New Dimeric Forms of Cyclo-octatetraene: Crystal Structures of Tricarbonylruthenium and Pentacarbonyldiruthenium Complexes containing Dimeric Cyclo-octatetraene

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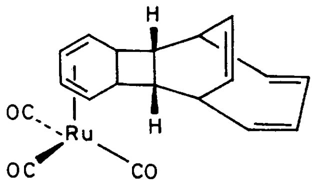
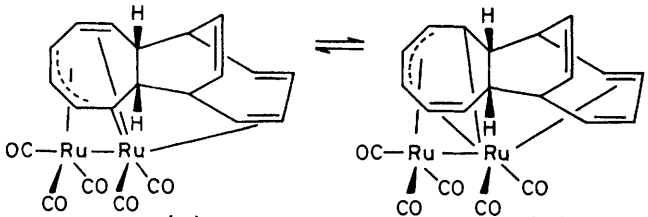
Reaction of $[Ru_3(CO)_{12}]$ or the cluster $[Ru_4H_4(CO)_{12}]$ with cyclo-octatetraene (cot) yields a mixture of products, several of which have already been identified. Among the hitherto unidentified species, however, are two complexes, $[Ru(CO)_3(C_{16}H_{16})]$ (1) and $[Ru_2(CO)_5(C_{16}H_{16})]$ (2). Both (1) and (2) have now been characterised by *X*-ray crystallography; they are metal carbonyl derivatives of two isomers of a new dimer of cot. Crystals of (1) are monoclinic, space group $P2_1/n$, with $Z = 4$ in a unit cell of dimensions $a = 12.801(4)$, $b = 6.640(1)$, $c = 19.678(5)$ Å, and $\beta = 103.06(2)°$. Crystals of (2) are also monoclinic, space group $P2_1/n$, with $Z = 8$ in a unit cell of $a = 7.010(1)$, $b = 24.965(8)$, $c = 22.021(7)$ Å, and $\beta = 101.03(2)°$. Both structures have been solved by heavy-atom methods for 1 899 independent observed intensities for (1), 3 812 for (2), and refined by least squares to *R* 0.037 for (1) and *R* 0.051 for (2). The structure of (1) shows the ruthenium atom to be η^4-bonded to a cyclohexadiene ring which is *cis*-fused to a planar cyclobutane ring which in turn is *cis*-fused in a 1,4 fashion to a cyclo-octatriene ring. The six-membered ring of the bicyclo-octadiene moiety and the eight-membered cyclo-octadiene ring are in an *anti* relationship to the central four-membered ring; the molecule as a whole has idealised mirror symmetry. In (2) the cot dimer takes the form that might be expected from Diels–Alder self addition, in that one of the C_8 rings remains unbridged. The link to the second C_8 ring is as in (1). The $Ru_2(CO)_5$ moiety adopts a ' sawhorse ' configuration; $Ru(CO)_3$ is η^4-bonded to ring 1, while $Ru(CO)_2$ is σ- and η^2-bonded to ring 1 and η^2-bonded to ring 2. The molecule is fluxional.

The unexpected formation of a new dimer of cyclo-octatetraene in two isomeric forms has been revealed by the crystallographic investigation of two products, $[Ru(CO)_3(C_{16}H_{16})]$ (1) and $[Ru_2(CO)_5(C_{16}H_{16})]$ (2), both of which result (among other products [1-3] previously identified) from the reaction of $[Ru_4H_4(CO)_{12}]$ with cyclo-octatetraene (cot). The molecular structures of (1) and (2) show that (1) is a tricarbonylruthenium complex of a bicyclo-octadiene–cyclo-octatriene system, while (2) is a fluxional pentacarbonyldiruthenium complex of a bis(cyclo-octatriene) system. A preliminary report of this work has already been made; [4] the synthetic and spectroscopic studies associated with it form the subject of a separate paper.[5] The free dimer $C_{16}H_{16}$ has been isolated in a pure state [4] but no crystals suitable for *X*-ray diffraction could be obtained. Spectroscopic studies [4,5] show, however, that the free dimer has the same structure as the ligand in (1).



(1)



(a) (b)

(2)

EXPERIMENTAL

Crystals of (1) grow as colourless plates elongated along *b* with well developed (001) faces. The crystal used for data collection was 0.20 × 0.50 × 0.05 mm and was cut from a larger crystal. Intensities were measured on a Syntex $P2_1$ four-circle diffractometer at scan rates depending upon the magnitude of a preliminary 2-s peak count, the rate varying from 0.033° s^{-1} for counts <250 to 0.983° s^{-1} for counts >750. Of the 3 088 independent reflections to $2\theta = 50°$, 1 899 had $I > 2.5\sigma(I)$ and only these were used in the solution and refinement of the structure. No significant crystal decay was observed during the 98 h of *X*-ray exposure. The data were corrected for absorption effects [6] ($A^*_{max.}$ 1.20 for 002, $A^*_{min.}$ 1.05 for $21\bar{1}$). Crystals of (2) grow as yellow prisms elongated along *a*. Intensities were measured as for (1) from a crystal of dimensions 0.35 × 0.08 × 0.08 mm. The 4 171 measured independent intensities gave rise to 3 812 ' observed ' reflections, and there was no crystal decomposition during the 210 h of *X*-ray exposure. The data were corrected for absorption effects [6] ($A^*_{max.}$ 1.14 for 741, $A^*_{min.}$ 1.12 for 2, 0, 22).

RESULTS

Crystal Data.—(1), $C_{19}H_{16}O_3Ru$, $M = 393.4$, Monoclinic, $a = 12.801(4)$, $b = 6.640(1)$, $c = 19.678(5)$ Å, $\beta = 103.06(2)°$ at 293 K, $U = 1\,629.4(7)$ Å^3, $D_m = 1.591$ g cm^{-3}, $Z = 4$, $D_c = 1.604$ g cm^{-3}, $F(000) = 792$, space group $P2_1/n$, Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 9.56$ cm^{-1}.

(2), $C_{21}H_{16}O_5Ru_2$, $M = 550.6$, Monoclinic, $a = 7.010(1)$, $b = 24.965(8)$, $c = 22.021(7)$ Å, $\beta = 101.03(2)°$ at 293 K, $U = 3\,782.3(18)$ Å^3, $D_m = 1.91$ g cm^{-3}, $Z = 8$, $D_c = 1.93$ g cm^{-3}, $F(000) = 2\,160$, space group $P2_1/n$, Mo-K_α *X*-radiation, $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 15.92$ cm^{-1}.

Structure Solution and Refinement.—Both structures were solved by conventional heavy-atom methods and refined by blocked-matrix least squares. For (1), anisotropic thermal parameters were ascribed to all non-hydrogen atoms, but in (2), for which the asymmetric unit comprises two molecules, anisotropy was confined to Ru and O atoms only. In both structures the H atoms were located by electron-density difference synthesis and were refined isotropically with $U_H = 1.10\ U_C$ for (1), and U_H fixed at 0.076 for (2). Refinement converged at R 0.037 (R' 0.040) for (1) and at R 0.051 (R' 0.065) for (2). Weights were applied according to the following schemes which gave satisfactory weight analyses: for (1), $1/w = 2.925$—

TABLE 1

Atomic positional parameters (fractional co-ordinates) for (1) with estimated standard deviations in parentheses

Atom	x	y	z
Ru	0.346 86(4)	1.122 37(9)	0.399 83(3)
C(1)	0.142 8(4)	0.368 0(12)	0.383 0(3)
C(2)	0.252 6(5)	0.372 1(12)	0.431 3(4)
C(3)	0.279 1(5)	0.228 2(17)	0.486 0(4)
C(4)	0.243 5(6)	0.029 0(14)	0.469 1(4)
C(5)	0.185 5(5)	0.000 1(11)	0.398 9(4)
C(6)	0.102 2(4)	0.151 3(11)	0.366 0(3)
C(7)	0.004 2(5)	0.194 3(12)	0.400 5(4)
C(8)	−0.112 3(6)	0.164 2(12)	0.360 9(5)
C(9)	−0.132 8(6)	0.159 9(14)	0.281 2(6)
C(10)	−0.116 3(7)	0.302 8(19)	0.238 9(5)
C(11)	−0.075 3(6)	0.501 6(19)	0.249 2(5)
C(12)	−0.041 7(6)	0.613 2(14)	0.305 0(5)
C(13)	−0.039 6(6)	0.572 7(10)	0.379 6(4)
C(14)	0.042 8(5)	0.414 7(12)	0.413 5(3)
C(15)	−0.148 7(6)	0.512 7(15)	0.387 9(4)
C(16)	−0.180 5(6)	0.329 7(15)	0.380 2(5)
C(01)	0.412 3(5)	−0.132 9(14)	0.389 6(4)
O(01)	0.449 4(5)	−0.283 2(10)	0.382 0(4)
C(02)	0.315 4(6)	0.198 1(12)	0.302 8(4)
O(02)	0.291 6(6)	0.241 2(12)	0.245 9(3)
C(03)	0.484 5(5)	0.249 5(12)	0.427 9(4)
O(03)	0.565 1(4)	0.327 4(9)	0.442 7(3)
H(1)	0.145(5)	0.447(10)	0.350(3)
H(2)	0.268(6)	0.472(11)	0.444(4)
H(3)	0.313(6)	0.248(12)	0.520(4)
H(4)	0.257(6)	−0.077(11)	0.502(4)
H(5)	0.171(5)	−0.115(11)	0.386(3)
H(6)	0.075(5)	0.139(11)	0.320(3)
H(7)	0.009(6)	0.095(12)	0.438(4)
H(8)	−0.129(6)	0.055(13)	0.373(4)
H(9)	−0.160(6)	0.000(14)	0.278(4)
H(10)	−0.132(7)	0.277(13)	0.193(4)
H(11)	−0.067(6)	0.567(13)	0.213(4)
H(12)	−0.028(7)	0.710(12)	0.299(4)
H(13)	−0.020(5)	0.687(9)	0.398(3)
H(14)	0.069(5)	0.442(10)	0.457(4)
H(15)	−0.176(6)	0.606(12)	0.395(4)
H(16)	−0.246(6)	0.283(12)	0.386(4)

TABLE 2

Interatomic distances (Å) and bond angles (°) for (1), showing where possible the similarities between the two halves of the molecule related by an approximate mirror plane of symmetry

(*a*) Distances

Ru–C(02)	1.927(8)	C(02)–O(02)	1.129(10)
Ru–C(01)	1.922(9)	Ru–C(03)	1.920(7)
C(01)–O(01)	1.129(11)	C(03)–O(03)	1.131(9)
Ru–C(2)	2.220(8)	Ru–C(5)	2.216(7)
Ru–C(3)	2.188(8)	Ru–C(4)	2.192(8)
C(1)–C(2)	1.509(8)	C(6)–C(5)	1.501(9)
C(2)–C(3)	1.422(12)	C(5)–C(4)	1.425(10)
C(7)–C(14)	1.548(11)	C(1)–C(6)	1.541(10)
C(1)–C(14)	1.561(10)	C(6)–C(7)	1.583(10)
C(14)–C(13)	1.530(10)	C(7)–C(8)	1.531(9)
C(13)–C(12)	1.487(13)	C(8)–C(9)	1.530(15)
C(12)–C(11)	1.314(14)	C(9)–C(10)	1.311(15)
C(3)–C(4)	1.414(14)	C(10)–C(11)	1.418(17)
C(13)–C(15)	1.497(11)	C(8)–C(16)	1.506(13)
C(15)–C(16)	1.279(14)		

TABLE 2 (*Continued*)

(*b*) Angles

C(01)–Ru–C(03)	91.4(3)	Ru–C(02)–O(02)	176.5(7)
C(02)–Ru–C(03)	98.2(3)	C(02)–Ru–C(01)	97.1(3)
Ru–C(03)–O(03)	178.0(7)	Ru–C(01)–O(01)	178.4(6)
C(2)–Ru–C(02)	94.4(3)	C(5)–Ru–C(02)	95.8(3)
C(3)–Ru–C(02)	130.8(3)	C(4)–Ru–C(02)	132.0(3)
C(2)–Ru–C(03)	96.5(3)	C(5)–Ru–C(01)	96.0(3)
C(3)–Ru–C(03)	97.7(3)	C(4)–Ru–C(01)	98.9(3)
C(1)–C(2)–C(3)	119.6(6)	C(6)–C(5)–C(4)	119.5(7)
C(2)–C(3)–C(4)	116.2(6)	C(5)–C(4)–C(3)	115.1(7)
C(6)–C(1)–C(2)	112.0(6)	C(1)–C(6)–C(5)	111.0(5)
C(6)–C(1)–C(14)	90.3(5)	C(1)–C(6)–C(7)	89.9(5)
C(2)–C(1)–C(14)	118.9(5)	C(5)–C(6)–C(7)	119.4(6)
C(1)–C(14)–C(7)	90.5(6)	C(6)–C(7)–C(14)	89.2(5)
C(1)–C(14)–C(13)	120.9(6)	C(6)–C(7)–C(8)	122.2(7)
C(7)–C(14)–C(13)	114.4(5)	C(14)–C(7)–C(8)	116.5(6)
C(14)–C(13)–C(12)	114.3(7)	C(7)–C(8)–C(9)	116.5(7)
C(14)–C(13)–C(15)	109.8(6)	C(7)–C(8)–C(16)	109.2(7)
C(12)–C(13)–C(15)	110.2(6)	C(9)–C(8)–C(16)	107.3(7)
C(13)–C(12)–C(11)	130.7(9)	C(8)–C(9)–C(10)	128.5(9)
C(12)–C(11)–C(10)	133.3(10)	C(9)–C(10)–C(11)	133.7(9)
C(13)–C(15)–C(16)	121.3(8)	C(8)–C(16)–C(15)	122.4(8)

TABLE 3

Equations of some least-squares planes for (1): distances (Å) of relevant atoms from these planes are given in square brackets

Plane (1)

C(2), C(3), C(4), C(5)

$$12.0403x - 1.3524y - 9.3939z = -1.5136$$

[C(2) 0.0002, C(3) −0.0004, C(4) 0.0004, C(5) −0.0002]

Plane (2)

C(1), C(2), C(5), C(6)

$$-7.6720x - 0.1331y + 18.0050z = 5.7684$$

[C(1) −0.016, C(2) 0.010, C(5) −0.010, C(6) 0.016]

Plane (3)

C(1), C(6), C(14), C(7)

$$4.3221x - 1.8614y + 15.7223z = 5.9336$$

[C(1) 0.020, C(6) −0.020, C(14) −0.020, C(7) 0.020]

Plane (4)

C(13), C(14), C(7), C(8)

$$-6.7082x + 0.2800y + 18.6365z = 7.5123$$

[C(13) −0.012, C(14) 0.022, C(7) −0.022, C(8) 0.012]

Plane (5)

C(13), C(15), C(16), C(8)

$$2.0772x - 0.1775y + 17.8839z = 6.0294$$

[C(13) 0.003, C(15) −0.006, C(16) 0.006, C(8) −0.003]

Plane (6)

C(12), C(13), C(8), C(9)

$$12.0258x - 2.1804y - 2.2916z = -2.5642$$

[C(12) 0.027, C(13) −0.030, C(8) 0.029, C(9) −0.026]

Plane (7)

C(9), C(10), C(11), C(12)

$$11.9943x - 2.2733y - 2.8220z = -2.7525$$

[C(9) 0.002, C(10) −0.005, C(11) 0.005, C(12) −0.002]

Angles (°) between planes:

(1)–(2)	141.0	(4)–(6)	115.0
(2)–(3)	121.5	(5)–(6)	103.8
(3)–(4)	125.1	(6)–(7)	178.2
(4)–(5)	137.2		

$0.125|F_o| + 0.002\,4|F_o|^2 - 0.000\,121|F_o|^3$; for (2), $1/w = 7.98 - 0.122|F_o| + 0.000\,8|F_o|^2$. In the final electron-density difference syntheses the largest peaks were <0.5 and >-0.2 e Å^{-3} for (1) and between $+0.5$ and -0.5 e Å^{-3} for (2). Positional parameters are in Table 1 for (1) and Table 5 for (2), interatomic distances and angles in Table 2 for (1), Table 6 for (2), while some least-squares planes and torsion angles for (1) are listed in Tables 3 and 4. Atomic scattering factors were of the analytical types of ref. 7 for ruthenium (corrected for anomalous dispersion: $\Delta f'$ -1.2, $\Delta f''$ 6.6),[8] oxygen, and carbon, and those of ref. 9 for hydrogen. All computational work was carried out (on the CDC 7600 of the University of London) by use of the '*X*-Ray' system of programs.[6] Observed and calculated structure factors and all thermal parameters are listed in Supplementary Publication No. SUP 22437 (27 pp.).*

TABLE 4

Some torsion angles (°) for the cyclo-octatetraene dimer in [Ru(CO)$_3$(C$_{16}$H$_{16}$)]

C(6)–C(1)–C(2)–C(3)	−38	C(1)–C(6)–C(5)–C(4)	43
C(1)–C(2)–C(3)–C(4)	41	C(6)–C(5)–C(4)–C(3)	−43
C(14)–C(1)–C(2)–C(3)	65	C(7)–C(6)–C(5)–C(4)	−59
C(13)–C(14)–C(1)–C(2)	128	C(8)–C(7)–C(6)–C(5)	−121
C(13)–C(14)–C(1)–C(6)	−116	C(8)–C(7)–C(6)–C(1)	124
C(7)–C(14)–C(1)–C(2)	−112	C(14)–C(7)–C(6)–C(5)	117
C(12)–C(13)–C(14)–C(1)	23	C(9)–C(8)–C(7)–C(6)	−20
C(15)–C(13)–C(14)–C(1)	147	C(16)–C(8)–C(7)–C(6)	−142
C(12)–C(13)–C(14)–C(7)	−83	C(9)–C(8)–C(7)–C(14)	87
C(15)–C(13)–C(14)–C(7)	41	C(16)–C(8)–C(7)–C(14)	−34
C(11)–C(12)–C(13)–C(14)	71	C(10)–C(9)–C(8)–C(7)	−62
C(11)–C(12)–C(13)–C(15)	−53	C(10)–C(9)–C(8)–C(16)	61
C(12)–C(13)–C(15)–C(16)	94	C(9)–C(8)–C(16)–C(15)	−93
C(14)–C(13)–C(15)–C(16)	−41	C(7)–C(8)–C(16)–C(15)	40

TABLE 5

Atomic positional parameters (fractional co-ordinates) for (2), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
(*a*) Molecule (i)			
Ru(11)	0.436 34(13)	0.043 31(4)	0.805 70(4)
Ru(12)	0.328 21(12)	0.029 91(3)	0.673 15(4)
C(111)	0.518 4(20)	0.045 0(5)	0.893 7(7)
O(111)	0.570 1(19)	0.045 8(5)	0.946 3(5)
C(112)	0.282 5(18)	0.106 8(5)	0.808 1(6)
O(112)	0.197 3(14)	0.144 2(4)	0.814 5(5)
C(113)	0.658 5(20)	0.080 4(5)	0.785 9(6)
O(113)	0.792 0(15)	0.100 2(5)	0.774 5(5)
C(121)	0.202 4(16)	0.096 4(5)	0.674 1(5)
O(121)	0.122 4(15)	0.136 9(4)	0.670 9(5)
C(122)	0.540 4(18)	0.062 9(5)	0.638 7(6)
O(122)	0.653 7(15)	0.082 8(4)	0.619 0(5)
C(101)	0.065 9(16)	−0.060 0(4)	0.680 2(5)
H(11)	−0.023(22)	−0.081(6)	0.695(7)
C(102)	−0.056 4(16)	−0.041 0(5)	0.618 5(5)
H(12)	−0.186(22)	−0.029(6)	0.619(7)
C(103)	0.053 6(17)	0.005 5(5)	0.593 3(5)
H(13)	−0.021(22)	0.038(6)	0.595(7)
C(104)	0.207 1(18)	0.002 0(5)	0.562 2(6)
H(14)	0.206(22)	0.026(6)	0.540(7)
C(105)	0.292 6(18)	−0.042 9(5)	0.536 8(6)
H(15)	0.384(22)	−0.030(6)	0.503(7)
C(106)	0.297 6(18)	−0.094 5(5)	0.551 8(6)
H(16)	0.388(22)	−0.113(6)	0.530(7)
C(107)	0.209 7(18)	−0.120 8(5)	0.603 5(6)
H(17)	0.266(22)	−0.147(6)	0.617(7)
C(108)	0.249 5(16)	−0.091 9(4)	0.668 0(5)
H(18)	0.262(22)	−0.127(6)	0.705(7)
C(109)	0.428 6(15)	−0.056 9(4)	0.672 6(5)
H(19)	0.491(22)	−0.059(6)	0.636(7)
C(1010)	0.545 7(15)	−0.035 3(4)	0.725 6(5)
H(110)	0.667(22)	−0.025(6)	0.722(7)
C(1011)	0.532 4(16)	−0.039 8(5)	0.790 4(5)
H(111)	0.654(22)	−0.062(6)	0.821(7)
C(1012)	0.356 9(17)	−0.041 5(5)	0.813 9(5)
H(112)	0.359(22)	−0.052(6)	0.859(7)
C(1013)	0.185 0(17)	−0.016 8(5)	0.786 1(5)
H(113)	0.090(22)	−0.017(6)	0.810(7)
C(1014)	0.119 1(15)	−0.009 1(4)	0.717 6(5)
H(114)	−0.024(22)	0.022(6)	0.715(7)
C(1015)	−0.119 7(17)	−0.087 9(5)	0.576 2(5)
H(115)	−0.242 6(22)	−0.088(6)	0.569(7)
C(1016)	0.000 4(20)	−0.126 6(6)	0.573 5(6)
H(116)	−0.026(22)	−0.162(6)	0.560(7)
(*b*) Molecule (ii)			
Ru(21)	0.058 63(15)	0.144 10(5)	−0.008 87(5)
Ru(22)	0.139 07(14)	0.226 53(4)	0.084 02(5)
C(211)	0.034 5(20)	0.084 1(6)	−0.062 5(7)
O(211)	0.025 9(20)	0.047 0(5)	−0.092 1(5)
C(212)	0.267 4(25)	0.178 4(7)	−0.039 9(8)
O(212)	0.393 1(22)	0.197 7(9)	−0.055 2(8)
C(213)	−0.141 0(25)	0.181 5(7)	−0.064 6(8)
O(213)	−0.254 4(20)	0.203 1(8)	−0.101 4(7)
C(221)	0.372 5(20)	0.262 4(5)	0.068 4(6)
O(221)	0.502 7(14)	0.282 8(5)	0.057 2(5)
C(222)	−0.014 5(24)	0.271 1(7)	0.024 6(8)
O(222)	−0.107 5(18)	0.299 3(6)	−0.010 1(7)
C(201)	0.133 7(17)	0.159 2(5)	0.200 1(5)
H(21)	0.174(22)	0.125(6)	0.204(7)
C(202)	0.198 9(19)	0.184 6(5)	0.267 1(6)
H(22)	0.219(22)	0.153(6)	0.285(7)
C(203)	0.343 9(19)	0.229 9(5)	0.271 6(6)
H(23)	0.428(22)	0.229(6)	0.299(7)
C(204)	0.332 5(21)	0.271 2(6)	0.233 5(7)
H(24)	0.415(21)	0.287(6)	0.244(7)
C(205)	0.187 0(20)	0.286 5(6)	0.180 6(7)
H(25)	0.187(22)	0.288(6)	0.156(7)
C(206)	−0.007(20)	0.272 2(6)	0.161 3(6)
H(26)	−0.078(22)	0.297(6)	0.143(7)
C(207)	−0.124 1(20)	0.230 4(6)	0.190 0(6)
N(27)	−0.239(22)	0.245(6)	0.171(7)
C(208)	−0.080 4(17)	0.175 6(5)	0.168 4(6)
H(28)	−0.050(22)	0.160(6)	0.192(7)
C(209)	−0.106 9(17)	0.178 5(5)	0.098 6(6)
H(29)	−0.221(22)	0.211(6)	0.084(7)
C(2010)	−0.125 9(18)	0.127 8(5)	0.064 6(6)
H(210)	−0.243(22)	0.117(6)	0.045(7)
C(2011)	0.015 6(20)	0.089 5(6)	0.064 4(6)
H(211)	0.072(22)	0.080(6)	0.077(7)
C(2012)	0.218 6(19)	0.102 2(5)	0.072 5(6)
H(212)	0.315(22)	0.080(6)	0.061(7)
C(2013)	0.316 3(18)	0.147 3(5)	0.107 6(6)
H(213)	0.443(22)	0.163(6)	0.088(7)
C(2014)	0.286 0(17)	0.172 7(5)	0.160 5(6)
H(214)	0.362(22)	0.178(6)	0.182(7)
C(2015)	0.037 3(20)	0.208 0(6)	0.294 2(6)
H(215)	0.083(22)	0.204(6)	0.331(7)
C(2016)	−0.100 9(21)	0.232 8(6)	0.260 4(7)
H(216)	−0.205(22)	0.251(6)	0.257(7)

DISCUSSION

The molecular structure of [Ru(CO)$_3$(C$_{16}$H$_{16}$)] (1) is given in Figure 1,† together with the crystallographic numbering system, while the contents of the monoclinic cell are shown in Figure 2. If the diene is regarded as a bidentate ligand attached to the ruthenium atom at the midpoints of the formal double bonds, the co-ordination about the metal atom is that of a tetragonal pyramid with C(02)–O(02) occupying the apical position. The

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

† Drawn with a modified version of C. K. Johnson's ORTEP, by R. Goddard.

TABLE 6

Bond lengths (Å) and angles (°) for (2)

(*a*) Distances

Around the metal atoms

Molecule (i)		Molecule (ii)	
Ru(11)–Ru(12)	2.891(1)	Ru(21)–Ru(22)	2.880(2)
Ru(11)–C(111)	1.91(1)	Ru(21)–C(211)	1.90(2)
C(111)–O(111)	1.15(2)	C(211)–O(211)	1.13(2)
Ru(11)–C(112)	1.92(1)	Ru(21)–C(213)	1.92(2)
C(112)–O(112)	1.13(2)	C(213)–O(213)	1.15(2)
Ru(11)–C(113)	1.93(1)	Ru(21)–C(212)	1.93(2)
C(113)–O(113)	1.13(2)	C(212)–O(212)	1.11(3)
Ru(11)–C(1011)	2.27(1)	Ru(21)–C(2010)	2.29(1)
Ru(11)–C(1012)	2.21(1)	Ru(21)–C(2011)	2.18(1)
Ru(11)–C(1013)	2.29(1)	Ru(21)–C(2012)	2.19(1)
Ru(12)–C(121)	1.88(1)	Ru(21)–C(222)	1.89(2)
C(121)–O(121)	1.15(2)	C(222)–O(222)	1.15(2)
Ru(12)–C(122)	1.97(1)	Ru(22)–C(221)	1.95(1)
C(122)–O(122)	1.09(2)	C(221)–O(221)	1.11(2)
Ru(12)–C(103)	2.42(1)	Ru(22)–C(206)	2.43(1)
Ru(12)–C(104)	2.53(1)	Ru(22)–C(205)	2.57(1)
Ru(12)–C(109)	2.28(1)	Ru(22)–C(2014)	2.24(1)
Ru(12)–C(1010)	2.37(1)	Ru(22)–C(2013)	2.34(1)
Ru(12)–C(1014)	2.15(1)	Ru(22)–C(209)	2.17(1)

(*a*) Distances

The dimer ligand

Molecule (i)		Molecule (ii)	
C(101)–C(102)	1.54(1)	C(208)–C(207)	1.50(2)
C(101)–C(108)	1.58(2)	C(208)–C(201)	1.58(2)
C(101)–C(1014)	1.52(2)	C(208)–C(209)	1.52(2)
C(102)–C(103)	1.55(2)	C(207)–C(206)	1.54(2)
C(102)–C(1015)	1.51(2)	C(207)–C(2016)	1.53(2)
C(103)–C(104)	1.38(2)	C(206)–C(205)	1.39(2)
C(104)–C(105)	1.43(2)	C(205)–C(204)	1.45(2)
C(105)–C(106)	1.33(2)	C(204)–C(203)	1.32(2)
C(106)–C(107)	1.54(2)	C(203)–C(202)	1.51(2)
C(107)–C(108)	1.57(2)	C(202)–C(201)	1.59(2)
C(107)–C(1016)	1.50(2)	C(202)–C(2015)	1.50(2)
C(1015)–C(1016)	1.29(2)	C(2016)–C(2015)	1.27(2)
C(108)–C(109)	1.52(2)	C(201)–C(2014)	1.54(2)
C(109)–C(1010)	1.40(1)	C(2014)–C(2013)	1.38(2)
C(1010)–C(1011)	1.45(2)	C(2013)–C(2012)	1.46(2)
C(1011)–C(1012)	1.42(2)	C(2012)–C(2011)	1.44(2)
C(1012)–C(1013)	1.39(2)	C(2011)–C(2010)	1.38(2)
C(1013)–C(1014)	1.50(2)	C(2010)–C(209)	1.46(2)

Carbon–hydrogen

C(101)	0.91(17)	C(208)	0.64(15)	C(109)	0.98(17)	C(2014)	0.64(14)
C(102)	0.96(16)	C(207)	0.91(15)	C(1010)	0.91(16)	C(2013)	1.12(16)
C(103)	0.96(16)	C(206)	0.84(15)	C(1011)	1.13(14)	C(2012)	0.96(16)
C(104)	0.78(16)	C(205)	0.54(16)	C(1012)	1.04(16)	C(2011)	0.48(15)
C(105)	1.12(17)	C(204)	0.71(15)	C(1013)	0.92(17)	C(2010)	0.89(15)
C(106)	0.98(17)	C(203)	0.76(14)	C(1014)	1.26(16)	C(209)	1.14(15)
C(107)	0.80(15)	C(202)	0.88(15)	C(1015)	0.85(15)	C(2016)	0.84(16)
C(108)	1.18(15)	C(201)	0.89(15)	C(1016)	0.94(16)	C(2015)	0.81(15)

(*b*) Angles

Molecule (i)		Molecule (ii)	
C(111)–Ru(11)–Ru(12)	174.2(4)	C(211)–Ru(21)–Ru(22)	171.7(4)
C(111)–Ru(11)–C(1011)	97.6(5)	C(211)–Ru(21)–C(2012)	95.9(6)
C(111)–Ru(11)–C(1012)	88.3(5)	C(211)–Ru(21)–C(2011)	87.6(6)
C(111)–Ru(11)–C(1013)	106.0(5)	C(211)–Ru(21)–C(2010)	107.7(6)
C(111)–Ru(11)–C(112)	90.9(5)	C(211)–Ru(21)–C(213)	91.0(7)
C(111)–Ru(11)–C(113)	96.9(6)	C(211)–Ru(21)–C(212)	96.6(7)
Ru(11)–C(111)–O(111)	179.0(13)	Ru(21)–C(211)–O(211)	176.6(13)
C(112)–Ru(11)–Ru(12)	94.8(4)	C(213)–Ru(21)–Ru(22)	97.3(5)
C(112)–Ru(11)–C(1011)	163.6(4)	C(213)–Ru(21)–C(2012)	162.4(7)
C(112)–Ru(11)–C(1012)	129.6(5)	C(213)–Ru(21)–C(2011)	126.3(7)
C(112)–Ru(11)–C(1013)	97.5(5)	C(213)–Ru(21)–C(2010)	95.6(6)
C(112)–Ru(11)–C(113)	95.3(6)	C(213)–Ru(21)–C(212)	93.8(7)
Ru(11)–C(112)–O(112)	174.5(11)	Ru(21)–C(213)–O(213)	175.3(17)
C(113)–Ru(11)–Ru(12)	83.9(4)	C(212)–Ru(21)–Ru(22)	82.8(5)
C(113)–Ru(11)–C(1011)	97.6(5)	C(212)–Ru(21)–C(2012)	101.4(6)
C(113)–Ru(11)–C(1012)	134.9(5)	C(212)–Ru(21)–C(2011)	139.7(6)
C(113)–Ru(11)–C(1013)	153.5(5)	C(212)–Ru(21)–C(2010)	153.7(6)
Ru(11)–C(113)–O(113)	117.2(12)	Ru(21)–C(212)–O(212)	176.8(15)
C(121)–Ru(12)–Ru(11)	85.4(3)	C(222)–Ru(22)–Ru(21)	85.4(5)
C(121)–Ru(12)–C(109)	169.9(5)	C(222)–Ru(22)–C(2014)	172.3(6)
C(121)–Ru(12)–C(1010)	149.2(4)	C(222)–Ru(22)–C(2013)	149.2(6)
C(121)–Ru(12)–C(1014)	91.9(5)	C(222)–Ru(22)–C(209)	93.7(6)
C(121)–Ru(12)–C(103)	85.4(4)	C(222)–Ru(22)–C(206)	87.0(6)
C(121)–Ru(12)–C(104)	100.5(4)	C(222)–Ru(22)–C(205)	101.4(6)
C(121)–Ru(12)–C(122)	91.5(5)	C(222)–Ru(22)–C(221)	89.6(7)
Ru(12)–C(121)–O(121)	175.9(10)	Ru(22)–C(222)–O(222)	177.9(15)
C(122)–Ru(12)–Ru(11)	105.6(3)	C(221)–Ru(22)–Ru(21)	105.0(4)
C(122)–Ru(12)–C(109)	97.9(5)	C(221)–Ru(22)–C(2014)	97.3(5)
C(122)–Ru(12)–C(1010)	90.7(4)	C(221)–Ru(22)–C(2013)	90.0(5)
C(122)–Ru(12)–C(1014)	174.4(4)	C(221)–Ru(22)–C(209)	173.7(5)
C(122)–Ru(12)–C(103)	112.2(5)	C(221)–Ru(22)–C(206)	112.8(5)
C(122)–Ru(12)–C(104)	83.2(5)	C(221)–Ru(22)–C(205)	84.1(5)
Ru(12)–C(122)–O(122)	177.3(11)	Ru(22)–C(221)–O(221)	177.3(12)

TABLE 6 (*Continued*)

The dimer ligand

Molecule (i)		Molecule (ii)	
C(102)–C(101)–C(108)	110.0(9)	C(207)–C(208)–C(201)	109.3(9)
C(102)–C(101)–C(1014)	104.9(8)	C(207)–C(208)–C(209)	106.5(10)
C(108)–C(101)–C(1014)	112.9(9)	C(201)–C(208)–C(209)	112.4(10)
C(101)–C(102)–C(103)	108.4(9)	C(208)–C(207)–C(206)	109.4(12)
C(101)–C(102)–C(1015)	110.7(9)	C(208)–C(207)–C(2016)	111.6(11)
C(103)–C(102)–C(1015)	117.8(10)	C(206)–C(207)–C(2016)	115.4(11)
C(102)–C(103)–C(104)	127.9(11)	C(207)–C(206)–C(205)	128.0(12)
C(103)–C(104)–C(105)	131.8(12)	C(206)–C(205)–C(204)	132.6(14)
C(104)–C(105)–C(106)	130.7(13)	C(205)–C(204)–C(203)	131.6(14)
C(105)–C(106)–C(107)	127.0(12)	C(204)–C(203)–C(202)	125.8(12)
C(106)–C(107)–C(108)	116.5(10)	C(203)–C(202)–C(201)	115.4(11)
C(106)–C(107)–C(1016)	102.2(10)	C(203)–C(202)–C(2015)	103.4(11)
C(108)–C(107)–C(1016)	115.7(11)	C(201)–C(202)–C(2015)	114.9(10)
C(107)–C(108)–C(101)	112.0(8)	C(202)–C(201)–C(208)	112.7(10)
C(107)–C(108)–C(109)	109.0(10)	C(202)–C(201)–C(2014)	109.3(9)
C(101)–C(108)–C(109)	113.0(9)	C(208)–C(201)–C(2014)	113.3(9)
C(108)–C(109)–C(1010)	128.5(10)	C(201)–C(2014)–C(2013)	127.8(11)
C(109)–C(1010)–C(1011)	130.8(10)	C(2014)–C(2013)–C(2012)	132.1(12)
C(1010)–C(1011)–C(1012)	125.6(9)	C(2013)–C(2012)–C(2011)	126.2(13)
C(1011)–C(1012)–C(1013)	124.3(11)	C(2012)–C(2011)–C(2010)	122.9(12)
C(1012)–C(1013)–C(1014)	125.0(11)	C(2011)–C(2010)–C(209)	127.3(11)
C(1013)–C(1014)–C(101)	115.6(9)	C(2010)–C(209)–C(208)	117.3(11)
C(102)–C(1015)–C(1016)	119.5(11)	C(207)–C(2016)–C(2015)	120.0(14)
C(107)–C(1016)–C(1015)	120.0(12)	C(202)–C(2015)–C(2016)	120.5(13)

butadiene fragment is itself extensively delocalised [C(2)–C(3) 1.422, C(3)–C(4) 1.414, C(4)–C(5) 1.425 Å] as is observed also, for example, in [$Ru(CO)_3(C_8H_8)$] [10] where the equivalent distances are 1.443, 1.394, and 1.443 Å.

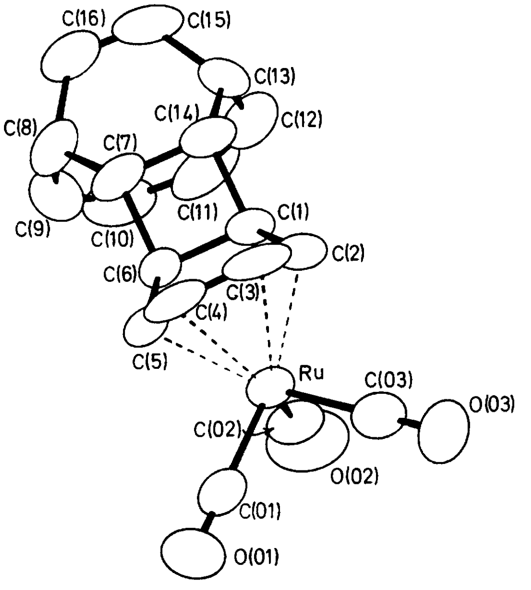

FIGURE 1 Molecular structure of [$Ru(CO)_3(C_{16}H_{16})$], showing the crystallographic numbering system

The saturated portion of the cyclohexadiene ring is at a dihedral angle of 141° with the butadiene moiety, and is *cis*-fused to a planar cyclobutane ring. This in turn is *cis*-fused in a 1,4 fashion to the cyclo-octatriene ring [C(8)—C(13), C(15), C(16)], giving rise to new six- and eight-membered rings. The molecule as a whole has an idealised plane of mirror symmetry through the ruthenium atom and bisecting all the rings (Figure 1). A view perpendicular to this mirror plane shows the folds between the successive rings (Figure 3). The computed dihedral angles are in Table 3. One implication of the presence of this mirror plane is that corresponding torsion angles for the two halves of the molecule should be equal in magnitude but opposite in sign. The extent to which this requirement is satisfied is revealed in Table 4.

The geometry of the η^4-bicyclo-octadiene fragment is closely similar to that found in both tricarbonyl(tricyclo-[6.2.0.0]deca-3,5-diene)iron, [$Fe(CO)_3(C_{10}H_{12})$],[11] and tricarbonyl(tricyclo[6.3.0.0]undeca-3,5-diene)iron, [$Fe(CO)_3(C_{11}H_{14})$],[12] but is significantly different from that in tricarbonyl(tricyclo[6.4.0.0]dodeca-3,5-triene)iron, [$Fe(CO)_3(C_{12}H_{16})$]; [13] here the cyclobutane ring is folded 15°

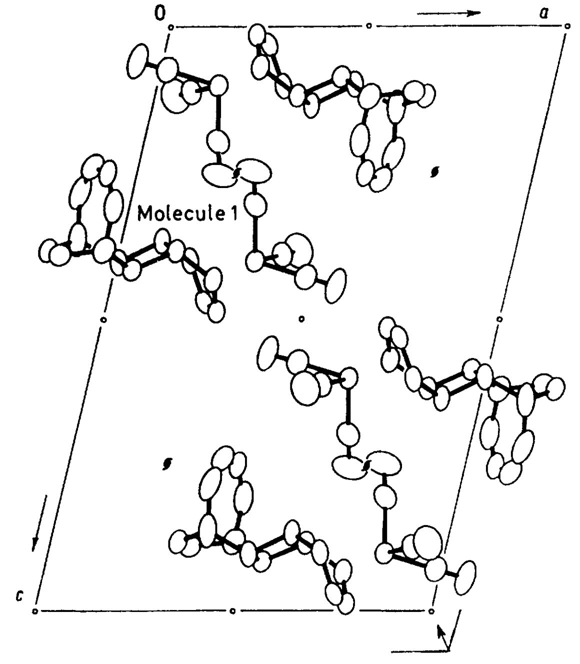

FIGURE 2 The contents of the monoclinic unit cell of [$Ru(CO)_3(C_{16}H_{16})$] seen in projection down *b* looking towards the origin

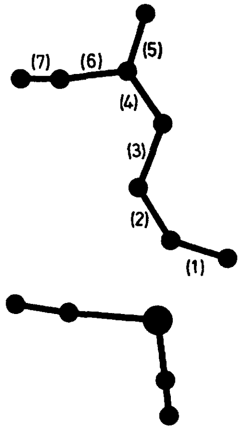

FIGURE 3 Cross section through the [Ru(CO)$_3$(C$_{16}$H$_{16}$)] molecule in its plane of mirror symmetry to show the dihedral angular relationships. Numbers in parentheses correspond to the least-squares planes in Table 3

along its diagonal to relieve strain from the twisted-chair cyclohexane ring to which it is fused. The mean C–C distance in the cyclobutane ring [1.558(11) Å] is very close to the estimated optimum value of 1.559(2) Å.[13]

The geometry of the C$_8$ ring approximates to that expected for the free cyclo-octatetraene dimer: the three C=C bonds [mean distance 1.30(1) Å] are significantly shorter than the other bonds in this ring and occur at C(9)–C(10), C(11)–C(12), and C(15)–C(16). The sequence C(8)–C(13) is approximately planar (Table 3).

The molecular structure of [Ru$_2$(CO)$_5$(C$_{16}$H$_{16}$)] (2) is given in Figure 4, together with the crystallographic numbering system. The contents of the monoclinic cell are in Figure 5, in which the two molecules of the crystallographic asymmetric unit labelled (i) and (ii) correspond to those whose co-ordinates are listed in Table 5. The unit cell contains, of course, four pairs of centrosymmetrically related molecules; (i) and (ii) are enantiomorphs related to one another as in (2).

Figure 4 shows that the ring systems have lost the simple mirror symmetry found in (1) and have become more contorted in order to bond to the two metal atoms. The C$_8$ section of the bifurcated ring system lies *endo* to the metal atoms so that η^2 bonding can be achieved between Ru(2) and C(03)–C(04).* The section of the ring C(02)–C(07) is substantially planar. All the other metal–carbon bonds are to the unbridged C$_8$ ring in the $\sigma:\eta^2:\eta^3$ manner shown in (2) and found also in [Ru$_2$(CO)$_6$(C$_8$H$_8$)] [14] and in [Fe$_2$(CO)$_6$(C$_8$H$_{10}$)].[15] In the case of [Ru$_2$(CO)$_5$(C$_{16}$H$_{16}$)], atom Ru(2) is σ-bonded to C(014) and η^2 bonded to C(09)–C(010), while Ru(1) is η^3-bonded to C(011)–C(013). All the bond lengths lie within the expected ranges, and there are no abnormally short intermolecular contacts. It is noteworthy that the hydrogen atoms attached to the bridgehead carbon atoms C(01) and C(08) are in a *cis,cis,anti* configuration with respect to the metal atoms and a *cis,cis,syn* configuration with respect to the double bond at C(015)–C(016). This is a conformation identical to that observed for the tricarbonyl complex (1). The Ru$_2$(CO)$_5$ fragment adopts an eclipsed (' sawhorse ') configuration with approximately orthogonal carbonyl groups (Table 6).

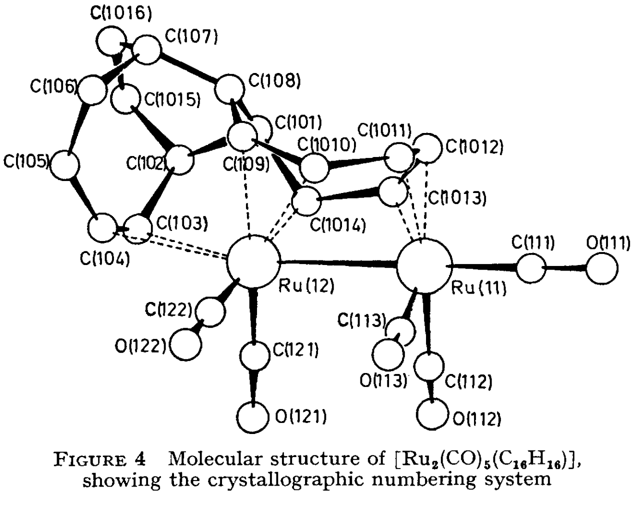

FIGURE 4 Molecular structure of [Ru$_2$(CO)$_5$(C$_{16}$H$_{16}$)], showing the crystallographic numbering system

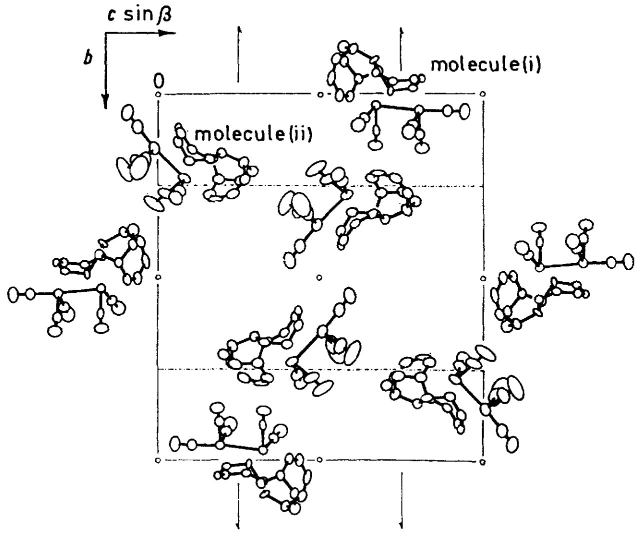

FIGURE 5 The contents of the monoclinic cell of [Ru$_2$(CO)$_5$-(C$_{16}$H$_{16}$)] seen in projection down *a* looking towards the origin. Molecules (i) and (ii) of the chosen crystallographic asymmetric unit are enantiomorphous

The ^{1}H n.m.r. spectrum of [Ru$_2$(CO)$_5$(C$_{16}$H$_{16}$)] between the limits of +100 and −30 °C shows changes [5] which are consistent with a (2a) $\rightleftharpoons$ (2b) interconversion. This fluxional process is, within the $\sigma:\eta^2:\eta^3$ bonded C$_8$ ring, similar to that postulated for [Ru$_2$(CO)$_6$(C$_8$H$_8$)] [14] and [Fe$_2$(CO)$_6$(C$_8$H$_{10}$)].[15]

The stereochemistry established here for the new cyclo-octatetraene dimers present in (1) and (2) provides valuable insight into the mechanism of formation of these dimers. A full discussion is given in ref. 5. The carbonylmetal groups appear to be able to sequester

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* In describing the molecule the numerical prefix 1 on all the atom numbers, indicative of molecule (i), has been omitted. In Table 6, corresponding values for bond distances and bond angles for molecules (i) and (ii) are listed in parallel for easy comparison.

(according to their electronic requirements) particular tautomers of the bicyclo-octadiene–cyclo-octatetraene system.

[8/1126 *Received*, 19*th June*, 1978]

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