0.670(1)	0.580(1)
O(5)	0.336(1)	0.378(1)	0.2392(9)
O(6)	0.3544(8)	0.389(1)	0.6948(7)
O(7)	0.3921(8)	0.816(1)	0.3912(8)
O(8)	0.3875(8)	0.814(1)	0.5698(8)
O	-0.5039(7)	0.496(1)	0.1872(6)
C(11)	0.132(1)	0.239(2)	0.339(1)
O(11)	0.085(1)	0.187(1)	0.279(1)
C(12)	0.319(1)	0.199(2)	0.462(1)
O(12)	0.3826(9)	0.121(1)	0.475(1)
C(13)	0.138(1)	0.234(2)	0.530(1)
O(13)	0.0930(9)	0.179(1)	0.5714(9)
C(21)	0.161(1)	0.767(2)	0.352(1)
O(21)	0.148(1)	0.854(2)	0.300(1)
C(22)	0.151(1)	0.739(2)	0.534(1)
O(22)	0.129(1)	0.810(2)	0.587(1)
C(23)	0.063(1)	0.530(2)	0.408(1)
O(23)	-0.0169(8)	0.498(1)	0.3839(8)
[(CO) ₃ RuC ₄ (CH ₂ CH ₂ OH) ₂ (C ₂ H ₅) ₂]Ru(CO) ₃ (II)			
Ru(1)	0.01265(6)	0.16290(3)	0.14662(4)
Ru(2)	0.23017(6)	0.13927(3)	0.06834(4)
C(1)	0.2487(7)	0.1281(4)	0.2230(4)
C(2)	0.3661(8)	0.1839(4)	0.2244(5)
C(3)	0.3042(9)	0.2519(4)	0.1618(5)
C(4)	0.1373(8)	0.2527(4)	0.1086(5)
C(5)	0.2961(8)	0.0566(4)	0.2900(5)
C(6)	0.2844(9)	0.0735(5)	0.3857(5)
O(6)	0.3381(7)	0.0090(4)	0.4536(4)
C(7)	0.055(1)	0.3204(4)	0.0401(5)
C(8)	-0.010(1)	0.3825(5)	0.0887(7)
O(8)	-0.0924(8)	0.4444(4)	0.0198(5)
C(11)	-0.0744(8)	0.0617(5)	0.1708(5)
O(11)	-0.1243(8)	0.0043(4)	0.1846(5)
C(12)	-0.0099(9)	0.2207(4)	0.2479(5)
O(12)	-0.0251(8)	0.2573(4)	0.3081(5)
C(13)	-0.1947(9)	0.1948(5)	0.0495(6)
O(13)	-0.3153(8)	0.2140(5)	-0.0034(6)
C(14)	0.5410(9)	0.1748(5)	0.2926(6)
C(15)	0.641(1)	0.1239(7)	0.2548(8)
C(16)	0.416(1)	0.3162(6)	0.1556(7)
C(17)	0.443(2)	0.3792(7)	0.229(1)

TABLE 3 (continued)

Atom	x/a	y/b	z/c
C(21)	0.331(1)	0.0389(5)	0.0688(6)
O(21)	0.3921(9)	-0.0189(4)	0.0664(5)
C(22)	0.2973(9)	0.1797(5)	-0.0283(5)
O(22)	0.3355(8)	0.2045(5)	-0.0864(5)
C(23)	0.0254(9)	0.1061(4)	-0.0241(6)
O(23)	-0.0832(7)	0.0849(4)	-0.0882(4)

TABLE 4

ANISOTROPIC THERMAL PARAMETERS OF COMPOUNDS I AND II (with e.s.d.'s in parentheses)

They enter the expression for the structure factor in the form: $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
[(CO) ₃ RuC ₄ (CH ₂ OH) ₄]Ru(CO) ₃ ·H ₂ O (I)						
Ru(1)	3.17(5)	2.02(4)	3.51(6)	-0.30(4)	0.11(4)	-0.07(4)
Ru(2)	2.79(4)	2.19(5)	2.91(5)	0.15(3)	0.14(3)	0.13(4)
C(1)	3.0(5)	3.4(5)	4.3(6)	-0.1(5)	0.9(5)	0.5(6)
C(2)	3.7(6)	3.2(5)	2.2(5)	0.2(4)	0.0(4)	0.5(4)
C(3)	3.2(5)	1.6(4)	4.4(7)	0.5(4)	-0.3(5)	0.2(4)
C(4)	2.0(6)	2.5(4)	2.7(5)	-0.0(5)	-0.4(4)	-0.4(5)
C(5)	5.2(8)	4.9(7)	4.0(6)	-0.8(7)	1.2(6)	0.4(7)
C(6)	4.9(8)	4.3(7)	3.7(6)	0.4(6)	-0.4(5)	0.2(6)
C(7)	4.9(7)	3.7(6)	7.1(10)	-1.1(6)	2.1(7)	-0.7(7)
C(8)	4.7(6)	2.1(5)	5.2(7)	-0.9(5)	-0.2(5)	-0.8(5)
O(5)	9.7(8)	4.3(5)	7.1(7)	-0.1(6)	5.0(6)	-1.5(5)
O(6)	6.6(5)	3.7(4)	4.4(5)	0.2(5)	-0.6(4)	1.2(4)
O(7)	5.9(5)	3.4(4)	6.6(6)	-0.1(4)	1.4(5)	0.2(4)
O(8)	6.2(5)	2.9(4)	5.5(5)	-0.3(4)	0.2(4)	-0.4(4)
O	4.7(4)	2.6(5)	5.3(4)	0.5(3)	0.2(4)	0.3(4)
C(11)	5.5(8)	3.5(7)	5.7(10)	-1.2(6)	0.6(7)	-1.7(7)
O(11)	10.6(9)	5.2(6)	6.1(7)	-1.2(7)	-1.6(7)	-1.0(6)
C(12)	5.5(8)	2.9(7)	4.4(7)	-0.4(6)	0.5(6)	-0.2(5)
O(12)	6.7(6)	3.9(5)	9.3(8)	1.9(5)	-0.2(6)	-0.0(6)
C(13)	3.9(7)	2.1(6)	6.6(10)	-0.9(5)	0.0(7)	-0.1(6)
O(13)	6.2(6)	5.9(6)	6.1(7)	-2.4(5)	1.5(5)	1.8(6)
C(21)	4.0(7)	4.1(7)	7.1(10)	1.0(6)	1.3(7)	2.4(7)
O(21)	9.3(9)	5.9(8)	9.7(10)	1.8(7)	1.7(7)	4.1(7)
C(22)	4.2(7)	4.0(8)	5.9(10)	1.5(6)	-0.2(7)	-0.4(7)
O(22)	9.8(9)	6.0(8)	6.4(8)	1.9(7)	1.0(7)	-2.6(7)
C(23)	4.2(7)	3.7(6)	4.4(7)	-0.4(6)	0.0(6)	0.6(6)
O(23)	3.7(5)	5.3(7)	7.1(6)	0.2(4)	-0.5(4)	0.2(5)
[(CO) ₃ RuC ₄ (CH ₂ CH ₂ OH) ₂ (C ₂ H ₅) ₂]Ru(CO) ₃ (II)						
Ru(1)	3.08(2)	2.99(2)	2.55(2)	0.14(2)	1.18(2)	0.08(2)
Ru(2)	3.60(2)	3.08(2)	2.55(2)	0.20(2)	1.54(2)	-0.01(2)
C(1)	3.2(2)	3.3(3)	2.4(2)	0.0(2)	1.3(2)	-0.2(2)
C(2)	3.5(3)	3.8(3)	3.0(3)	-0.2(2)	1.4(2)	-0.1(2)

TABLE 4 (continued)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(3)	5.6(4)	3.0(3)	3.3(3)	-0.5(2)	2.2(3)	-0.1(2)
C(4)	4.5(3)	2.8(3)	2.9(2)	0.3(2)	1.0(2)	0.0(2)
C(5)	3.7(3)	3.0(3)	3.4(3)	0.3(2)	1.3(2)	0.1(2)
C(6)	4.7(3)	4.5(3)	3.3(3)	0.3(3)	1.6(3)	0.6(3)
O(6)	5.5(3)	6.7(3)	4.6(3)	0.5(2)	1.6(2)	2.6(2)
C(7)	6.0(4)	3.4(3)	3.0(3)	0.9(3)	2.7(3)	0.7(2)
C(8)	7.3(5)	4.3(4)	6.0(4)	1.9(3)	3.8(4)	0.8(3)
O(8)	7.8(4)	4.4(3)	8.0(4)	2.5(2)	3.9(3)	1.8(3)
C(11)	3.8(3)	4.2(3)	3.6(3)	-0.4(3)	1.5(2)	-0.4(2)
O(11)	6.8(3)	4.9(3)	7.0(4)	-1.2(2)	4.4(3)	0.1(3)
C(12)	4.1(3)	4.4(3)	3.7(3)	-0.3(2)	1.8(2)	-0.2(3)
O(12)	7.8(4)	7.3(3)	5.2(3)	-0.1(3)	3.7(3)	-1.5(3)
C(13)	3.8(3)	5.5(4)	3.9(3)	0.7(3)	1.1(3)	0.6(3)
O(13)	4.7(3)	10.4(5)	6.0(4)	1.7(3)	-0.2(3)	2.5(4)
C(14)	3.7(3)	4.8(4)	4.7(3)	-0.3(3)	1.2(3)	0.2(3)
C(15)	3.5(3)	8.5(6)	7.1(5)	-0.4(4)	2.4(3)	-0.6(4)
C(16)	5.2(4)	5.0(5)	6.7(5)	-1.2(3)	2.6(4)	1.6(4)
C(17)	11.1(9)	6.4(6)	9.6(8)	-4.6(6)	4.3(7)	-2.2(5)
C(21)	5.9(4)	3.9(3)	3.9(3)	1.4(3)	2.1(3)	0.1(3)
O(21)	9.1(4)	4.7(3)	6.7(3)	2.4(3)	3.4(3)	0.1(2)
C(22)	4.7(3)	4.8(3)	2.6(3)	-0.1(3)	1.5(2)	0.2(2)
O(22)	7.0(3)	10.1(5)	5.4(3)	0.0(3)	3.9(3)	1.0(3)
C(23)	4.6(4)	3.6(3)	4.6(4)	-0.4(3)	2.4(3)	-0.5(3)
O(23)	5.6(3)	6.9(3)	4.6(3)	-1.7(2)	1.7(2)	-1.9(2)

TABLE 5

INTERATOMIC DISTANCES OF COMPOUNDS I AND II (Å) (with e.s.d.'s in parentheses)

	I	II		I	II
Ru(1)-C(1)	2.06(3)	2.089(6)	Ru(2)-Ru(1)	2.743(3)	2.717(1)
Ru(1)-C(2)	2.08(3)	2.101(6)	Ru(2)-C(1)	2.21(3)	2.250(6)
Ru(1)-C(11)	1.97(3)	1.967(8)	Ru(2)-C(2)	2.25(2)	2.281(6)
Ru(1)-C(12)	1.90(3)	1.874(7)	Ru(2)-C(3)	2.27(3)	2.279(7)
Ru(1)-C(13)	2.00(3)	1.950(7)	Ru(2)-C(4)	2.25(3)	2.259(6)
Ru(1)···C(23)	2.76(2)	2.762(7)	Ru(2)-C(21)	1.93(3)	1.918(7)
C(11)-O(11)	1.11(2)	1.118(9)	Ru(2)-C(22)	1.92(3)	1.904(7)
C(12)-O(12)	1.13(2)	1.140(9)	Ru(2)-C(23)	1.90(2)	1.916(8)
C(13)-O(13)	1.08(2)	1.119(9)	C(21)-O(21)	1.13(2)	1.125(9)
C(1)-C(2)	1.44(3)	1.420(9)	C(22)-O(22)	1.12(2)	1.135(9)
C(2)-C(3)	1.42(2)	1.44(1)	C(23)-O(23)	1.13(2)	1.128(9)
C(3)-C(4)	1.43(2)	1.42(1)			
<i>Compound I</i>			<i>Compound II</i>		
C(1)-C(5)	1.57(2)		C(1)-C(5)	1.506(9)	
C(5)-O(5)	1.38(2)		C(5)-C(6)	1.50(1)	
C(2)-C(6)	1.50(3)		C(6)-O(6)	1.426(9)	
C(6)-O(6)	1.49(2)		C(4)-C(7)	1.508(9)	
C(3)-C(7)	1.50(3)		C(7)-C(8)	1.52(1)	
C(7)-O(7)	1.41(2)		C(8)-O(8)	1.44(1)	
C(4)-C(8)	1.51(2)		C(2)-C(14)	1.53(1)	
C(8)-O(8)	1.44(2)		C(14)-C(15)	1.52(1)	
			C(3)-C(16)	1.51(1)	
			C(16)-C(17)	1.47(2)	

TABLE 6

BOND ANGLES (°) OF COMPOUNDS I AND II (with e.s.d.'s in parentheses)

	I	II		I	II
C(1)–Ru(1)–C(4)	76.8(6)	77.7(2)	C(21)–Ru(2)–C(22)	90.3(8)	90.6(3)
C(1)–Ru(1)–C(11)	95.3(8)	94.0(3)	C(21)–Ru(2)–C(23)	95(1)	94.9(3)
C(1)–Ru(1)–C(12)	97(1)	97.5(3)	C(22)–Ru(2)–C(23)	95(1)	94.7(3)
C(1)–Ru(1)–C(13)	165.9(7)	166.8(3)	C(21)–Ru(2)–C(1)	99.7(8)	94.9(3)
C(1)–Ru(1)–C(23)	79.1(9)	89.3(2)	C(21)–Ru(2)–C(2)	96(1)	102.5(3)
C(4)–Ru(1)–C(12)	96(1)	95.5(3)	C(21)–Ru(2)–C(3)	121(1)	134.1(3)
C(4)–Ru(1)–C(13)	94.3(6)	94.6(3)	C(21)–Ru(2)–C(4)	158.0(6)	165.7(3)
C(4)–Ru(1)–C(11)	165.9(7)	166.3(3)	C(21)–Ru(2)–Ru(1)	138.1(9)	124.4(2)
C(4)–Ru(1)–C(23)	85(1)	76.6(2)	C(22)–Ru(2)–C(1)	161.9(7)	152.9(3)
C(11)–Ru(1)–C(12)	96(1)	96.4(3)	C(22)–Ru(2)–C(2)	127(1)	116.4(3)
C(11)–Ru(1)–C(13)	91.0(7)	91.3(3)	C(22)–Ru(2)–C(3)	97(1)	93.5(3)
C(11)–Ru(1)–C(23)	82(1)	92.5(3)	C(22)–Ru(2)–C(4)	94.9(7)	100.0(3)
C(12)–Ru(1)–C(13)	95(1)	93.8(3)	C(23)–Ru(2)–C(1)	99(1)	111.2(3)
C(12)–Ru(1)–C(23)	175.0(6)	168.3(3)	C(23)–Ru(2)–C(2)	136.2(8)	143.8(3)
C(13)–Ru(1)–C(23)	89(1)	78.4(3)	C(23)–Ru(2)–C(3)	141.4(7)	130.2(3)
			C(23)–Ru(2)–C(4)	106(1)	93.9(3)
			C(23)–Ru(2)–Ru(1)	70.4(7)	70.8(2)
			C(22)–Ru(2)–Ru(1)	129(1)	142.2(9)
Ru(1)–C(11)–O(11)	180(2)	180(2)	Ru(2)–C(21)–O(21)	177(2)	177.5(7)
Ru(1)–C(12)–O(12)	177(2)	178.4(7)	Ru(2)–C(22)–O(22)	179(2)	179.1(7)
Ru(1)–C(13)–O(13)	176(2)	177.3(8)	Ru(2)–C(23)–O(23)	169(1)	169.0(6)
<i>Compound I</i>			<i>Compound II</i>		
Ru(1)–C(1)–C(2)	117.8(9)		Ru(1)–C(1)–C(2)	116.2(4)	
Ru(1)–C(1)–C(5)	123(1)		Ru(1)–C(1)–C(5)	123.0(4)	
C(2)–C(1)–C(5)	118(2)		C(2)–C(1)–C(5)	119.7(5)	
C(1)–C(2)–C(3)	113(2)		C(1)–C(2)–C(3)	114.2(6)	
C(1)–C(2)–C(6)	128(1)		C(1)–C(2)–C(14)	122.4(6)	
C(3)–C(2)–C(6)	124(2)		C(3)–C(2)–C(14)	123.2(6)	
C(2)–C(3)–C(4)	114(2)		C(2)–C(3)–C(4)	115.4(6)	
C(2)–C(3)–C(7)	120(2)		C(2)–C(3)–C(16)	120.0(7)	
C(4)–C(3)–C(7)	126(1)		C(4)–C(3)–C(16)	124.5(7)	
C(3)–C(4)–Ru(1)	117(1)		C(3)–C(4)–Ru(1)	115.3(4)	
C(3)–C(4)–C(8)	118(2)		C(3)–C(4)–C(7)	121.4(6)	
Ru(1)–C(4)–C(8)	124(1)		Ru(1)–C(4)–C(7)	122.7(5)	
C(1)–C(5)–O(5)	112(2)		C(1)–C(5)–C(6)	111.7(5)	
C(2)–C(6)–O(6)	110(1)		C(5)–C(6)–O(6)	113.4(6)	
C(3)–C(7)–O(7)	113(1)		C(4)–C(7)–C(8)	112.1(6)	
C(4)–C(8)–O(8)	109(2)		C(7)–C(8)–O(8)	110.2(7)	
			C(2)–C(14)–C(15)	116.3(7)	
			C(3)–C(16)–C(17)	112.4(8)	

tallography [17] including $\Delta f'$ and $\Delta f''$ for ruthenium atoms. The agreement factors were defined in the usual way as $R = \Sigma(|F_0 - F_c|) / \Sigma|F_0|$ and $R_w = \{\Sigma(w|F_0 - F_c|)^2 / \Sigma(w|F_0|^2)\}^{1/2}$.

In all least squares refinements the quantity minimized was $\Sigma(w|F_0 - F_c|)^2$ and the full matrix was inverted. A weighting scheme based on counting statistics, $w = \Delta I / 2F$ was used in least squares refinement.

Both structures were solved by heavy-atom techniques. Ru atoms were unambigu-

ously revealed by Patterson functions. The subsequent F_0 syntheses showed the position of all non-hydrogen atoms. Refinement of their coordinates using full-matrix least-squares procedure with isotropic temperature factors, then anisotropic, gave convergence at $R = 0.058$ (I) and $R = 0.049$ (II). H atoms were then included as a fixed contribution at their calculated idealized positions (C–H 1.0 Å). They were assigned isotropic thermal parameters 1.0 Å² higher than those of the C atoms to which they are attached. Final least-squares refinements led to the agreement factors of $R = 0.056$ and $R_w = 0.052$ and a GOF = 1.16 ($N_o = 1911$, $N_v = 244$) for compound I, and $R = 0.044$ and $R_w = 0.042$, and a GOF = 2.03 ($N_o = 2865$, $N_v = 254$) for compound II. The goodness of fit (GOF) is defined as $\sum(w|F_o - F_c|)^2 / (N_o - N_v)$.

Atomic coordinates and thermal parameters are given in Tables 3 and 4, bond lengths and angles with e.s.d.'s calculated from the full variance-covariance matrix and including contribution due to errors in the unit cell parameters, in Tables 5 and 6, and details of important molecular planes in Table 7. Tables of calculated and observed structure factors may be obtained from the authors.

Results and discussion

Both crystals are built up from binuclear units as shown in Figures 1 and 2; in addition, the asymmetric unit of compound I contains a water molecule. Each binuclear unit can be regarded as a Ru(CO)₃ fragment (this Ru referred as Ru(2)) π -bonded to a cycloruthenapentadienyl ring. The ruthenium (referred as Ru(1)) engaged in the ring also is σ -bonded to three CO groups. The Ru₂C₄ fragment of each molecule (i.e. the RuC₄ ring and the Ru(2)) is similar to those found in the metallocycle complexes shown in Table 8.

The butadiene chain is essentially planar with equal C–C distances within the experimental deviation [1.43(1) Å]; this corresponds with delocalized electrons as found in other diene complexes, but the delocalization in this case seems to be fairly complete, since the central and terminal C–C bond lengths are equal.

Among all the known metallocycles, only Cr₂(CO)(η -C₅H₅)₂(C₆H₅)₂C₄H₂ [12] has been regarded as containing C(1) and C(4) bridging carbene-type bonds with identical C(1)–Cr(1), C(1)–Cr(2), Cr(1)–C(4) and Cr(2)–C(4) bond lengths of 2.02 Å. In the other compounds the M(1)–C(1) and M(1)–C(4) linkages have just been defined as single bonds. However in our compounds these lengths correspond rather to lengths appropriate to metal-stabilized carbenes in which the metal–carbon bond is close to a double bond. From Table 9, it appears that the metal–carbon bond length in all the metallocycles is just as close to a double bond. In this respect the following typical single bond values are relevant:

Fe–CH₃–2.079(5)–Fe(CO)₂(CH₃NC)(CH₃(PPh₃)₂) [23]; W–CH₂C(CH₃)₃–2.258(8)–W(CMe₃)(CHCMe₃)(CH₂CMe₃)(dmpe) [24].

π -Bonding between Ru(1)–C(1) and Ru(1)–C(4) implies ruthenium t_{2g} orbitals. If z is the Ru(1)–C(12) axis, those t_{2g} orbitals do not lie in the Ru(1)–C(23) plane. Indeed Ru(1)–C(11) and Ru(1)–C(13) where C(11) and C(13) are carbonyl in *trans* positions with respect to C(1) and C(4), are longer than the Ru(1)–C(12) bond, suggesting again that a part of the electron density of this orbital is used for π -bonds with the ring. These π -bonds bring the Ru(1) C₄ fragment close to planarity. The Ru(1) atom is only slightly lifted above the perfect plane defined by the butadiene fragment, by 0.28 and 0.26 Å for compounds I and II, respectively (Table 7). It is

TABLE 8
STRUCTURAL PARAMETERS FOR Ru_2C_4 FRAGMENT IN COMPOUNDS I AND II AND RELATED PARAMETERS IN SOME CYCLOMETALLAPENTADIENE COMPLEXES

Compound	Reference	M(1)-C(σ)	M(2)-C(π) (terminal)	M(2)-C(π) (central)	C-C (terminal)	C-C (central)	M(1)-M(2)
$(CO)_6Ru_2(C_4(CH_2OH)_4) \cdot H_2O$	^a	2.07(4)	2.23(6)	2.26(5)	1.44(2)	1.42(2)	2.743(3)
$(CO)_6Ru_2(C_4(C_2H_4OH)_2(C_2H_5)_2)$	^a	2.095(8)	2.25(1)	2.28(1)	1.42(1)	1.44(1)	2.717(1)
$(CO)_6Fe_2(C_6H_8O_2)$	[3]	1.95(1)	2.12(1)	2.15(1)	1.42(2)	1.43(1)	2.493
$(CO)_6Fe_2(CH_3)_3SiOC_4$	[4]	1.92(2)	2.13(2)	2.19(2)	-	-	2.500(3)
$(CO)_6Fe_2(C_{12}H_{16})$	[5]	1.96(2)	2.07(2)	2.18(2)	1.41(2)	1.43(2)	2.462(3)
$(CO)_6Fe_2C_4(C_6H_5)_4$	[6]	1.97(1)	2.10(1)	2.14(1)	-	-	2.505(1)
$(CO)_5Fe_2PPh_3(C_6H_5)_4C_4$	[7]	1.99(1)	2.12(2)	2.15(2)	1.43(2)	1.43(1)	2.515(2)
$(CO)_6W_2(C_6H_{14})$	[10]	2.17(3)	2.36(3)	2.35(3)	1.42(3)	1.48(3)	2.900(2)
$(CO)_4Ir_2PPh_3C_4(C_2H_5)_2CO_4$	[11]	2.071(8)	2.23(2)	2.27(4)	1.435(4)	1.43(1)	2.737(1)
$(\eta-C_5H_5)_2CoCr_2(C_4(C_6H_5)_2H_2)$	[12]	2.028(7)	2.022(7)	2.23(1)	1.42(1)	1.428(11)	2.377(2)
$(\eta-C_5H_5)_2(CO)_2W(C_4H_4)Co(CO)_2$	[13]	2.13(1)	2.03(1)	2.12(1)	1.43(1)	1.42(1)	2.664(1)

^a This work.

TABLE 9
COMPARISON OF METAL-CARBON BOND LENGTHS (Å) IN METAL-STABILIZED CARBENES AND IN CYCLOMETALLAPENTADIENYL COMPLEXES

Compound	M-C (Carbene)	M-C	Metallobicyclic complexes	Reference
$(C_5H_5)_2Ru_2(CO)_2=C_2(CH_3)_2CHO$	2.080(4) (18)	2.07(3)	$Ru_2(CO)_6C_4(CH_2OH)_4 \cdot H_2O$	This work
$Fe_3(CO)_6(\mu-Sc)=COS$	1.949(2) (10)	2.095(6)	$Ru_2(CO)_6C_4(CH_2CH_2OH)_2Et_2$	This work
$W(CO)_5=C(C_6H_5)_2$	2.14(2) (20)	1.97(1)	$Fe_2(CO)_6(C_6H_5)_4C_4$	[6]
$W(=O)(=CHCMe_3)(PMMe_3)_2Cl_2$	1.99(2) (21)	1.96(2)	$Fe_2(CO)_6C_{12}H_{16}$	[5]
$W(CO)_5=C(OC_2H_5)_2C_6H_8CHC(C_6H_5)_2$	2.18(2) (22)	2.16(2)	$W_3(CO)_8C_9H_{14}$	[10]

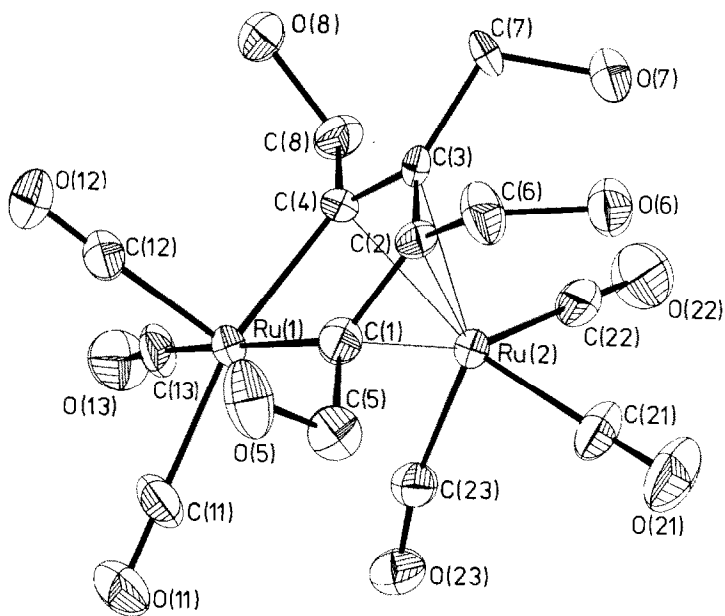


Fig. 1. The $[(\text{CO})_3\text{RuC}_4(\text{CH}_2\text{OH})_4]\text{Ru}(\text{CO})_3$ molecule. Ellipsoids of 50% probability are shown.

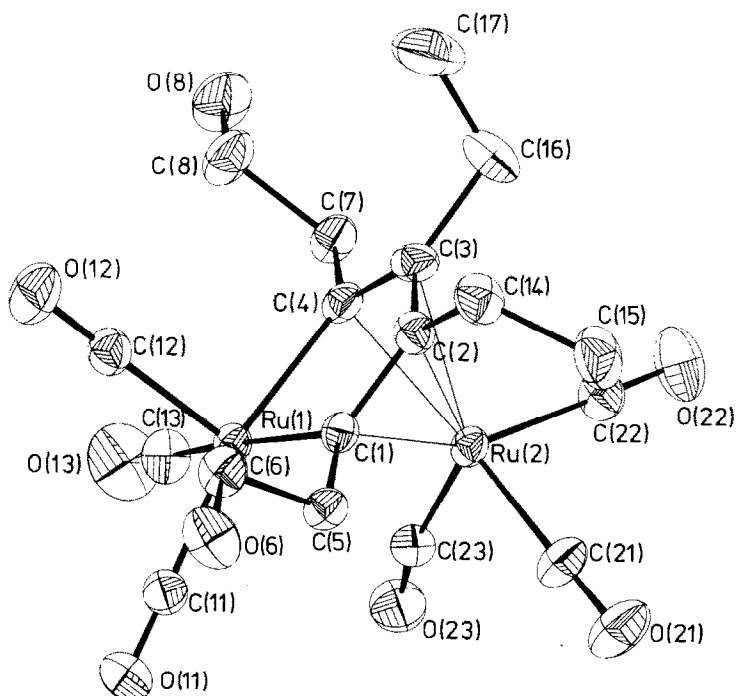


Fig. 2. The $[(\text{CO})_3\text{RuC}_4(\text{CH}_2\text{CH}_2\text{OH})_2(\text{C}_2\text{H}_5)_2]\text{Ru}(\text{CO})_3$ molecule. Ellipsoids of 50% probability are shown.

noteworthy that a cyclodimethylsilapentadienyl ring is known to act as a ligand to Ru [25]. In such a case, Si cannot give such π -bonds and indeed it lies 0.72 Å above the butadiene plane. Thus electron delocalization is assumed for all the bonds of that cycloruthenapentadiene ring.

Besides the C(1) and C(4) atoms, Ru(1) is also bonded to three CO groups with a square pyramidal coordination: the C(1), C(4), C(11) and C(13) atoms define the basal plane, and C(12) is in the apical position. The three CO ligands bonded to Ru(1) and the two σ -bonds make it a sixteen electron atom (neglecting the metal-metal bond). A 18 electrons configuration is achieved through the formation of a metal-metal donor-acceptor Ru(2) \rightarrow Ru(1) bond; such bonding causes a build up of electron density on Ru(1). Cotton [26] considers that this charge build up is relieved by the formation of a weak bond to the C(23) carbon atom which lies below Ru(1). This would explain why the Ru(2)-C(23)-O line is bent; such a CO ligand is called "semi-bridging" [27]. This point will be discussed later on.

We now consider the coordination around Ru(2). It is strikingly similar to that described for the mononuclear compounds [Fe(CO)₃(1,4-diphenylbutadiene)] [28] and for [Fe(CO)₃(butadiene)] [29]. This Ru(2) atom (or Fe(2) in similar complexes) receives three doublets from the three CO ligands and two doublets from the substituted butadiene group, and thus is a 18 electron atom. Ru(2) has a square pyramidal environment with two carbonyl groups and the midpoint of C(1)-C(2) and C(4)-C(3) on the base vertices, and one CO group (C(23)-O(23)) on the apex. This CO group lies nearly in the symmetry plane of the butadiene fragment; the angle between this Ru-C-O line and the normal to the mean plane of the butadiene fragment can be compared to the corresponding angle observed in [Fe(CO)₃(butadiene)] complexes and cycloferrapentadienyl complexes.

		M(2)-C(23)	Reference
[Fe(CO) ₃ (1,4-diphenylbutadiene)]	100°(2)	1.782(5)	[28]
[Fe(CO) ₃ (butadiene)]	99°(1)	1.74(4)	[29]
[Fe ₂ (CO) ₆ (C ₄ (C ₆ H ₅) ₄)]	105°(2)	1.784(5)	[6]
[Ru ₂ (CO) ₆ (C ₄ (CH ₂ OH) ₄)]	125°(2)	1.90(2)	this work
[Ru ₂ (CO) ₆ (C ₄ (CH ₂ CH ₂ OH) ₂ (C ₂ H ₅) ₂)]	109°(1)	1.916(8)	this work

Thus it seems that the Ru-Ru bond does not strongly influence the overall geometry of Ru(2)(CO)₃ with respect to the butadiene fragment. Furthermore, the metal-CO distance is not noticeably changed, as is evident from the table above. If the Ru(2)-C(23) is regarded as the *z* axis for this ruthenium, then the d_{xz} and d_{yz} orbitals of Ru(2) may be involved in π -bonding with the ligands, C(23)-O included. It thus appears that this CO has no π^* orbitals in the plane Ru(1)-Ru(2)-C(23). Furthermore, this carbonyl group is geometrically *trans* to C(12)-O attached to Ru(1), but the Ru(1)-C(12) distance is normal, suggesting that no significant interaction between Ru(1) and C(23) occurs through the Ru(1) d_{yz} orbital used for the Ru(1)-C(12) bond.

The Ru-Ru bond has now to be discussed. From the way in which the two squares pyramids are arranged, it appears that there is no direct metal-metal overlap. The d_{z^2} orbital of Ru(1) is mainly engaged in the Ru(1)-C(12)-O bond and its extension down Ru(1) in the Ru(1)-Ru(2)-C(23) plane is very probably quite low. Moreover Ru(2) has no orbitals extending in the Ru(1)-Ru(2)-C(23) plane, as

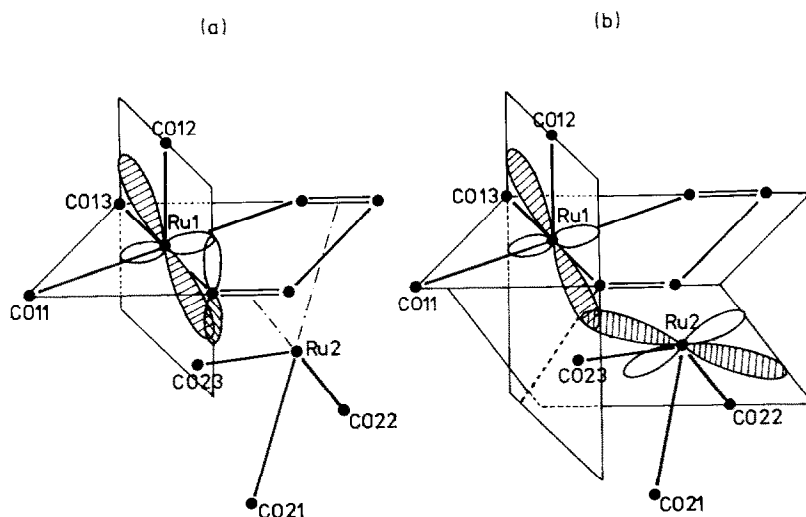


Fig. 3. Scheme of possible overlaps between: (a) the d_{xz} and d_{yz} orbitals of Ru(1) and the ring; (b) the d_{xz} and d_{yz} orbitals of Ru(1) and Ru(2).

pointed out earlier, except the one already used to make the Ru(2)–C(23) bond. How then does the Ru–Ru overlap occur? In the light of what has been said about the various π orbitals in which t_{2g} ruthenium orbitals are involved, it appears that an overlap of those orbitals is possible. The d_{xz} orbital of Ru(1) extends down (Fig. 3) into the C(13)–Ru(1)–C(12)–C(1) plane; the d_{xz} orbital of Ru(2) extends into the C(22)–Ru(2)–C(23) plane. These two planes intersect along the dotted line, and so these two orbitals may overlap. The same situation occurs for d_{yz} orbitals. This would be the interaction through which Ru(2) gives electrons to Ru(1). Then, due to the π bonding between the d_{xz} and d_{yz} of Ru(1) and the ring, and the bonds between that ring and Ru(2), the charge release might occur quite easily following the path Ru(2) \rightarrow Ru(1) \rightarrow ring π -electrons \rightarrow Ru(2). Thus the semi-bridging CO is not necessarily involved in that charge release to the extent as suggested by Cotton.

The last question to be discussed is why the Ru(2)–C(23)–O linkage is bent. Two points may be considered. First, there is quite a lot of steric crowding around this C(23)–O bond, the Ru(1)–C(23) distance is only 2.73 Å and there may be some repulsion between the π -CO electron density and the d_{z^2} part of Ru(1) which lies below Ru(1), *trans* to C(12)–O. The second point is the nonsymmetrical influence of the d_{xz} and d_{yz} orbitals of Ru(1) on C(23)–O(23), thus several kinds of overlaps occur together: d_{xz} and d_{yz} of Ru(1) with d_{xz} and d_{yz} of Ru(2); d_{xz} and d_{yz} of Ru(1) with p_z of C(1) and C(4); and d_{xz} and d_{yz} of Ru(2) with some parts of the C(23)–O π orbitals. It is noteworthy that this last overlap does not occur in the Ru(1)–Ru(2)–C(23) plane, and thus must be quite weak. In this respect we note that Fig. 4 shows that C(23)–O seems to be trying to escape the influence of Ru(1), since the projected Ru(2)–C(23)–O line does not go exactly through Ru(1) in projection, suggesting that the steric hindrance may dominate.

This scheme would be valid for all the described cases of iron and ruthenium. However an interesting case is that of the tungsten-metalloctetrahedron $[(CO)_4W(C_9H_{14})W(CO)_4]$ [10]. In this case each tungsten is bonded to four carbonyl

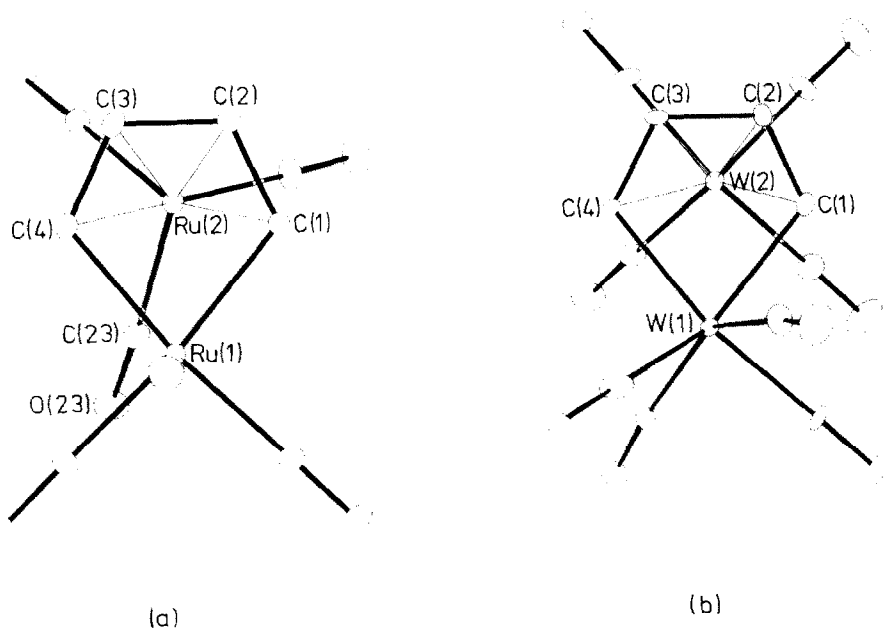


Fig. 4. Projection of the $\text{Ru}_2\text{C}_4(\text{CO})_6$ (a) and $\text{W}_2\text{C}_4(\text{CO})_8$ (b) onto the butadiene fragment.

groups. One of them is involved in a cyclotungstapentadiene ring which is π -bonded to the second one. Electron counting again suggest that the tungsten of the ring receives an electron pair from the other metal centre. However there is no semi-bridging CO. It is relevant to note that in $(\eta\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{Cl}$ compound [30], one CO group and the chlorine atom *trans* to it lie in the symmetry plane as shown on Fig. 5. If a similar disposition had been retained in the cyclotungstapentadiene complex, the semi-bridging would have occurred. However, since this is not observed for the ditungsten complex, we feel that what has been described as a semi-bridging CO group is not essential to the stability of the molecule. The steric crowding would thus be the predominant influence on the bending of the $\text{Ru}(2)\text{-C}(23)\text{-O}(23)$ linkage.

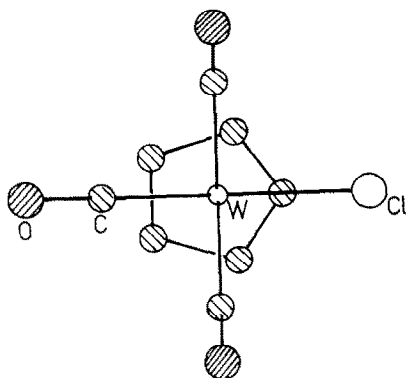


Fig. 5. $(\eta\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{Cl}$ molecule projected onto the cyclopentadienyl plane.

Another interesting feature of the ruthenium compounds is the geometry of the lateral chains. In compound I four hydroxymethyl groups are attached to the carbon atoms of the cycloruthenapentadienyl ring, whereas in compound II there are two hydroxyethyl groups and two ethyl groups in an arrangement such that the two ethyl groups are adjacent. The carbon atoms attached to the ring are essentially coplanar with the ring, showing that there is no distortion from sp^2 hybridization for the four carbon atoms of that ring. The lateral chains show some peculiarities. If the molecule is orientated in such a way that Ru(2) is below the metallaring, then in the butyne diol complexes I the oxygen atoms of the alcohol functions attached to C(1) and C(4) atoms are above the ring, while the two other oxygen atoms are below it. In the hexynol compound II, the CH_2OH groups are attached to C(1) and C(4) and are also above the ring. The reason for such a disposition might lie in the fact that if the OH or CH_2OH groups were below the plane, the alcoholic H atoms would be brought too close to the C(22)–O(22) and C(21)–O(21) carbonyl groups. The chair conformation of the OH groups in the butyne diol complexes minimizes repulsion between them. In the hexynol complexes II the methyl carbons of the ethyl groups are arranged in such a way that they point away from each other; one is above the butadiene plane and the other is below it; this arrangement, quite different from that in the butyne diol compound, might be attributable to the fact that CH_3 is bulkier than OH.

Although some intermolecular oxygen contacts (2.70 Å mean value) might suggest hydrogen bonds, infrared spectra indicate no significant changes in the OH stretching frequency. Moreover, in our experience when hydrogen atoms are engaged in hydrogen bonding they are often easier to locate, probably because their temperature factor is somewhat lowered; in fact the hydrogen atoms attached to oxygen could not be located.

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