Transition Metal Complexes of Cyclic π-Ligands. IV.* The Crystal and Molecular Structure of Bis(hexamethylbenzene)ruthenium(0), a Complex Containing a Bent *tetrahapto* Benzene Nucleus

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A three-dimensional X-ray structure analysis of bis(hexamethylbenzene)ruthenium(0), $C_{24}H_{36}Ru$, has been carried out. The crystals are monoclinic, space group $P2_1/c$ with $a = 15·508$, $b = 8·068$, $c = 16·734$ Å, $\beta = 90·00°$ and $Z = 4$. An approximate solution of the structure was obtained from data collected from a twinned or disordered crystal by standard procedures. The final solution is based on 2696 non-zero, independent structure factors obtained from measurements using two different untwinned crystals. Refinement of the structure by the least-squares method led to an agreement factor of $R_1 = 0·043$. The structure consists of discrete monomeric molecules. The two hexamethylbenzene rings are non-equivalent in the compound. One of them is planar and is bonded to the metal by six carbon–metal linkages. The other one is bent along the 1,4-axis by 42·8°. Only four adjacent carbon atoms are involved in bonding to the metal; they thus form a butadiene-like fragment. This fragment is nearly parallel to the planar ring. The remaining two ring carbon atoms are displaced from the 'butadiene' plane by equal amounts so that the contacts made by them to the metal atom are essentially non-bonding. The distance [1·33(1) Å] between these two carbon atoms corresponds to that of a pure double bond.

Introduction

Bis(hexamethylbenzene)ruthenium(0), $C_{24}H_{36}Ru$, has been prepared by Fischer & Elschenbroich (1970). If this complex were isostructural with bis-(π-arene)chromium compounds the electron configuration of the central atom would exceed the electron number of the noble gas Xe by two electrons. ¹H-n.m.r. spectroscopic investigations showed that the molecule exhibits fluxional behaviour in solution. Fischer & Elschenbroich inferred structures with one planar and one bent ring for the individual valence tautomeric forms. Thus the planar ring will formally donate six electrons to the central metal and the bent one only four as is common with butadiene complexes. The central metal will reach the inert gas electron configuration in this way.

Bending of a benzene nucleus along the 1,4 axis has already been observed for π-cyclopentadienylhexakis-(trifluoromethyl)benzenerhodium (Churchill & Mason, 1966) and for π-pentamethylcyclopentadienylhexakis-carbomethoxybenzene complexes of Rh and Ir (Kang, Childs & Maitlis, 1970). In these cases, however, the benzene nucleus is substituted by strongly electron withdrawing groups which may be supposed to have a determining influence on the structure of these compounds.

A similar possible influence seems unlikely for the permethylated benzene nuclei in bis(hexamethylbenzene)ruthenium(0). Therefore, the structure of this compound was determined in order to show that distortions of this kind are mainly due to the properties of the central metal and not to those of the groups substituting the benzene nucleus. A preliminary account of this work has already been published (Huttner, Lange & Fischer, 1971).

Crystal data

Bis(hexamethylbenzene)ruthenium(0), [$C_{24}H_{36}Ru$], M.W. 425·6. Diffraction symmetry $2/m$, monoclinic, $a = 15·508$ (10), $b = 8·068$ (8), $c = 16·734$ (12) Å, $\beta = 90·00$ (7)°, $V = 2094$ (5) Å³, $Z = 4$, $d_{calc} = 1·350$ (4), $d_{exp} = 1·339$ (10) g.cm⁻³ (measured by flotation in aqueous K_2HgI_4), space group $P2_1/c$ (C_{2h}^5, No. 14, *International Tables for X-ray Crystallography*), $F_{000} = 1472$, absorption coefficient $\mu = 8·13$ cm⁻¹ (for Mo $K\alpha$ radiation, $\lambda = 0·71069$ Å).

The determination of the structure

Preliminary investigations

In a first attempt to solve the structure orange-coloured needle-shaped crystals kindly supplied by Dr Elschenbroich were used. These had been grown from a concentrated solution of the compound in n-hexane by controlled cooling (Fischer & Elschenbroich, 1970). Precession photographs of the layers *nkl*, *hnl*, and *hkn* with *n*=0,1 revealed perfect orthorhombic diffraction symmetry (*mmm*), thus indicating an orthorhombic space group. Systematic absences occurred for:

(1)	*h0l*	$l = 2n + 1$
[(1a)	*0k0*	$k = 2n + 1$]
(2)	*hk0*	$h + k = 2n + 1$

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* Part III: G. Huttner & O.S. Mills, *Chem. Ber.* (1972), **105**, 301.

In addition, reflexions for which

$$(3) \qquad k+2l=4n+2$$

were found to be considerably weakened.

Conditions (1) and (2) are consistent with space groups Pmcn or $P2_1cn$ [standard setting Pnma (No. 62) and $Pna2_1$ (No. 33) respectively (International Tables for X-ray Crystallography, 1962)]. Comparison of the observed and calculated densities indicated four molecules per unit cell.

However, photographs of the hk0 layer taken with an exposure time ten times longer than usual showed some weak reflexions of the|type forbidden by condition (2). This observed violation of condition (2) might be explained by several arguments: If the 'forbidden' reflexions were due to multiple diffraction these could be neglected to a first approximation in solving the structure. Reasonable results should be expected for calculations based on space groups Pmcn or $P2_1cn$.

With the observed diffraction symmetry mmm only one space group [Pmcm, standard setting Pmma (No. 51)] would conform to the presence of extinction condition (1) alone. However, this space group is not a subgroup of Pmcn and therefore does not allow for an approximate diagonal glide as indicated by condition (2) for a structure not disordered with respect to the heavy atoms. A Patterson synthesis (see next section) clearly revealed a strictly ordered arrangement of the four ruthenium atoms in the unit cell. Thus space group Pmcn could definitely be excluded.

The only subgroup of Pmcn which indeed would allow for conditions (1) and [1(a)] as the sole strict extinction conditions is the monoclinic space group $P2_1/c$ (No. 14). As the diffraction symmetry observed for the crystals was mmm, the assumption of this space group necessarily implies the presence of either twinning or disorder of the light atoms or both. When examined under the polarizing microscope the crystals showed perfect optical extinction, as would be expected for a disordered arrangement of the molecules in space group $P2_1/c$. If the crystals were twinned, the law of twinning should be a very special one.

At this point we decided to try a solution of the structure in an orthorhombic space group and to delay all decisions concerning the problem of twinning or disorder. It was hoped that an approximate solution of the structure would perhaps yield further hints.

A crystal (approximate dimensions $0.39 \times 0.15 \times 0.45$ mm, longest axis parallel to b) was mounted in a thin-walled glass capillary in an atmosphere of dry, purified nitrogen. Diffraction intensities were measured at room temperature on a Stoe two-circle Weissenberg diffractometer using Zr-filtered Mo $K\alpha$ radiation. A scintillation counter was used and the pulse height discriminator of the Philips counting chain was set so as to receive 90% of the Mo $K\alpha$ radiation. Data were collected in the first octant of the reciprocal lattice in a range of $0 < \sin \theta/\lambda \leq 0.7$. Ten layers were measured (hnl, $0 \leq n \leq 9$). For the subsequent calculations only those

data were used for which the standard deviation based on counting statistics did not exceed 30% of the measured intensity. After Lorentz and polarization corrections the data were transformed to structure factors. Repeatedly measured reference reflexions showed that no decomposition of the crystal had occurredduring the period of exposure to X-rays.

A three-dimensional Patterson synthesis in space group Pmmm clearly revealed the positions of the heavy atoms. The value of $\frac{1}{4}$ was assigned to the x coordinate of the ruthenium atom. In the centric space group Pmcn this coordinate must necessarily have this value (which corresponds to the location of the heavy atom on a mirror plane); in the acentric space group $P2_1cn$ this value can be assigned to the x coordinate arbitrarily. The y coordinate was determined as $\frac{1}{8}$ and thus was completely consistent with the observed weakening condition (3) (see before). The z coordinate was determined as 0.110.

Subsequent Fourier syntheses led to a structural model which was in general agreement with the molecular conformation proposed by Fischer & Elschenbroich (1970). Isotropic least-squares refinement converged at $R_1 = 12\%$. Whereas distances and angles were reasonable for the final model, the temperature factors of all the light atoms assumed rather high values. A difference electron-density synthesis clearly demonstrated an elongation of almost all the light atom peaks in the x direction. This peak shape could not be explaned by rotational disorder of the benzene nuclei which is often observed with π-complexes of five-membered rings (see e.g. Bailey & Dahl, 1965; Hock & Mills, 1961). The acentric space group $P2_1cn$ had been excluded by Fourier syntheses phased with different acentric parts of the molecule. In all cases these syntheses had led to the centric arrangement already observed.

A disordered or twinned structure based on $P2_1/c$ was inferred from these experiments. As the refinement of the twinned structure could not be expected to yield parameters of the quality necessary for the discussion of the bonding in the complex we decided to tackle the problem by trying to obtain untwinned, ordered single crystals of the same compound.

Solution of the structure

The compound was prepared essentially following the method described by Fischer & Elschenbroich (1970). As high concentrations and low temperatures favour twinning we tried to grow crystals by sublimation of the compound in a high vacuum at temperatures between 60 and 90 °C. These experiments were unsuccessful, but we finally obtained good crystals by the diffusion method. The compound was dissolved in toluene and an excess of n-hexane was allowed to diffuse into the toluene solution at 20 °C. Four crystals were chosen from one preparation and examined by the precession method. All of them were found to exhibit monoclinic $(2/m)$ diffraction symmetry with the unique angle β

equal to 90° within the limits of error. Reflexion conditions (1) and (1a) were strictly obeyed thus uniquely establishing space group $P2_1/c$ (C_{2h}^5, No. 14, *Interna-*

Table 1. *Fractional coordinates and thermal parameters for the non-hydrogen atoms*

Standard deviations are given in parentheses; they refer to the least significant figure. The atomic numbering scheme refers to Fig. 1 throughout.

(a) The final coordinates and their standard deviations

	x/a	y/b	z/c
Ru	0·24752 (3)	0·12504 (6)	0·10806 (3)
C(11)	0·3086 (5)	−0·0760 (8)	0·2496 (4)
C(61)	0·3733 (7)	−0·1226 (15)	0·3130 (5)
C(12)	0·3392 (4)	−0·0372 (9)	0·1675 (4)
C(62)	0·4363 (5)	−0·0094 (13)	0·1565 (7)
C(13)	0·2956 (4)	−0·1157 (9)	0·1035 (4)
C(63)	0·3400 (7)	−0·2006 (11)	0·0323 (6)
C(14)	0·2054 (4)	−0·1289 (9)	0·1107 (3)
C(64)	0·1485 (6)	−0·2113 (10)	0·0505 (6)
C(15)	0·1737 (4)	−0·0444 (9)	0·1835 (4)
C(65)	0·0780 (5)	−0·0237 (12)	0·1941 (6)
C(16)	0·2236 (5)	−0·0803 (8)	0·2582 (4)
C(66)	0·1769 (7)	−0·1316 (14)	0·3337 (5)
C(21)	0·2946 (4)	0·3911 (8)	0·1241 (4)
C(71)	0·3542 (7)	0·4568 (13)	0·1866 (7)
C(22)	0·3286 (4)	0·3191 (8)	0·0511 (5)
C(72)	0·4242 (6)	0·3288 (12)	0·0320 (8)
C(23)	0·2729 (6)	0·2577 (9)	−0·0085 (4)
C(73)	0·3073 (9)	0·1932 (14)	−0·0881 (5)
C(24)	0·1827 (5)	0·2605 (9)	0·0061 (5)
C(74)	0·1207 (8)	0·1960 (14)	−0·0584 (6)
C(25)	0·1514 (4)	0·3185 (9)	0·0767 (5)
C(75)	0·0535 (5)	0·3343 (13)	0·0909 (7)
C(26)	0·2043 (4)	0·3823 (9)	0·1370 (4)
C(76)	0·1659 (7)	0·4615 (13)	0·2120 (6)

tional Tables for X-ray Crystallography, 1962). Conditions (2) and (3) now both appeared as weakening rules corresponding to a rather special distribution of the heavy atoms. Obviously the ruthenium atoms were distributed in a nearly perfect orthorhombic arrangement with $x = \frac{1}{4}$ since for many reflexions $|F|_{hkl} \simeq |F|_{\bar{h}kl}$ was still observed. Weakening condition (3) is a consequence of the ruthenium atom having $y \simeq \frac{1}{8}$. The apparent *mmm* Laue symmetry observed with the formerly used crystals now could be definitely ascribed to twinning or disorder such that reflections hkl and $\bar{h}kl$ coincide. This explanation was further substantiated by the final solution of the untwinned structure (see below). Similar phenomena are not too uncommon with nearly orthorhombic structures (*e.g.* Dunitz, 1964).

Two crystals (bound by $\{102\}$ and $\{221\}$) were mounted in thin-walled glass capillaries in an atmosphere of dry purified nitrogen. Lattice constants were determined from precession photographs and were found to be identical within the limits of error with the ones obtained from the twinned crystals.

In general, the collection of data proceeded in the same way as described above with the exception that a graphite monochromator was used to eliminate the white radiation. From the first crystal ($0.38 \times 0.25 \times 0.4$ mm, longest dimension parallel to **a**) ten layers were measured (nkl, $0 \le n \le 9$), the second crystal ($0.13 \times 0.33 \times 0.55$ mm, longest dimension along **b**) was used to collect intensities in the layers hnl, $0 \le n \le 17$. A range of $0 < \sin\theta/\lambda \le 0.77$ was covered. Lorentz, polarization and empirical absorption cor-

Table 1 (*cont.*)

(b) The final anisotropic thermal parameters and their standard deviations. All values $\times 10^4$. The temperature factor is of the form:

$$T = \exp\left[-(h^2 b_{11} + k^2 b_{22} + l^2 b_{33} + 2hk b_{12} + 2hl b_{13} + 2kl b_{23})\right].$$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ru	19 (0)	83 (1)	21 (0)	−2 (0)	0 (0)	4 (0)
C(11)	44 (3)	119 (12)	30 (3)	0 (5)	−14 (2)	2 (4)
C(61)	86 (6)	242 (19)	49 (4)	9 (11)	−36 (4)	11 (9)
C(12)	25 (2)	122 (11)	39 (3)	0 (4)	−9 (2)	22 (5)
C(62)	25 (3)	273 (21)	81 (6)	7 (6)	−9 (3)	52 (9)
C(13)	38 (3)	71 (9)	29 (2)	21 (5)	5 (2)	25 (4)
C(63)	86 (6)	154 (14)	47 (4)	43 (8)	23 (4)	4 (6)
C(14)	40 (3)	71 (8)	29 (2)	−9 (5)	−3 (2)	0 (5)
C(64)	72 (5)	118 (13)	55 (4)	−25 (7)	−23 (4)	8 (6)
C(15)	24 (2)	123 (11)	35 (3)	−1 (4)	5 (2)	16 (4)
C(65)	29 (3)	242 (19)	74 (5)	0 (6)	15 (3)	61 (8)
C(16)	62 (4)	97 (11)	19 (2)	6 (5)	4 (2)	7 (4)
C(66)	103 (6)	232 (18)	31 (3)	−3 (11)	25 (4)	13 (8)
C(21)	48 (3)	57 (9)	37 (3)	−15 (5)	−16 (2)	8 (4)
C(71)	83 (6)	184 (17)	73 (6)	−52 (9)	−41 (5)	23 (8)
C(22)	32 (3)	95 (10)	55 (4)	−4 (4)	13 (3)	26 (5)
C(72)	40 (4)	194 (20)	129 (9)	−12 (7)	31 (5)	44 (10)
C(23)	78 (5)	102 (12)	27 (3)	7 (6)	15 (3)	3 (4)
C(73)	128 (9)	277 (22)	28 (3)	10 (11)	27 (4)	6 (7)
C(24)	47 (4)	112 (12)	42 (3)	−13 (5)	−13 (3)	26 (5)
C(74)	101 (7)	246 (20)	57 (5)	−16 (10)	−47 (5)	21 (8)
C(25)	26 (3)	121 (11)	47 (3)	9 (4)	−5 (2)	29 (5)
C(75)	35 (3)	221 (21)	102 (7)	23 (7)	1 (4)	38 (9)
C(26)	50 (3)	96 (10)	31 (2)	18 (6)	8 (2)	25 (5)
C(76)	92 (6)	208 (18)	47 (4)	51 (9)	19 (4)	1 (7)

rections (North & Phillips, 1968) were applied to the data. 58 weak and 14 very strong reflexions were discarded after a critical inspection of the graphical records prepared during the intensity measurements. The two sets of data were then brought to a common scale ($R_1 = 0.026$). At a later stage another 34 weak reflexions which obviously suffered from multiple diffraction inherent in the Weissenberg setting used were discarded. The remaining 2969 independent non-zero structure factors form the basis of this structure determination.

The structure was solved by the heavy atom method and refined by least squares. At the stage of refinement at which $R_1 = 0.073$, a difference Fourier synthesis showed the positions of most of the hydrogen atoms. Their coordinates were fitted to the positions found for them by a least-squares procedure with the constraint of tetrahedral symmetry around the methyl carbon atoms and a C–H bond length of 1·08 Å (r.m.s. deviation: 0·19–0·64 Å). By insertion of the hydrogen atoms R_1 was reduced to 0·069. Anisotropic refinement of all except the hydrogen atoms converged

Table 2. *Hydrogen atom coordinates*

The hydrogen atom positions were fitted to electron density peaks from difference Fourier syntheses by a least squares procedure assuming a C–H bond length of 1·08 Å and tetrahedral bonding angles (109·5°). The first two digits of a hydrogen atom label refer to the carbon atom to which it is bonded.

	x/a	y/b	z/c
H(611)	0·4325	−0·0553	0·3032
H(612)	0·3478	−0·0919	0·3712
H(613)	0·3859	−0·2541	0·3100
H(621)	0·4505	0·0064	0·0938
H(622)	0·4558	0·1003	0·1888
H(623)	0·4712	−0·1153	0·1792
H(631)	0·3019	−0·1824	−0·0209
H(632)	0·4033	−0·1476	0·0237
H(633)	0·3462	−0·3317	0·0442
H(641)	0·1070	−0·1200	0·0233
H(642)	0·1879	−0·2687	0·0049
H(643)	0·1099	−0·3047	0·0795
H(651)	0·0655	0·0829	0·2314
H(652)	0·0480	−0·0059	0·1365
H(653)	0·0516	−0·1331	0·2221
H(661)	0·2233	−0·1620	0·3794
H(662)	0·1367	−0·0306	0·3540
H(663)	0·1371	−0·2385	0·3215
H(711)	0·4197	0·4239	0·1717
H(712)	0·3484	0·5900	0·1896
H(713)	0·3375	0·4038	0·2439
H(721)	0·4454	0·2125	0·0068
H(722)	0·4355	0·4273	−0·0104
H(723)	0·4599	0·3534	0·0862
H(731)	0·2758	0·0774	−0·1026
H(732)	0·2941	0·2828	−0·1345
H(733)	0·3759	0·1736	−0·0837
H(741)	0·0573	0·2472	−0·0486
H(742)	0·1438	0·2327	−0·1167
H(743)	0·1175	0·0624	−0·0553
H(751)	0·0401	0·3237	0·1540
H(752)	0·0315	0·4533	0·0695
H(753)	0·0203	0·2368	0·0591
H(761)	0·2074	0·4364	0·2626
H(762)	0·1607	0·5937	0·2035
H(763)	0·1028	0·4102	0·2232

at $R_1 = 0.043$. The least-squares matrix was approximated by two large blocks each corresponding to the parameters of one ring. The metal atom was exchanged between the two after each cycle. The maximum shift over error was 0·02 for the last cycle. The final difference electron density map showed a random electron density fluctuation reaching maxima of ± 0.7 e.Å^{-3} at positions having no relation to the geometry of the molecule. The final coordinates and temperature factors for the non-hydrogen atoms are shown in Table 1. The coordinates of the hydrogen atoms are given in Table 2. The observed and calculated structure factors are given in Table 3.

Spectroscopic measurements

Since it is known that the preparation of the complex may be accompanied by demethylation of the hexamethylbenzene ligand (Fischer & Elschenbroich, 1970), a mass spectrum was kindly taken by Dr J. Müller. It indicated that no detectable demethylation had occurred for the crystals used. For an independent test of the purity of the compound we refined the site occupation numbers of the methyl carbons in addition to their thermal and positional parameters. The refined site occupation numbers were equal to unity within one standard deviation and did not show any systematic trend. It follows that the positional and thermal parameters were equally unaltered.

As the molecule shows fluxional behaviour in solution (Fischer *et al.*) we were interested in the activation energy of the rearrangement process. ^{1}H-n.m.r. spectra of the compound in the temperature range of −20 to +40°C were kindly measured by Dr C. G. Kreiter on a Varian A60 spectrometer. We did a line-width analysis of the spectrum and obtained an energy barrier of 10 ± 3 kcal.mole^{-1} (for details of the method see *e.g.* Pople, Schneider & Bernstein, 1959).

Programs

All calculations were performed on a Telefunken TR440 computer using the programming system *TUMXR* written by Huttner, Lange & Krieg (1971). The Fourier program and the program for the evaluation of best planes utilized by this system are modified local versions of algorithms developed at the University of Manchester. The least-squares program *TUMLS* was written by Huttner, Schelle & Berghammer (1970). It allows for the use of blocked matrices of any dimension from the diagonal to the full-matrix approximations and at the same time automatically applies all constraints imposed by any space group symmetry. The program includes a function and error calculation part. The scaling program *TUMSC* was written by Huttner (1970*a*) according to the method of Hamilton, Rollett & Sparks (1965). The graphical representations were performed on a Benson plotter using the program *TUMGR* written by Huttner (1970*b*). All the remaining calculations were made with programs written by members of this group.

Table 3. *Observed and calculated* $|F|$ $(\times 10)$

The molecular structure

Bis(hexamethylbenzene)ruthenium(0) exists in the solid state as discrete monomeric molecules. The conformation of the complex is shown in Fig. 1. The two rings are non-equivalent in the compound; one of the benzene nuclei is bonded by all six carbon atoms in the manner commonly found in π-benzene metal complexes, the other is bound by a sequence of only four carbon atoms. The molecule as a whole has approximate mirror symmetry: this mirror is plane D of Table 4. (Atom labels refer to Fig. 1 throughout). Selected bond distances, contact distances and angles are shown in Table 5.

Table 4. Least-squares planes and deviations

The direction cosines refer to natural axes.

Plane A

Defined by atoms: C(11), C(12), C(15), C(16)
Direction cosines: 0·0006, 0·9746, 0·2238
Distances of atoms from plane:

C(11)	0·0014	C(61)	−0·1274
C(12)	−0·0007	C(62)	0·1774
C(13)	−0·8586	C(63)	−1·7923
C(14)	−0·9362	C(64)	−1·8100
C(15)	0·0007	C(65)	0·2027
C(16)	−0·0014	C(66)	−0·1225
Ru	1·0512		

Plane B

Defined by atoms: C(12), C(13), C(14), C(15)
Direction cosines: 0·0796, −0·8665, 0·4928
Distances of atoms from plane: see Fig. 4(a).

Plane C

Defined by atoms: C(21), C(22), C(23), C(24), C(25), C(26)
Direction cosines: 0·0720, −0·9078, 0·4132
Distances of atoms from plane: see Fig. 2(a).

Plane D

Defined by all non-hydrogen atoms
Direction cosines: −0·1333, −0·7022, −0·6994
Distances of atoms from plane:

C(11)	0·6060	C(16)	−0·7173
C(12)	1·2911	C(15)	−1·2825
C(13)	0·8160	C(14)	−0·5809
C(21)	0·6459	C(26)	−0·7674
C(22)	1·3803	C(25)	−1·4000
C(23)	0·7047	C(24)	−0·7158
Ru	0·0217		

Dihedral angles between planes:

A∧B	137·2°	A∧C	142·4°
B∧C	5·2	C∧D	70·2

The planar hexamethylbenzene ring

One of the hexamethylbenzene rings bonded to the central metal is approximately planar. Fig. 2(a) shows the deviations of all twelve carbon atoms from the best molecular plane defined by the six ring carbon atoms (r.m.s. deviation 0·009 Å). By the steric or electronic influence of the metal atom, the methyl

groups are slightly forced out of the plane of the aromatic ring in a direction opposite to the metal atom. The deviations from planarity are small (maximum about 4°) and with the exception of C(71) are all in the

Table 5. Selected distances and angles

Standard deviations are given in parentheses; they refer to the least significant digit. Only values not given in the figures are presented.

(a) Bonding distances		(b) Bonding angles	
Ru——C(12)	2·173 (6) Å	C(12)-Ru——C(15)	72·6(2)°
Ru——C(13)	2·082 (7)	Ru——C(12)-C(11)	110·0(4)
Ru——C(14)	2·151 (7)	Ru——C(12)-C(62)	120·0(5)
Ru——C(15)	2·185 (6)	Ru——C(12)-C(13)	67·2(3)
Ru——C(21)	2·283 (6)	Ru——C(15)-C(16)	109·4(4)
Ru——C(22)	2·223 (6)	Ru——C(15)-C(65)	121·1(5)
Ru——C(23)	2·259 (7)	Ru——C(15)-C(14)	68·8(3)
Ru——C(24)	2·262 (7)		
Ru——C(25)	2·221 (6)		
Ru——C(26)	2·234 (7)	(d) Contact angles	

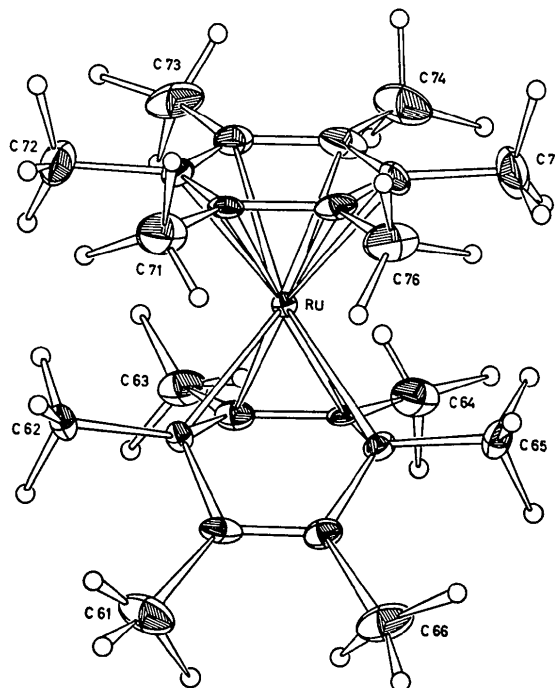| (c) Contact distances			
		C(61)-C(62)-C(63)	107·0 (4)°
		C(62)-C(63)-C(64)	116·2 (4)
Ru——C(11)	3·023 (7) Å	C(63)-C(64)-C(65)	115·0 (4)
Ru——C(16)	3·032 (6)	C(64)-C(65)-C(66)	107·1 (4)
C(12)-C(15)	2·581 (8)	C(65)-C(66)-C(61)	115·0 (3)
C(22)-C(25)	2·782 (9)	C(66)-C(61)-C(62)	116·0 (3)
		C(71)-C(72)-C(73)	120·0 (4)
		C(72)-C(73)-C(74)	119·5 (4)
		C(73)-C(74)-C(75)	119·9 (4)
		C(74)-C(75)-C(76)	121·6 (4)
		C(75)-C(76)-C(71)	119·7 (4)
		C(76)-C(71)-C(72)	119·2 (4)

Fig. 1. The molecular geometry of bis(hexamethylbenzene)-ruthenium(0): The 68% probability vibrational ellipsoids are at the scale of the molecule. The name of a ring carbon atom to which a methyl group with the central atom. C(mn) is bonded is given by C(m − 5)n.

same sense. Similar features were found in (hexamethyl-benzene)tricarbonylchromium (Bailey & Dahl, 1965) and are quite common with arenes π-bonded to a transition metal (Wheatley, 1967).

Fig. 2(b) shows the molecular parameters found for the planar ring. The six C–C distances within the benzene nucleus range from 1·361 (11) to 1·453 (11) Å. The average C–C$_{ring}$ bond length (1·410 Å) is in good agreement with the mean separation of the ring carbon atoms found in (hexamethylbenzene)tricarbonyl-chromium (1·42 Å, Bailey & Dahl, 1965) and dibenzenechromium (1·42 Å, Keulen & Jellinek, 1966).

The pattern of C–C distances within the ring seems to indicate some distortion of the aromatic nucleus from hexagonal symmetry in this compound. There is one extremely long [1·453 (11) Å] bond between atoms C(21) and C(22) and opposite to it a rather short

distance between C(24) and C(25) [1·361 (11) Å] whereas the remaining distances are equal to within 0·02 Å. Consistent with the large distance between C(21) and C(22) the methyl carbon atoms linked to these atoms show the largest separation between two neighbouring methyl groups in this ring. The symmetry of this distortion does not coincide with the approximate overall symmetry of the molecule.

The standard deviations for the C–C bonds derived from the partitioned least-squares moment matrix (see experimental section) are about 0·01 Å. If the values found for the distances of the methyl carbons to the carbon atoms of the planar benzene nucleus are taken as a sample of one distribution we get an average value of 1·524 Å for these bond lengths. The standard error of a single observation is then estimated as 0·017 Å (95% confidence interval $0·004 \le \sigma \le 0·0172$ Å by χ^2). The e.s.d.'s derived from the least-squares calculations thus would seem somewhat low as is frequently observed in single-crystal diffraction studies (Hamilton, 1965). The hypothesis that the long bond distance of 1·453 Å and the short one of 1·361 Å are from a normal population with a mean value of 1·41 Å and a standard deviation of 0·017 Å can be rejected at 2·5% and 1·0% significance levels respectively.

The Ru–C$_{ring}$ distances average at 2·25 Å. Again the individual values appear to vary significantly: three of them are identical (2·22 Å), the bonds Ru–C(23) and Ru–C(24) seem to be somewhat lengthened (2·26 Å both) and C(21) is the most distant of the ring carbon atoms involved in bonding to the metal (2·28 Å). The long distances of C(23) and C(24) to the ruthenium atom might be explained by steric crowding, although this argument does not hold for C(21).

It is obvious that the field induced to the metal by the bent hexamethylbenzene ring has at most m (C_s) symmetry and that an axially symmetric bonding of the metal to the planar ring can therefore not be expected. However, the observed deviations from axially symmetric bonding do not seem to conform even approximately to any symmetry higher than 1 (C_1). Similar seemingly irregular deviations among bond lengths which would be expected to be equal for chemical reasons are also found for the bonds between the bent ring and the metal atom. In view of the reported standard deviations the observed differences among bond lengths which seem to be comparable for chemical reasons are at least partially to be taken as real.

An explanation for the observed asymmetry may be found in the low internal conformational potential of the molecule. The molecule shows fluxional behaviour in solution (Fischer & Elschenbroich, 1970) which corresponds to a transition between the twelve valence tautomeric forms characterized by one planar and one bent ring. The activation energy for the rearrangement process has been determined as only 10 ± 3 kcal.mole^{-1} by an Arrhenius plot (see experimental section). This is far less than the activation energy of 20 kcal.mole^{-1} observed for the rearrangement of the bent benzene
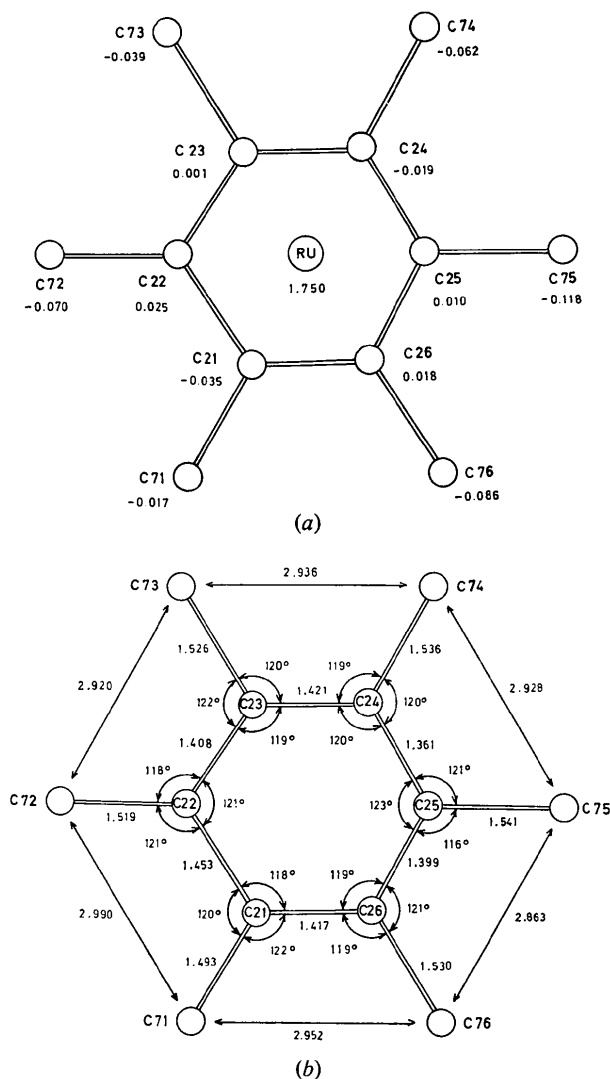

Fig. 2. (a) Deviations (in Å) from the mean plane formed by the six carbons of the planar ring. (b) Parameters found for the planar ring.

nucleus in π-pentamethylcyclopentadienylhexakis-carbomethoxybenzenerhodium (Kang *et al.*, 1970) and would suggest different mechanisms for the rearrangement processes in the two compounds [1,2 shifts in the rhodium compound, 1,2 shifts and/or concerted movement of the two rings in bis(hexamethylbenzene)-ruthenium(0)]. The determined activation energy, however, is well within the range of lattice energies observed for comparable complex molecules, *e.g.* 13·4 kcal.mole^{-1} for bis(hexamethylbenzene)chromium(0) (Röhrscheid, 1964) and 15·4 kcal.mole^{-1} for bis-(mesitylene)chromium(0) (Fischer, Schreiner & Reck-ziegel, 1961). Thus it cannot be excluded that the geometry found for bis(hexamethylbenzene)ruthenium-(0) in the solid state does not exactly correspond to the equilibrium configuration of the free molecule. Furthermore, if we assume a synchronous mechanism for the transition from one tautomeric form to another we should expect a strong mutual dependence of the distances and angles in one ring with respect to the geometry of the other. The same argument then applies to the interdependence of metal to carbon distances for the two hexamethylbenzene moieties. It appears therefore that a slight variation from the equilibrium conformation induced on one point of the molecule will also influence the geometry of other parts of the complex. We thus feel that these arguments might explain most of the unexpected minor deviations from the idealized symmetric geometry in the present complex.

It is worth while noting that the energy barrier observed for the rearrangement process is far less than the difference in the energies of a bent and a planar hexamethylbenzene ring. A *MINDO*-2 calculation based on the positional parameters found for the planar and the bent ring in the complex gave 36·2 kcal.mole^{-1} as the difference between the energies of the two ring conformations. A simple Hückel approximation leads to a value of 1·52 β for the separation of a benzene nucleus into a butadiene and an ethylene fragment. For $\beta = 20$ kcal (Cotton, 1963) these estimates correspond closely.

The distance of the ruthenium atom from the best plane defined by the carbon atoms of the benzene nucleus is 1·75 Å. It is much shorter than the corresponding value reported for bis(cyclopentadienyl)-ruthenium (1·84 Å, Hardgrove & Templeton, 1959) whereas the mean Ru–C$_{ring}$ distances are comparable. They amount to 2·21 Å in Ru(C$_5$H$_5$)$_2$ and to 2·25 Å in the present structure. This reflects the purely geometrical requirements for locating a metal atom above ring systems of different size (Wheatley, 1967).

The non-planar hexamethylbenzene ring

The non-planar hexamethylbenzene ring [atoms C(11) to C(16) and C(61) to C(66)] is eclipsed with respect to the planar one. A schematic sketch of the molecule (Fig. 3) gives a clear idea of the conformation observed for this ring. It is bonded to the metal by only four carbon atoms [C(12), C(13), C(14), and C(15)] which
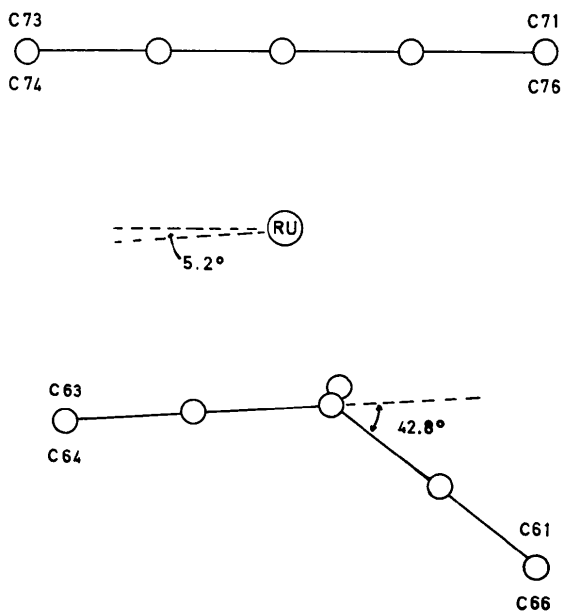
Fig. 3. Schematic sketch of the molecule as seen from the side.

are coplanar to within 0·009 Å (Fig. 4a) and is bent along the axis C(12)–C(15) so as to assume an essentially non-planar conformation.

The plane defined by atoms C(11), C(12), C(15), and C(16) (r.m.s. deviation 0·001 Å) is inclined to the plane defined by the bonded atoms. The angle of tilt (42·8°) is only slightly smaller than the corresponding one reported for the hexakis(trifluoromethyl)benzene ring in [(CF$_3$)$_6$C$_6$] (C$_5$H$_5$)Rh where the perfluorinated analogue of hexamethylbenzene is bonded to the metal in rather the same fashion (Churchill & Mason, 1963, 1966). However, whereas in the rhodium complex the bending of the benzene nucleus has been ascribed at least partially to the strong electron-withdrawing influence of the fluorine atoms (Churchill & Mason, 1963; Mingos, 1971) the present structure shows that it is probably a consequence of the 'inert gas rule' alone. The metal reaches the inert gas electron configuration by taking 6 π-electrons from the planar and 4 π-electrons from the bent ring in the ruthenium complex. In the rhodium compound 5 electrons from the cyclopentadienyl radical and 4 electrons from the bent six-membered ring together with the electrons of the metal give a total of 54 electrons corresponding to the electron number of xenon.

The distances between the ruthenium atom and the carbon atoms C(11) and C(16) are 3·023 (7) and 3·032 (6) respectively, and are thus essentially non-bonding contacts. This conclusion is confirmed by the pattern of distances and angles observed for the bent ring [Fig. 4(b)]; the distance C(11)–C(16) of 1·327 (10) Å is in close agreement with the C=C double bond distance (1·330–1·335 Å) reported for ethylene (Lide, 1962). However, the environment of these carbon atoms deviates slightly from planarity; the methyl

carbon atoms C(61) and C(66) are bent out of the plane defined by C(11), C(12), C(15), and C(16) by 4·9 and 4·6° respectively. The distances C(11)–C(12) of 1·487 (10) Å and C(15)–C(16) of 1·498 (10) Å average at 1·49 Å thus indicating a π-bond order of approximately zero for these bonds.

The part of the ring which is bonded to the metal atom may roughly be classified as a butadiene moiety. However, the individual C–C distances deviate from the symmetric pattern expected for a complexed butadiene; the central bond C(13)–C(14) (1·408 (8) Å) is the shortest, the distance C(12)–C(13) at 1·415 (10) Å is only marginally longer than this, whereas the bond C(14)–C(15) at 1·480 (9) Å seems to be significantly lengthened with respect to the other two distances. The distance between the methyl carbon atoms, C(64) and C(65), which are linked to the 'long' bond is correspondingly large [Fig. 4(b)].

Some general trends have been observed for complexed butadiene-like ligands and some implications with respect to the bonding in these complexes have been given (Churchill & Mason, 1967). It is generally noted that the distance between the terminal carbon atoms of the butadiene moiety is decreased in the complex with respect to the free ligand. This fact has been explained as a consequence of maximizing overlap between the orbitals on the terminal carbons and the metal d orbitals (Churchill, 1965). Correspondingly, the internal angles are generally less than 120° in complexed, butadiene-like fragments. In the present complex these angles are 116·3 (6) and 111·5 (5)° whose average of 113·9° is considerably less than the value of 120° expected for an sp^2-hybridized carbon atom. The distance [2·581 (8) Å] between the terminal carbon atoms C(12) and C(15) is markedly shorter than the average 1,4 distances in the planar hexamethylbenzene ring (2·82 Å).

It is also generally observed that the overlap between the orbitals of the terminal carbon atoms and the metal atom is further increased in these complexes by a rotation about the terminal C–C bonds. In sorbic acid iron tricarbonyl, for instance, a twisting of 9° about the terminal bonds has been reported (Eiss, 1970). In the present complex the torsion angles C(62)–C(12)–C(13)–C(14) and C(65)–C(15)–C(14)–C(13) are 15° and 9° respectively.

In all butadiene complexes in which the butadiene fragment is part of a cyclic ligand the non-coordinated part of the ligand is bent away from the metal as is observed for the compound studied here. As a general rule it has been noted that the bonds from the metal to the terminal carbon atoms of the butadiene ligand are longer than those to the central ones (Robson & Truter, 1968). This rule is also obeyed by the present complex; the terminal carbon atoms C(12) and C(15) are bonded to the metal at 2·173 (6) and 2·185 (6) Å respectively. The central carbon atom C(13) is at a distance of 2·08 (7) Å from the central metal. The distance Ru–C(14), however, although still shorter than the average Ru–C$_{terminal}$ distance (2·18 Å) is considerably longer [2·151 (7) Å]. It is worth while noting that this comparably long Ru–C bond is *trans* to the longest bond made from the metal to the planar ring: Ru–C(21) at 2·283 (6) Å which is at the same time the longest Ru–C bond in the complex. Adjacent to the carbon atoms which are involved in these long Ru–C bonds we find the considerably lengthened C–C bonds C(21)–C(22), and C(14)–C(15).

The average Ru–C distance to the atoms of the planar ring amounts to 2·25 Å; the mean distance of the 'butadiene' carbon atoms from the metal is only 2·15 Å. It is thus considerably shorter than the average Ru–C distance in (cyclooctatetraene)tricarbonylruthenium (Cotton & Eiss, 1969) amounting to 2·23 Å. The observed shortening may be ascribed to enhanced backbonding to the butadiene moiety in the present complex due to the absence of strongly backbonding
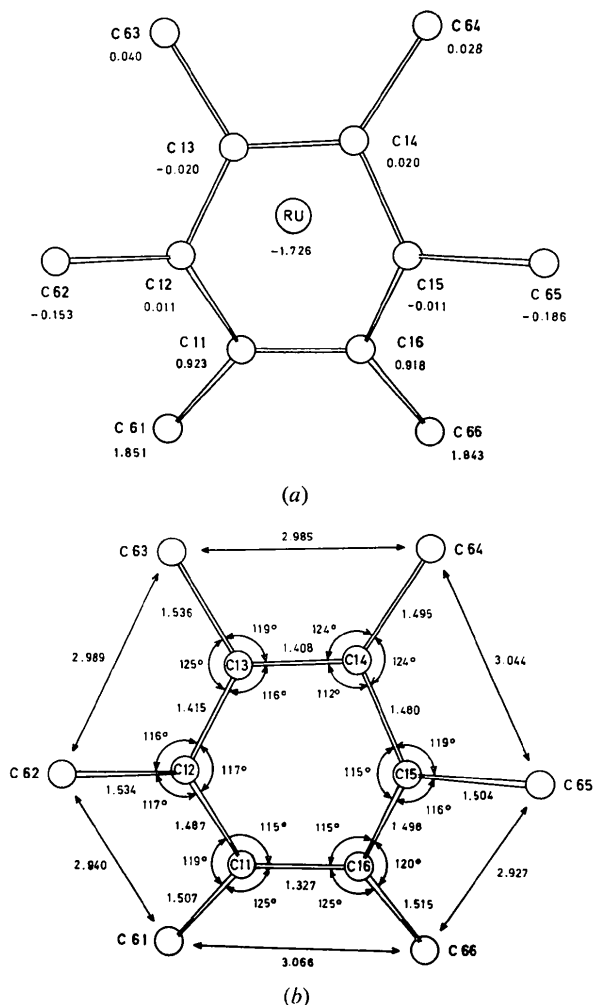

Fig. 4. (a) Deviations (in Å) from the mean plane formed by the four carbon atoms of the 'butadiene' moiety, C(12), C(13), C(14), and C(15). (b) Parameters observed for the bent ring.

carbonyl groups. This corresponds to the observed shortening of Cr–C bonds when going from (benzene)-tricarbonylchromium (Bailey & Dahl, 1965; average Cr–C$_{ring}$ distance 2·22 Å) to dibenzenechromium (average Cr–C$_{ring}$ distance 2·14 Å; see, *e.g.* Keulen & Jellinek, 1966).

The distance of the metal atom from the plane defined by the four carbon atoms of the butadiene fragment is, at 1·73 Å, only marginally shorter than the distance of the ruthenium atom to the planar ring (1·75 Å). The considerable difference between the lengths of the bonds made from the metal atom to the carbon atoms of the two ligands (see above) is obviously largely compensated for by their different geometries. The planar parts of the two ligand systems which are directly involved in bonding to the metal are nearly parallel to each other (dihedral angle 174·8°).

As with the planar benzene nucleus the methyl groups bonded to the central atoms C(13) and C(14) of the butadiene fragment are bent away from the metal by about 1·5°.

The methyl groups

The relative orientations of the methyl groups as inferred from the final difference Fourier synthesis are shown in Fig. 5. As expected the accuracy obtained for these parameters is not very good. This is evidenced by some rather short distances between hydrogen atoms of neighbouring methyl groups especially for the planar ring. Free rotation for all of the methyl groups, however, is in clear contrast to the observed difference electron density distribution. In this context it may be noted that heat capacity measurements (Pauling, 1930) as well as ^{1}H-n.m.r. results (Andrew, 1950) and ultra-violet spectra of crystalline hexamethylbenzene (Schnepp, 1958) have been interpreted in terms of an

onset of free rotation of the methyl groups at about 100°K. A rotational disorder is also probable in the case of crystalline (hexamethylbenzene)tricarbonyl-chromium (Bailey & Dahl, 1965).

Analysis of thermal vibration

Fig. 1 shows the thermal vibrational ellipsoids of the molecule. The overall symmetry of the thermal motions closely corresponds to the idealized mirror symmetry of the molecule. The Ru atom moves nearly isotropically. Its vibrational amplitudes are far smaller than those of the ring carbon atoms, and the motion of the methyl groups is still more pronounced. The vibrations of the bent nucleus closely resemble those in (cyclooctatetraene)tricarbonylruthenium (Cotton & Eiss, 1969). The longest axes of the thermal ellipsoids for the atoms C(13) and C(14), and for the carbon atoms of the 'ethylene' fragment are nearly parallel to their coordination planes, whereas the terminal carbon atoms C(13) and C(14) have their largest components out of the butadiene plane. The same pattern of thermal motions is observed for the surrounding methyl groups. A rigid body model thus does not seem to be an appropriate approximation for a more detailed analysis of the thermal motions.

Packing considerations

The packing of the molecule in the crystal is demonstrated in Figs. 6 and 7. The molecules are held together by mere van der Waals forces and form layers at $x = \pm \frac{1}{4}$ (see Fig. 7). The planes $x = \pm \frac{1}{4}$ are only approximate mirror planes with respect to the individual molecules as well as to the whole structure. They would be exact if the space group were *Pmcn*.
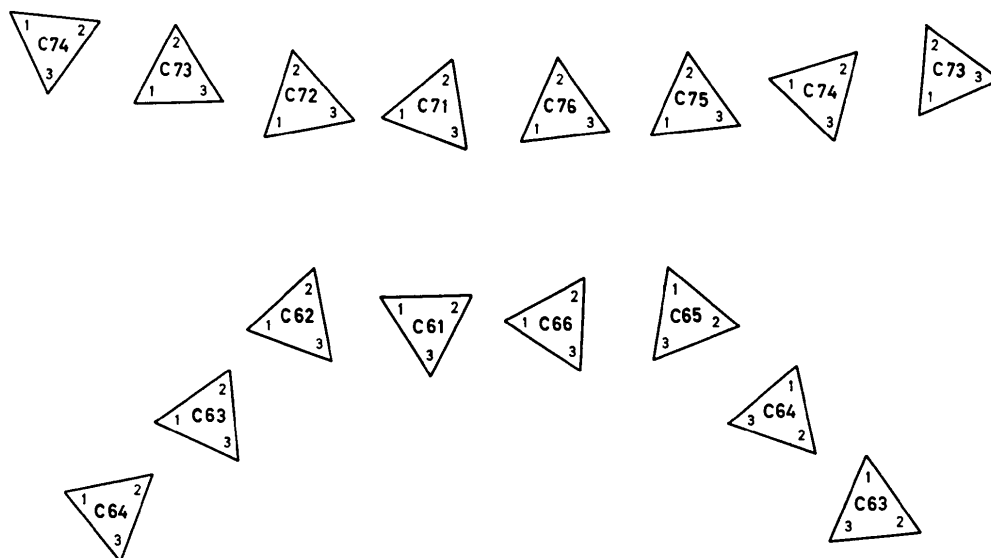
Fig. 5. The relative arrangement of the methyl groups as derived from difference Fourier synthesis.

The twinning or disorder phenomena encountered during the preliminary investigations of this structure are easily understood by inspection of Fig. 7. The intermolecular contacts would only slightly change when inserting the mirror image of a molecule at $x=\frac{1}{4}$ instead of its original image. The observed phenomenon might either correspond to a statistical random arrangement of images and mirror images within the crystal or to twinning along (100).
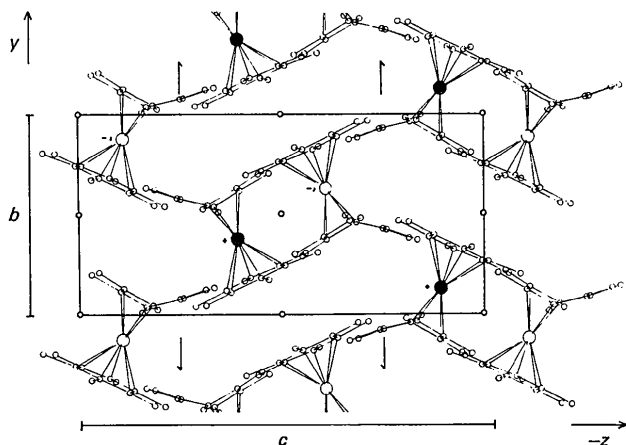
Fig. 6. Projection of the unit cell down the *a* axis. Molecules with black (white) central metal atoms form a layer.
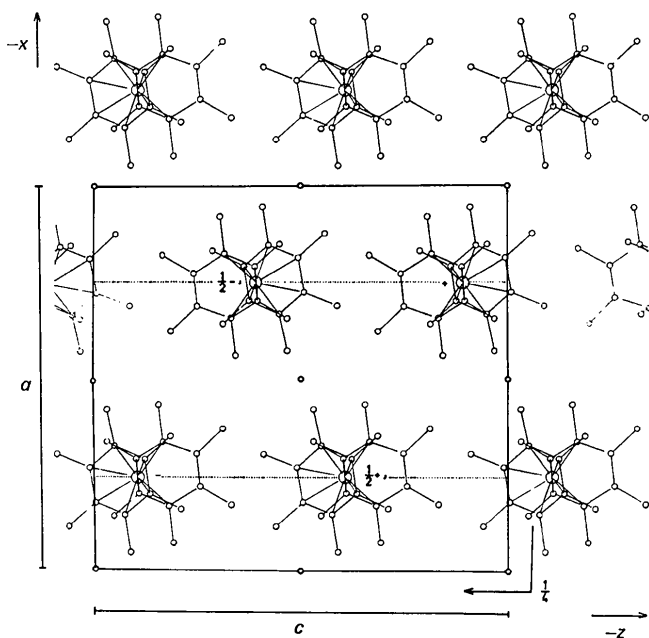
Fig. 7. Projection of the unit cell down the unique axis *b*. The dotted lines indicate the only approximate mirrors at $x=\frac{1}{4}$ and $x=\frac{3}{4}$.

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The Crystal and Molecular Structure of Photoaldrin, C12H8Cl6

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Photoaldrin $C_{12}H_8Cl_6$ is monoclinic, space group $P2_1/n$ with cell constants $a = 9\cdot344$ (4), $b = 15\cdot756$ (18), $c = 8\cdot952$ (4) Å and $\beta = 91\cdot31$ (4)°. The crystal structure has been determined and refined using counter diffractometer data to $R = 0\cdot045$ for 2787 observed reflections. The single C–C bonds exhibit a wide range of variation, from $1\cdot51$ to $1\cdot62$ Å. The longest among these bonds appears to be the longest ever reported as a C–C bonding distance.

Introduction

Investigations of the toxicity and metabolism of photoaldrin (II), a photoisomer of aldrin (I), have shown recently that it is more toxic to house flies and mosquito larvae than the parent compound (Sutherland & Rosen, 1968; Khan, Sutherland, Rosen & Carey, 1970). Because of its toxic properties, the photoisomer has potential as an insecticide.

(I)   (II)

The structure of (II) has been established from spectrographic data only (Rosen, 1967). The frameworks of the saturated hydrocarbons are flexible enough to deviate appreciably from an expected model. An X-ray diffraction study has therefore been carried out to confirm the molecular structure of photoaldrin and to determine, in detail, the stereochemical features.

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Experimental

Photoaldrin was obtained from the photolysis of aldrin (Rosen, 1967). It was separated by chromatography on thick layer silica gel *G* plates, scrapped and extracted with petroleum ether and then recrystallized from hexane. Crystal symmetry and the approximate cell parameters were determined from precession photographs. A nearly spherical crystal with an average diameter of 0·4 mm was used for the collection of the intensity data on an automatic diffractometer. Ag *Kα* radiation monochromated by a graphite crystal was used and θ–2θ scans were made. Details of the technique are reported elsewhere (Baur & Kahn, 1970). Cell parameters were measured from well resolved reflections using only the α_1 component. 7250 reflections, measured in two quadrants with $\sin \theta/\lambda$ values up to $0\cdot68$ Å^{-1}, were averaged to give 3636 reflections. Of these, 849 were considered to be of zero intensity because their magnitudes were smaller than 2σ. Lorentz–polarization corrections were applied but absorption corrections were neglected.

Crystal data

Photoaldrin, $C_{12}H_8Cl_6$, is monoclinic with $a = 9\cdot344$ (4), $b = 15\cdot756$ (18), $c = 8\cdot952$ (4) Å, $\beta = 91\cdot31$ (4)°, $V = 1317\cdot6$ Å^3, $Z = 4$, the pycnometric $D_m = 1\cdot83$, $D_c = 1\cdot84$ g.cm^{-3}, F.W. 365·0, μ(Ag *Kα*) = 6·4 cm^{-1}, $\mu R = 0\cdot13$. Space group $P2_1/n$ was established from systematic absences ($h + l = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$) and by the successful refinement of the structure.