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PREPARATION AND STRUCTURE OF BIS[ETHYLTETRAMETHYLCYCLOPENTADIENYLDICARBONYLRUTHENIUM(I)]

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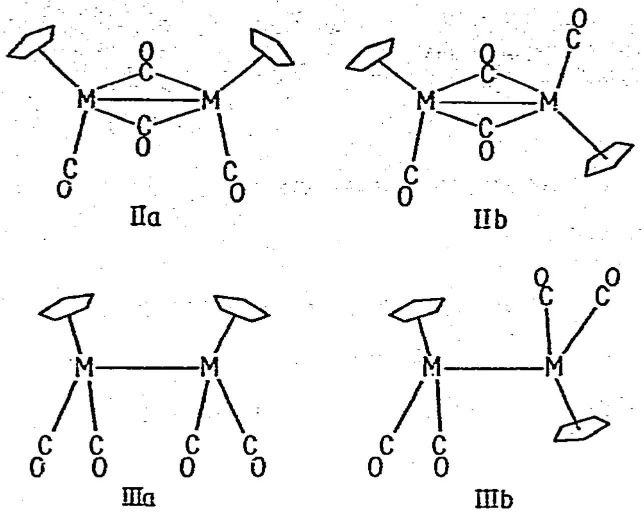
Summary

The preparation of $[Ru(\eta^5\text{-}C_5Me_4Et)(CO)_2]_2$ has been described and its structure determined by X-ray crystallography. The crystals are monoclinic with space group C2/m and a = 11.934(2), b = 12.158(2), c = 9.433(2)Å and β = 113.95(1)°. In the solid state the dimeric molecule has crystallographically imposed C_{2h} symmetry (i.e. trans conformation) with two bridging and two terminal carbonyl ligands; this structure is retained in solution. The structure is compared with those of the related complexes, $[M(\eta^5\text{-}C_5H_5)(CO)_2]_2$ (M = Fe and Ru).

Introduction

As part of a detailed investigation of the chemistry of ethyltetramethylcyclopentadienylruthenium complexes we have prepared the complex $[Ru(C_5Me_4Et)(CO)_2]_2$ (I). There has been considerable interest over many years in the structures of related complexes having the general formula $[M(Cp)(CO)_2]_2$ (M = Fe, Ru or Os; Cp = η^5-cyclopentadienyl derivative)[1-3] and therefore we have investigated the structure of the complex (I), both in solution and in the solid state.

The complexes $[M(Cp)(CO)_2]_2$ may adopt a carbonyl bridged structure (II) or a non-carbonyl bridged structure (III); further, each of these structural types can exist as cis- or trans-isomers (designated and and b respectively, Figure 1). In practice in solution all the isomers may be in equilibrium



IIa IIb

IIIa IIIb

Fig. 1

with each other and elegant infrared[1] and ^{13}C n.m.r.[2,3] studies have shown that the relative proportions of each isomer depend upon the nature of the metal, M, the substituents on the cyclopentadienyl ring, the solvent and the temperature. The only other penta-alkylcyclopentadienyl derivative of this type which has been prepared is the iron complex $[Fe(C_5Me_5)(CO)_2]_2$ but unfortunately only the infrared spectrum in cyclohexane was reported.[4] This spectrum did suggest, however, that in this medium the complex exists exclusively as the trans-carbonyl bridged isomer (IIb). The structure of the ruthenium analogue $[Ru(C_5Me_4Et)(CO)_2]_2$ is of interest because of the possibility of detecting a non-carbonyl bridged isomer since the complexes $[M(Cp)(CO)_2]_2$ show a preference for this structure as the atomic mass of M increases.[5] It also provides a useful comparison with the structure of the unsubstituted analogue $[Ru(C_5H_5)(CO)_2]_2$[6] in order to observe the influence of the alkyl ring-substituents upon the rest of the molecule.

Experimental

Preparation

1-Ethyl-2,3,4,5-tetramethylcyclopentadiene was prepared by the method of Feitler and Whitesides.[7] The complex $[Ru(C_5Me_4Et)(CO)_2]_2$ was prepared by the following modification of the procedure described for $[Ru(C_5H_5)(CO)_2]_2$.[8]

A heptane ($150\ cm^3$) solution of $Ru_3(CO)_{12}$ (1 g, 1.56 mmol) and excess $C_5Me_4(Et)H$ (1 g) was refluxed in air for 20 h. The solution was allowed to cool, filtered and the dark brown residue washed with petroleum ether (b.pt. 40-60°C, $2 \times 10\ cm^3$) to remove excess C_5Me_4EtH. Washing with dichloromethane ($2 \times 10\ cm^3$) removed traces of $Ru(C_5Me_4Et)(CO)_3$ and gave pure tetracarbonylbis(η^5-ethyltetramethylcyclopentadienyl)diruthenium. (720 mg, 50% Yield). Recrystallisation from ethyl acetate afforded orange crystals suitable for X-ray diffraction studies.

(Found C, = 51.1; H, = 5.8; $C_{26}H_{34}O_4Ru_2$ requires C, 51.0; H = 5.6) I.r. (nujol) = 1929 and 1744 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 2.32q (2H, J = 7.5 Hz), 1.87s (6H), 1.78s (6H), and 1.02t (3H).

<u>Crystal Data</u> $C_{26}H_{34}O_4Ru_2$, M = 612.69. Monoclinic, a = 11.934(2), b = 12.158(2), c = 9.433(2)Å, β = 113.95(1)°, U = 1250.8(4)Å^3; D_m = 1.62, Z = 4, D_c = 1.626, F(000) = 620. Space group C2/m (C^3_{2h}, No. 12) from reflection conditions {hkl}, k+l = 2n; confirmed by structural analysis: MoK_α X-radiation ($\bar{\lambda}$ = 0.71069Å), $\mu(MoK_\alpha)$ = 12.1 cm^{-1}.

X-ray data ($6.5 < 2\theta < 50°$) were collected on a Stoe Stadi-2 X-ray diffractometer by the moving-crystal, stationary-counter method from a small, irregularly shaped crystal (approx. dimensions 0.15 x 0.08 x 0.12 mm) mounted along a C-face diagonal of the monoclinic unit cell. A total of 1068 independent reflections, for which $I/\sigma(I) > 3.0$ were corrected for the usual effects but, in view of the small crystal dimensions, no correction for absorption was applied. The positions of all non-hydrogen atoms were clearly revealed on the Patterson map and the molecular C_{2h} symmetry was confirmed (see Discussion section). Block-diagonal, least-squares refinement converged at R 0.032, anisotropic thermal parameters being allowed for all atoms. Difference Fourier syntheses revealed all hydrogen atoms, including those of the methyl groups, in substantially ordered positions which were consistent with the crystallographically imposed symmetry and which showed no unacceptable intramolecular contacts. Hydrogen atoms were included, in fixed, optimized positions (C-H = 0.95Å) with isotropic thermal parameters of 7.0Å^2, in subsequent least-squares refinement which converged, after allowance for the anomalous scattering of ruthenium, at R 0.0259. Unit weights were used throughout the refinement (analysis of structure factor agreement having suggested no clearly preferable scheme) and atomic scattering factors were taken from reference

Atomic positions and thermal vibrations, together with their e.s.ds. are collected in Table 1 (hydrogen atoms are labelled according to the carbon atom to which they are attached): observed structure amplitudes and calculated structure factors are available from the authors. Table 2 gives details of the molecular geometry which is illustrated in Figure 2.

TABLE 1

Atomic parameters for bis[(ethyltetramethylcyclopentadienyl)dicarbonylruthenium(I)]

(a) Positional Parameters and estimated standard deviations

	X/a	Y/b	Z/c
Ru(1)	0.12644(4)	0	0.06250(5)
O(1)	0	0.2219(4)	0
O(2)	0.1564(5)	0	-0.2398(6)
C(1)	0	0.1238(5)	0
C(2)	0.1400(5)	0	-0.1280(7)
C(3)	0.3293(5)	0	0.2015(7)
C(4)	0.2803(4)	0.0964(4)	0.2464(5)
C(5)	0.2015(4)	0.0591(4)	0.3158(5)
C(6)	0.4297(6)	0	0.1403(8)
C(7)	0.5547(8)	0	0.2779(11)
C(8)	0.3142(5)	0.2133(5)	0.2319(6)
C(9)	0.1387(5)	0.1303(5)	0.3897(6)
H(61)	0.4220	0.0638	0.0773
H(71)	0.6183	0	0.2427
H(72)	0.5602	0.0644	0.3400
H(81)	0.3682	0.2391	0.3314
H(82)	0.2408	0.2566	0.1928
H(83)	0.3532	0.2160	0.1614
H(91)	0.1805	0.1245	0.4988
H(92)	0.0557	0.1056	0.3564
H(93)	0.1400	0.2043	0.3564

TABLE 1 (Continued)

(b) Anisotropic Thermal Vibrational Parameters and estimated standard deviations [expression used is $\exp(-(h^2b_{11}+k^2b_{22}+l^2b_{33}+klb_{23}+hlb_{12}+hkb_{23}))$]

	$b_{11}\times10^5$	$b_{22}\times10^5$	$b_{33}\times10^5$	$b_{23}\times10^5$	$b_{13}\times10^5$	$b_{12}\times10^5$
Ru(1)	333(0)	327(0)	576(1)	0	396(1)	0
O(1)	810(7)	315(5)	1473(12)	0	734(16)	0
O(2)	934(8)	938(8)	969(11)	0	1363(17)	0
C(1)	470(8)	436(7)	763(12)	0	674(17)	0
C(2)	376(8)	471(7)	894(14)	0	388(17)	0
C(3)	319(7)	681(9)	759(13)	0	456(16)	0
C(4)	469(6)	526(5)	743(9)	-229(12)	201(12)	-245(9)
C(5)	537(6)	562(5)	562(9)	-212(11)	282(12)	4(9)
C(6)	431(9)	1068(12)	1158(17)	0	830(21)	0
C(7)	527(11)	1996(23)	1768(25)	0	787(28)	0
C(8)	963(9)	626(7)	1341(13)	-412(16)	923(18)	-649(12)
C(9)	760(7)	730(7)	1041(11)	-597(15)	912(15)	-137(12)

Results and Discussion

In the solid state the molecule has precise C_{2h} symmetry and, therefore, adopts a trans conformation with the ruthenium atoms and the terminal carbonyls lying in, and the (C_4Me_4Et) ring lying across, the mirror plane. The two, mirror-related, bridging carbonyl groups lie along the crystallographic 2-fold axis.

The molecular geometry may be usefully compared to that of $[Ru(\eta^5\text{-}C_5H_5)(CO)_2]_2$[6] which possesses the same molecular conformation and an almost identical skeletal geometry; however, of the molecular C_{2h} symmetry, only the inversion centre is crystallographically imposed. In both molecules the bonding of the five-membered ring is almost symmetric η^5 with a very similar range of Ru-C distances (2.23 - 2.30Å in I; 2.22 - 2.28Å in reference 6). The five-membered ring is planar (r.m.s. deviation 0.003Å); the substituent carbon atoms lie, on average, 0.12Å from this mean plane in a direction away from the ruthenium which is 1.92Å away from the mean plane. In I, the geometries of both terminal and bridging carbonyls show the expected

TABLE 2

Molecular geometry and estimated standard deviations for bis[(ethyltetramethylcyclopentadienyl)dicarbonylruthenium(I)]

(a) Bond Lengths (Å)

Bond	Length	Bond	Length
Ru(1) – Ru(1)^a	2.7584(5)	C(2) – O(2)	1.149(7)
Ru(1) – C(1)	2.042(4)	C(3) – C(4)	1.448(7)
Ru(1) – C(2)	1.868(5)	C(3) – C(6)	1.527(8)
Ru(1) – C(3)	2.237(5)	C(4) – C(5)	1.421(6)
Ru(1) – C(4)	2.273(5)	C(4) – C(8)	1.499(7)
Ru(1) – C(5)	2.300(5)	C(5) – C(5)^b	1.437(6)
Ru(1) – Cp*	1.922(5)	C(5) – C(9)	1.490(7)
C(1) – O(1)	1.192(4)	C(6) – C(7)	1.529(10)

(b) Bond Angles (°)

	Angle		Angle
C(1) – Ru(1) – C(1)^b	95.01(10)	C(4) – C(3) – C(6)	125.7(4)
C(1) – Ru(1) – C(2)	93.70(11)	C(3) – C(4) – C(5)	107.3(4)
C(1) – Ru(1) – Cp*	119.93(16)	C(3) – C(4) – C(8)	125.8(4)
C(2) – Ru(1) – Cp*	126.91(19)	C(5) – C(4) – C(8)	126.8(4)
Ru(1) – C(1) – Ru(1)^a	84.99(14)	C(4) – C(5) – C(5)^b	108.6(4)
Ru(1) – C(1) – O(1)	137.50(26)	C(4) – C(5) – C(9)	125.6(4)
Ru(1) – C(2) – O(2)	175.5(5)	C(9) – C(5) – C(5)^b	125.5(4)
C(4) – C(3) – C(4)^b	108.1(4)	C(3) – C(6) – C(7)	108.9(5)

a related by symmetry operation [–x, y, –z]

b related by symmetry operation [x, –y, z]

* position of centre-of-gravity of cyclopentadienyl ring

features. The ruthenium-ruthenium distance of 2.76Å is very similar to that in the unsubstituted compound, suggesting that the presence of more bulky substituents has no detectable effect on the geometry of the bridge system.

The infrared spectrum of [Ru(η^5-C_5Me_4Et)$(CO)_2$]$_2$ was recorded in heptane, cyclohexane, m-xylene, bromoform, chloroform, carbon disulphide, dichloromethane and tetrahydrofuran. In all these solvents the compound exhibited

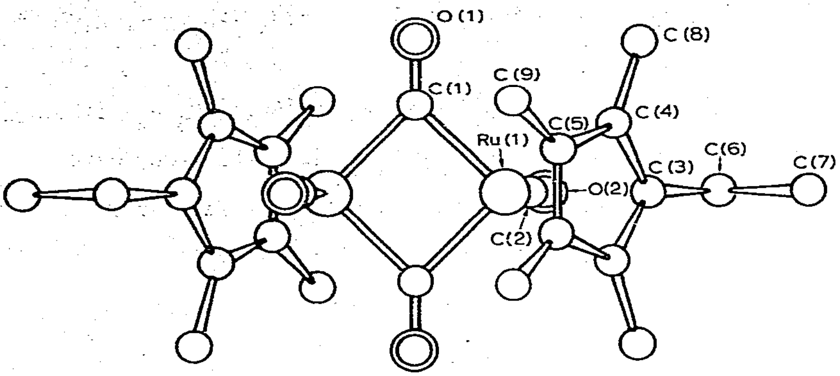


Fig. 2. The molecular structure of Bis[(ethyltetramethylcyclopentadienyl)-dicarbonylruthenium(I)].

only one band (1923-1936 cm^{-1}) in the terminal metal carbonyl region together with only one band (1742-1765 cm^{-1}) in the bridging metal carbonyl region. It appears, therefore, that in all these solvents the complex exists exclusively as the trans-carbonyl bridged isomer (IIb) as in the solid state. Further, the spectrum in cyclohexane (1937 and 1765 cm^{-1}) is very similar to that of the isostructural complex $[Fe(\eta^5\text{-}C_5Me_5)(CO)_2]_2$ (1932 and 1764 cm^{-1}).[4] Unfortunately the complex proved too insoluble for ^{13}C n.m.r. studies.

In certain solvents a slow reaction between $[Ru(C_5Me_4Et)(CO)_2]_2$ and the solvent occurred. For example, in chloroform the initial carbonyl bands at 1933 and 1748 cm^{-1} disappeared over a period of 4 days to be replaced by new bands at 2040 and 1990 cm^{-1}; this change is accelerated by irradiating the solution with visible light. A similar but slower reaction occurred in dichloromethane. The new product has been fully characterised as $[Ru(C_5Me_4Et)(CO)_2Cl]$ and the corresponding bromide complex may be prepared by the analogous reaction with bromoform.[9] We, and others, have reported similar reactions of chloroform and bromoform with $[Mo(C_5H_5)(CO)_3]_2$ and $[Fe(C_5H_5)(CO)_2]_2$.[10] In refluxing tetrahydrofuran over a period of several weeks the initial carbonyl bands at 1923 and 1754 cm^{-1} were replaced by two bridging carbonyl peaks at 1776 and 1724 cm^{-1}. Unfortunately, at present we have been unable to isolate this product in a pure form but we believe it to be a ruthenium cluster compound in view of its infrared spectrum and the known tendency of $[Ru(C_5H_5)(CO)_2]_2$ to form $[Ru(C_5H_5)(CO)]_4$ (ν_{CO} = 1616 cm^{-1}) on heating.[11]

Finally, it is worth considering why the molecule $[Ru(\eta^5\text{-}C_5Me_4Et)(CO)_2]_2$ only exists in the trans-carbonyl bridged structure IIb. The X-ray data show that the co-ordination polyhedron around the ruthenium is that of a symmetric 'piano stool' with (O)C-Ru-C(O) angles all close to 94.5°. If a similar coordination geometry were to be adopted in a cis conformation of the molecule an unacceptably short C(methyl)-C(methyl) contact of 2.33Å would occur. This may be compared with 2.75Å, the calculated shortest H-H contact for a cis conformation of $[Ru(\eta^5\text{-}C_5H_5)(CO)_2]_2$, IIa. It seems likely, however, that bond angle deformation of the 'piano stool' polyhedron and, perhaps, bridge plane deformation as observed in cis-$[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$[12] could ease the intramolecular interaction. Models suggest that appreciable deformation would be required to increase the C(methyl)-C(methyl) distance to an acceptable value and such a conformation would be energetically unfavourable. Similar considerations for the trans-non-carbonyl bridged structure, IIIb, again suggest that there would be considerable ligand congestion in the ruthenium coordination hemisphere remote from the metal-metal interaction, this time between the substituted cyclopentadienyl and the terminal carbonyl ligands.

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