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XXI *. REACTIONS OF $Ru_3(CO)_{12}$ WITH DIMETHYL ACETYLENEDICARBOXYLATE: CRYSTAL AND MOLECULAR STRUCTURES OF $Ru_2(CO)_6[C_4(CO_2Me)_4]$

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Summary

One of the products from reactions between $Ru_3(CO)_{12}$ and $C_2(CO_2Me)_2$ is $Ru_2(CO)_6[C_4(CO_2Me)_4]$. A single-crystal structure determination shows this to be a (tricarbonylruthenacyclopentadiene)$Ru(CO)_3$ complex; the two crystallographically independent molecules have different orientations of the CO group which semi-bridges the Ru–Ru bond. Crystal data: monoclinic, space group $C2/c$, a 37.479(23), b 7.509(6), c 32.91(3) Å, β 90.97(2)°, $Z = 16$; 6250 data were refined to R 0.045.

The tricarbonylferracyclopentadiene-$Fe(CO)_3$ moiety (I) is a common feature of many complexes obtained from reactions between alkynes and iron carbonyls: structural studies of nine examples have been reported [1]. The osmium analogue is found in a reaction product from $Os_3(CO)_{12}$ and 2,3-dimethylbutadiene, and the bicyclic derivative $Os_2(CO)_6(C_8H_6)$ [2]. Few ruthenium complexes of this type have been described, the most recent being obtained from reactions between $Ru_3(CO)_{12}$ and $HC{\equiv}CCR_2(OH)$ ($R = H$ or Me) [3], and none have been structurally characterised.

The $Fe_2(CO)_6$(ligand) structure has been theoretically examined by extended Hückel methods [4]. The $Fe_2(CO)_6$ moiety may adopt the sawhorse geometry (Ia), or an alternative in which the $Fe(CO)_3$ group π-bonded to the carbons is rotated by

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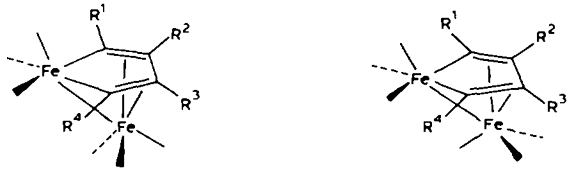
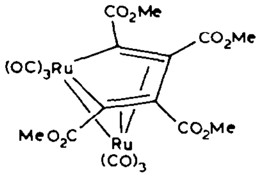
* For Part XX, see ref. 5.



(a) (b)

(I)



(V)

	R^1	R^2	R^3	R^4
(II)	OH	Me	Me	OH
(III)	OH	Et	Et	OH
(IV)	$CHPh_2$	H	OMe	OMe
(VI)	Ph	Ph	Ph	Ph

60°, as in Ib. In this instance, one CO group is positioned to interact with the second iron atom, forming a semi-bridging CO group, which has been rationalised as enabling the electron-deficient ferrole metal atom to recover some electron density. Energy differences between these two arrangements are calculated as only 0.2 eV in the parent compound, favouring Ib; experimental results confirm that there is only a low energy difference, since $Fe_2(CO)_6[C_4(OH)_2Me_2]$ (II) adopts structure b, whereas the corresponding ethyl derivative (III) is found to have structure a. In solution, ^1H and ^{13}C NMR measurements show that the CO groups are fluxional.

Of the known structures of iron complexes of this type, only two (III and IV) adopt conformation a; on the other hand, both osmium complexes mentioned above have this conformation. It was therefore of some interest to establish the molecular structure of a ruthenium complex of this type, and this paper describes the synthesis and structure of $Ru_2(CO)_6[C_4(CO_2Me)_4]$ (V).

Experimental

General experimental conditions were similar to those reported in other papers from these laboratories [5]. All reactions were carried out under nitrogen, although reaction products were worked up in air.

Reaction between $Ru_3(CO)_{12}$ and $C_2(CO_2Me)_2$: isolation of $Ru_2(CO)_6[C_4(CO_2Me)_4]$

A mixture of $Ru_3(CO)_{12}$ (600 mg, 0.94 mmol) and $C_2(CO_2Me)_2$ (400 mg, 2.82 mmol) in tetrahydrofuran (50 ml) was heated at reflux point for 5 h. Evaporation and separation of the products by thin layer chromatography (adsorbent: Kieselgel H; developed in 85/15 ethyl acetate/acetone) gave the following fractions: (a) a yellow band which moved with the solvent front; (b) an orange band (R_f 0.79) which afforded $Ru_3(CO)_7[C_2(CO_2Me)_2]_4$ (45 mg, 4.4%), purified by recrystallisation from hexane/dichloromethane mixtures (Found: C, 35.13; H, 2.93; M (acetone), 1110; $C_{31}H_{24}O_{23}Ru_3$ calcd.: C, 34.86; H, 2.25%; M, 1067; ν(CO) (CH_2Cl_2) 2111m, 2085s, 2058vs, 2042vs, 2020s, 1986(sh) cm^{-1}); (c) an orange band (R_f 0.22), presently unidentified (31 mg; ν(CO) (CH_2Cl_2) 2104sh, 2087m, 2050vs, 1982vs cm^{-1}). The brown baseline (144 mg) also contained metal carbonyl complexes. Further separation of fraction a (using 70/30 cyclohexane/acetone) gave $Ru_3(CO)_{12}$ (21 mg, 3.5%) and a pale yellow fraction (R_f 0.48) which afforded pure

TABLE 1

NON-HYDROGEN ATOM COORDINATES

Atom	Molecule 1			Molecule 2		
	x	*y*	*z*	*x*	*y*	*z*
Ru(A)	0.05983(2)	0.55719(8)	0.12891(2)	0.18453(1)	0.39384(7)	0.38800(2)
C(A1)	0.0291(2)	0.4798(11)	0.1723(3)	0.2030(2)	0.1792(9)	0.3642(3)
O(A1)	0.0110(2)	0.4386(9)	0.1971(2)	0.2131(2)	0.0557(7)	0.3483(2)
C(A2)	0.0884(2)	0.3477(10)	0.1348(2)	0.2086(2)	0.3487(10)	0.4387(2)
O(A2)	0.1062(2)	0.2253(8)	0.1386(2)	0.2229(2)	0.3239(9)	0.4687(2)
C(A3)	0.0301(2)	0.4577(12)	0.0874(3)	0.1425(2)	0.2793(10)	0.4057(2)
O(A3)	0.0112(2)	0.3905(10)	0.0653(2)	0.1193(2)	0.1953(8)	0.4170(2)
Ru(B)	0.06329(2)	0.78274(9)	0.06386(2)	0.13272(2)	0.64906(8)	0.37569(2)
C(B1)	0.0174(3)	0.8014(13)	0.0358(3)	0.0873(2)	0.5396(12)	0.3568(3)
O(B1)	−0.0097(2)	0.8098(12)	0.0200(2)	0.0614(2)	0.4797(11)	0.3480(2)
C(B2)	0.0853(3)	0.6621(14)	0.0175(3)	0.1116(2)	0.7310(12)	0.4257(3)
O(B2)	0.0981(3)	0.5934(12)	−0.0084(2)	0.0990(2)	0.7858(11)	0.4548(2)
C(B2)	0.0778(2)	1.0132(13)	0.0501(3)	0.1247(2)	0.8632(10)	0.3482(2)
O(B3)	0.0868(2)	1.1546(10)	0.0430(2)	0.1214(2)	0.9909(8)	0.3308(2)
Ligand						
C(1)	0.0425(2)	0.8426(9)	0.1201(2)	0.1633(2)	0.5275(9)	0.3316(2)
C(11)	0.0048(2)	0.9016(10)	0.1279(2)	0.1509(2)	0.4163(9)	0.2963(2)
O(11)	−0.0147(2)	0.8366(10)	0.1518(2)	0.1675(2)	0.2959(7)	0.2817(2)
O(12)	−0.0046(1)	1.0323(9)	0.1043(2)	0.1190(1)	0.4647(8)	0.2831(2)
C(12)	−0.0409(3)	1.0938(15)	0.1079(4)	0.1033(3)	0.3578(16)	0.2505(3)
C(2)	0.0659(2)	0.8356(9)	0.1537(2)	0.2007(2)	0.5571(9)	0.3346(2)
C(21)	0.0565(2)	0.9032(11)	0.1954(2)	0.2273(2)	0.4932(9)	0.3031(2)
O(21)	0.0478(2)	1.0532(9)	0.2010(2)	0.2507(1)	0.3908(7)	0.3096(2)
O(22)	0.0589(2)	0.7801(8)	0.2236(2)	0.2202(1)	0.5754(7)	0.2683(1)
C(22)	0.0515(3)	0.8338(17)	0.2649(3)	0.2400(3)	0.5116(13)	0.2334(2)
C(3)	0.1006(2)	0.7668(9)	0.1449(2)	0.2125(2)	0.6456(8)	0.3704(2)
C(31)	0.1303(2)	0.7469(10)	0.1765(2)	0.2509(2)	0.6813(10)	0.3815(2)
O(31)	0.1496(2)	0.6203(8)	0.1779(2)	0.2629(2)	0.6679(11)	0.4144(2)
O(32)	0.1325(1)	0.8878(7)	0.1998(2)	0.2690(1)	0.7277(8)	0.3493(2)
C(32)	0.1606(2)	0.8822(14)	0.2307(3)	0.3072(2)	0.7430(15)	0.3543(3)
C(4)	0.1044(2)	0.7169(10)	0.1038(2)	0.1838(2)	0.6871(9)	0.3974(2)
C(41)	0.1392(2)	0.6483(11)	0.0893(2)	0.1916(2)	0.7916(10)	0.4355(2)
OO(41)	0.1447(2)	0.5032(8)	0.0757(2)	0.2010(2)	0.9427(8)	0.4353(2)
O(42)	0.1639(2)	0.7742(9)	0.0935(2)	0.1845(2)	0.6994(7)	0.4682(1)
C(42)	0.1995(3)	0.7269(18)	0.0811(5)	0.1903(3)	0.7914(16)	0.5070(3)
C(X)[a]	0.0783(−)	0.7900(−)	0.1306(−)	0.1901(−)	0.6044(−)	0.3584(−)

[a] C(X) is the centroid of the C_4 moiety.

$Ru_2(CO)_6[C_4(CO_2Me)_4]$ (V; 78 mg, 13%) from hexane or on sublimation (65°C/0.01mmHg) (Found: C, 33.29; H, 1.59; *M* (mass spectrometry), 654; $C_{18}H_{12}O_{14}Ru_2$ calcd.: C, 33.04; H, 1.85%; *M*, 654). Infrared (cyclohexane): ν(CO) 2114m, 2090vs, 2050s, 2038s, 2021vs cm^{-1}. Mass spectrum: 654 (M^+).

Crystallography

Crystal data. $C_{18}H_{12}O_{14}Ru_2$, $M = 654.4$, Monoclinic, space group C_2/c (C_{2h}^6, No. 15), *a* 37.479(23), *b* 7.509(6), *c* 32.91(3) Å,β 90.97(2)°, *U* 9260(11) Å^3. D_m

TABLE 2

RUTHENIUM ATOM ENVIRONMENTS (The two values in each entry are for molecules **1**, **2** respectively. *r* is the relevant ruthenium–ligand distance; the other entries in the matrix are the angles subtended at the ruthenium by the two relevant atoms. Carbonyl carbon atoms are *italicized*.)

Ru(A)	*r*(Ru–L)	*C(2)*	*C(3)*	C(1)	C(2)	C(3)	C(4)	C(X) [a]
C(1)	1.938(8)	91.0(3)	93.6(4)	101.9(3)	94.0(3)	116.6(3)	153.4(3)	118.7(–)
	1.927(7)	92.2(3)	93.0(3)	99.3(3)	92.0(3)	115.3(3)	153.0(3)	116.9(–)
C(2)	1.911(8)		94.0(4)	162.6(3)	132.4(3)	100.1(3)	93.3(3)	123.8(–)
	1.914(7)		92.0(3)	162.9(3)	130.7(3)	99.2(3)	93.5(3)	123.2(–)
C(3)	1.901(9)			96.7(3)	132.7(3)	146.1(3)	112.3(3)	126.7(–)
	1.896(7)			99.9(3)	136.7(3)	148.9(3)	113.2(3)	130.1(–)
C(1)	2.257(7)				36.2(2)	63.8(2)	69.9(3)	39.3(–)
	2.244(7)				37.0(2)	64.5(2)	70.6(2)	39.9(–)
C(2)	2.254(7)					37.1(2)	64.1(3)	24.8(–)
	2.235(6)					36.9(2)	64.6(2)	24.9(–)
C(3)	2.250(7)						36.8(3)	25.1(–)
	2.242(7)						37.7(2)	25.3(–)
C(4)	2.226(7)							39.8(–)
	2.224(7)							40.3(–)
C(X) [a]	1.881(–)							
	1.870(–)							

Ru(B)	*r*(Ru–L)	*C(2)*	*C(3)*	C(1)	C(4)	C(X)
C(1)	1.943(10)	92.6(4)	94.4(4)	93.7(3)	164.4(3)	131.7(3)
	1.982(8)	92.1(4)	94.3(4)	94.6(3)	163.5(3)	132.5(3)
C(2)	1.967(10)		96.4(4)	164.3(3)	93.7(4)	131.6(3)
	1.938(9)		94.2(4)	166.3(3)	93.0(3)	131.7(2)
C(3)	1.872(10)			97.5(3)	99.1(3)	98.3(3)
	1.866(8)			97.3(3)	101.0(3)	98.7(3)
C(1)	2.070(7)				76.8(3)	38.5(2)
	2.076(7)				77.4(3)	38.7(2)
C(4)	2.067(7)					38.5(2)
	2.051(7)					38.9(2)
C(X) [a]	2.258(–)					
	2.258(–)					

[a] C(X) is the centroid of the C_4 moiety.

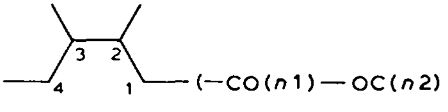
TABLE 3

CARBONYL GEOMETRIES (The two values in each entry are for molecules **1**, **2** respectively.)

	Ru–C (Å)	C–O (Å)	Ru–C–O (°)
Ru(A)			
CO(1)	1.938(8)	1.11(1)	178.5(8)
	1.927(7)	1.13(1)	176.4(7)
CO(2)	1.911(8)	1.14(1)	178.2(7)
	1.914(7)	1.13(1)	179.3(10)
CO(3)	1.901(9)	1.13(1)	174.1(8)
	1.896(7)	1.14(1)	173.0(7)
Ru(B)			
CO(1)	1.943(10)	1.14(1)	178.5(9)
	1.982(8)	1.10(1)	176.7(8)
CO(2)	1.967(10)	1.11(1)	179.3(13)
	1.938(9)	1.15(1)	177.5(8)
CO(3)	1.872(10)	1.14(1)	177.8(10)
	1.866(8)	1.12(1)	176.7(7)

1.87(1), D_c (Z 16) 1.88 g cm^{-3}. $F(000) = 5120$. Specimen size: $0.07 \times 0.40 \times 0.19$ mm. μ(Mo) 12.8 cm^{-1}.

Structure determination. A unique data set measured at 295(1) K to $2\theta_{max}$55° using a Syntex P2_1 four circle diffractometer, fitted with a monochromatic Mo-K_α radiation source, and operating in conventional $2\theta/\theta$ scan mode, yielded 10681 independent reflections, 6250 of which with $I > 3\sigma(I)$ were considered 'observed' and used in the structure determination after the application of analytical absorption correction. 9×9 block diagonal least squares refinement was employed, anisotropic thermal parameters being used for the non-hydrogen atoms (see Tables 1–4). Hydrogen atom (x, y, z, U) were included as constrained estimates. At convergence, residuals were 0.045, 0.053 (R, R'). Neutral atom scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion (f', f'') [6]. Computation used the X-ray 76 program system [7], implemented on a Perkin–Elmer 7240 computer. Within molecules **1**, **2** group labelling is as shown in the Figures; non-hydrogen atom labelling in the ligands is as follows:



(n = 1–4)

Results and discussion

Reactions between $Ru_3(CO)_{12}$ and $C_2(CO_2Me)_2$ readily afford at least four complexes, two of which can be separated easily by chromatographic methods, to

TABLE 4

LIGAND NON-HYDROGEN GEOMETRIES

	Molecule 1	Molecule 2
Distances (Å)		
C(1)-C(2)	1.400(9)	1.420(9)
C(2)-C(3)	1.433(9)	1.416(9)
C(3)-C(4)	1.414(10)	1.442(9)
C(1)-C(11)	1.505(10)	1.498(9)
C(2)-C(21)	1.513(10)	1.529(9)
C(3)-C(31)	1.519(10)	1.504(9)
C(4)-C(41)	1.488(11)	1.503(10)
C(11)-O(11)	1.19(1)	1.20(1)
C(21)-O(21)	1.19(1)	1.18(1)
C(31)-O(31)	1.19(1)	1.17(1)
C(41)-O(41)	1.20(1)	1.19(1)
C(11)-O(12)	1.30(1)	1.32(1)
C(21)-O(22)	1.31(1)	1.32(1)
C(31)-O(32)	1.31(1)	1.31(1)
C(41)-O(42)	1.33(1)	1.31(1)
O(12)-C(12)	1.44(1)	1.46(1)
O(22)-C(22)	1.45(1)	1.46(1)
O(32)-C(32)	1.45(1)	1.45(1)
O(42)-C(42)	1.45(1)	1.47(1)
Angles (deg)		
Ru(B)-C(1)-C(2)	117.2(5)	116.0(5)
C(1)-C(2)-C(3)	114.5(6)	115.1(6)
C(2)-C(3)-C(4)	113.2(6)	113.0(6)
C(3)-C(4)-Ru(B)	117.3(5)	117.1(5)
Ru(B)-C(1)-C(11)	125.8(5)	128.3(5)
C(2)-C(1)-C(11)	117.0(6)	115.7(6)
C(1)-C(2)-C(21)	123.5(6)	124.0(6)
C(3)-C(2)-C(21)	122.0(6)	120.9(6)
C(2)-C(3)-C(31)	123.8(6)	124.7(6)
C(4)-C(3)-C(31)	123.0(6)	122.2(6)
C(3)-C(4)-C(41)	120.1(6)	119.4(6)
Ru(B)-C(4)-C(41)	121.7(5)	122.1(5)
C(1)-C(11)-O(11)	125.6(7)	125.0(6)
C(2)-C(21)-O(21)	121.9(7)	124.9(6)
C(3)-C(31)-O(31)	122.7(7)	124.0(7)
C(4)-C(41)-O(41)	126.5(7)	123.3(7)
C(1)-C(11)-O(12)	111.6(6)	111.7(6)
C(2)-C(21)-O(22)	113.0(7)	108.4(5)
C(3)-C(31)-O(32)	111.1(6)	110.9(6)
C(4)-C(41)-O(42)	109.5(7)	111.6(6)
O(11)-C(11)-O(12)	122.8(7)	123.3(7)
O(21)-C(21)-O(22)	125.1(7)	126.6(6)
O(31)-C(31)-O(32)	126.1(7)	125.1(7)
O(41)-C(41)-O(42)	124.1(7)	124.9(7)
C(11)-O(12)-C(12)	116.1(8)	116.4(7)
C(21)-O(22)-C(22)	117.0(7)	115.5(6)
C(31)-O(32)-C(32)	115.2(6)	116.9(6)
C(41)-O(42)-C(42)	116.2(8)	115.9(7)

TABLE 5

LEAST-SQUARES PLANES

A least-squares plane is calculated through the C_4 skeleton of each ring and given in the form $pX + qY + rZ = s$, where the R.H. orthogonal (Å) frame (X, Y, Z) is defined with X parallel to a, Z in the ac plane. σ(defining atoms) and atom deviations (δ) are in Å. θ_n° is the dihedral angle to the $C \cdot CO_2(n)$ carboxyl plane.

	Molecule 1	Molecule 2
$10^4 p$	3234	1123
$10^4 q$	9222	−8843
$10^4 r$	−2122	4532
s	5.488	2.110
σ	0.003	0.003
δRu(B)	0.242	−0.283
δC(1)	0.002	−0.002
δC(2)	−0.004	0.003
δC(3)	0.004	−0.003
δC(4)	−0.002	0.002
δC(11)	−0.102	0.160
δC(21)	0.051	0.072
δC(31)	0.000	0.085
δC(41)	0.049	−0.094
δO(11)	−0.960	0.813
δO(21)	0.945	0.946
δO(31)	−0.654	0.714
δO(41)	−0.792	−1.060
δO(21)	0.858	−0.492
δO(22)	−0.973	−1.021
δO(32)	0.835	−0.624
δO(42)	1.190	0.973
δC(12)	0.818	−0.331
δC(22)	−0.987	−1.032
δC(32)	0.916	−0.490
δC(42)	1.383	0.964
θ_1	56.4	36.2
θ_2	59.9	61.7
θ_3	42.1	37.4
θ_4	64.0	66.5
δRu(A)	−1.828	1.812

give deep red $Ru_3(CO)_7[C_2(CO_2Me)_2]_4$ and yellow $Ru_2(CO)_6[C_4(CO_2Me)_4]$ (V). The former complex probably has an open-chain ligand formed by oligomerisation of the alkyne, and may be similar to complexes obtained with 1-alkynes such as HC_2Bu^t. A structural study will be reported separately.

Complex V is obtained as well-formed crystals. The composition was indicated by analysis, the ν(CO) spectrum, which was characteristic of an $M_2(CO)_6$ system, and by the ^1H NMR spectrum, which contained two singlets for the two pairs of CO_2Me groups. In addition, the mass spectrum contained a molecular ion centred on m/e 654, and fragment ions formed by the loss of the six CO ligands. Further breakdown of the $[Ru_2C_4(CO_2Me)_4]^+$ ion occurred by loss of OMe and CO fragments.

The structure determination confirms the assignment of the molecular formula (Fig. 1). The asymmetric unit of the structure contains two molecules, however, neither of which contains a crystallographically imposed symmetry element; the conformations of both molecules differ slightly (Fig. 2). As can be seen from Fig. 2, the molecular structure is in accord with arrangement Ia, closely resembling the archetypal $Fe_2(CO)_6(C_4H_4)$ molecule, with a tetrasubstituted tricarbonylruthenacyclopentadiene ligand π-bonded to the second $Ru(CO)_3$ group. The environment of both ruthenium atoms can be considered to be six-coordinate, although the interaction of Ru(B) with the semi-bridging CO group gives that atom *pseudo*-seven coordination.

The C_4 skeleton of each $[C_4(CO_2Me)_4]^{2-}$ ligand is closely planar in each molecule; although some irregularities are observed in the distances throughout the C(1)-C(4) string, these are not systematic. The mean C-C distance is 1.42_1 Å and the mean C-C-C angle $114._0°$, cf. 1.39_5 Å and $112._8°$ in $Fe_2(CO)_6(C_4H_4)$ (neither geometry is corrected for libration). In each molecule Ru(B) lies appreciably out of

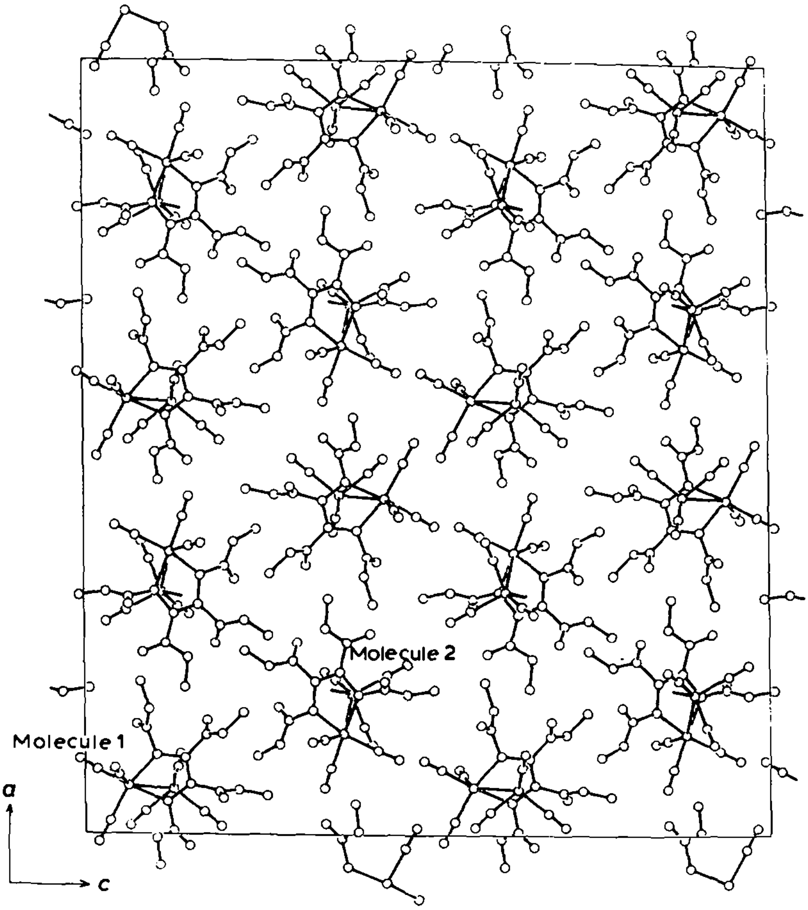


Fig. 1. Unit cell contents of $[C_4(CO_2Me)_4(Ru(CO)_3)_2]$ projected down *b*.

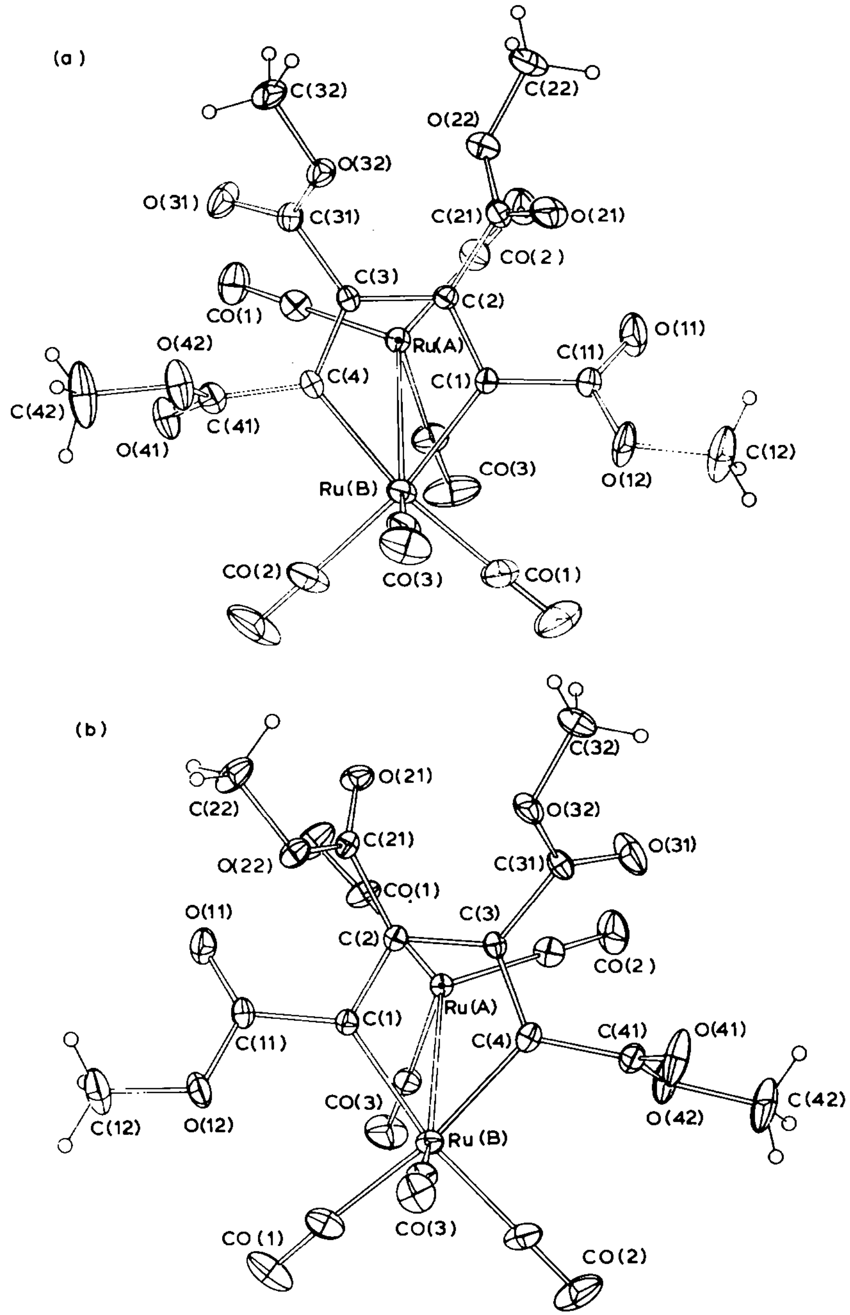


Fig. 2. Projections of molecules 1 and 2 of $[C_4(CO_2Me)_4(Ru(CO)_3)_2]$ on the C_4 plane of each ligand. 20% thermal ellipsoids are shown, together with atom labelling.

the C_4 plane, away from Ru(A) (Table 5, Fig. 3). All carboxyl groups are tilted well out of the C_4 plane; as in the previously studied $[C_5(CO_2Me)_5]^-$ derivatives [8], the C(*n*1) (*n* = 1–4) atom deviations are often considerable, the largest, C(11) (molecule

B), in this case being 0.160 Å. In the $[C_5(CO_2Me)_5]^-$ derivatives C(n)–C(n1) distances exceeding 1.50 Å are quite rare; in the present molecule, most of these bonds are longer than this suggesting the C(n)–C(n1) bond in this complex to be

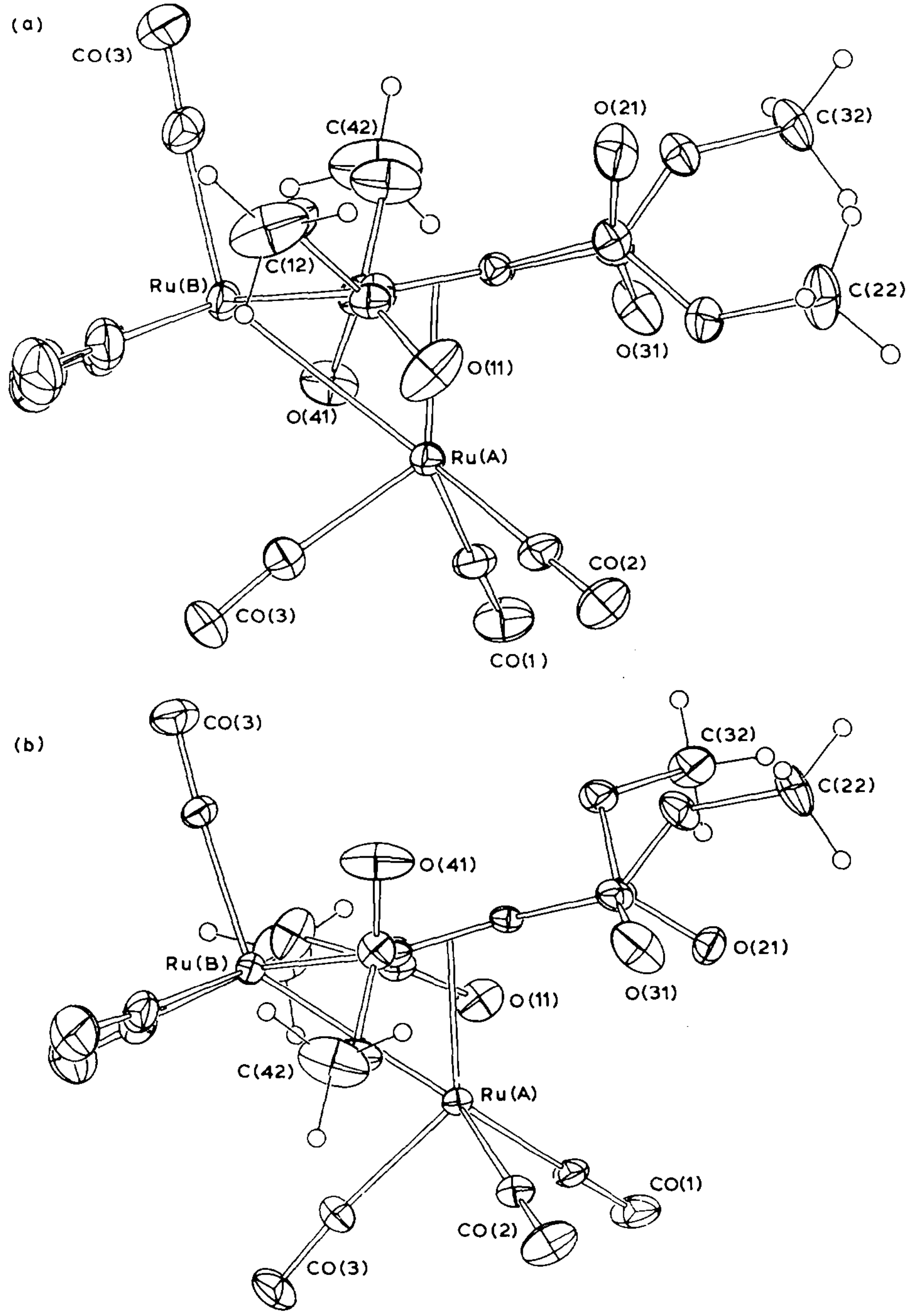


Fig. 3. Projection of molecules 1 and 2 of $[C_4(CO_2Me)_4(Ru(CO)_3)_2]$ along the C(1)–C(4) line.

appreciably weaker than in the $[C_5(CO_2Me)_5]^-$ adducts. Paralleling this, we also observe changes in the carboxylate angular geometry: in the $[C_5(CO_2Me)_5]$ complexes, O–C–O rarely exceeds 125°, whereas in the present complex values greater than 125° appear to be the norm, compensated by a diminution in C(*n*)–C(*n*1)–O(*n*2). This may be related to some extent to the considerable tendency of $[C_5(CO_2Me)_5]^-$ to form chelate derivatives, so that a greater proportion of carboxylate groups are constrained to be *pseudo*-parallel with the ring and offer increased scope for π-interactions.

The Ru–Ru distances are significantly different (2.734(2), 2.753(2) Å) in the two molecules, but not outside the usual range of such distances (e.g. $[Ru(CO)_2(\eta\text{-}C_5H_5)]_2$, 2.735(2) Å [9]; $Ru_3(CO)_{12}$, 2.852 Å [10]). The CO ligands on Ru(A) are staggered with respect to those on Ru(B), with Ru(A)–C–O 174.1(8), 173.0(7)° in the two molecules. This results in Ru–C(3) distances of 2.852(9), 2.968(8) Å, respectively, which suggests there to be a much smaller interaction than that found in the iron analogues, even when the differing covalent radii of Fe and Ru are considered. Thus, in VI, the corresponding distance is 2.374(9) Å, with angle Fe–C–O of 162.1(8)°, a difference of 0.48–0.62 Å from that found in V (half difference in M–M bond lengths is ca. 0.12 Å). Consequently, we should expect the electron deficiency of Ru(B) to be less well compensated. The Ru(B)–C(3) distance of 1.872(10), 1.866(8) Å is found to be shorter than the other two, as found for the iron complexes, and is a result of increased back-bonding to ruthenium, again as a partial compensation for its electron deficiency.

It is of some interest that the two crystallographically independent molecules differ significantly in the disposition of the three CO groups about Ru(A), and of the semi-bridging CO group towards Ru(B) (Fig. 2). This underlines the conclusion of Thorn and Hoffmann [4] that a delicate balance of forces affects the choice of conformation Ia or Ib, and suggests that the steric constraints associated with the packing of molecules of V into the crystal lattice are sufficient to perturb the minimum energy geometry.

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