Dewar Benzene Complexes: the Crystal Structure of Tetracarbonyl(hexamethyl[2,2,0]hexa-2,5-diene)chromium

By G. HUTTNER
(*Anorganisch-Chemisches Laboratorium der Technischen Hochschule München, 8 München 2, West Germany*)
and O. S. MILLS*
(*Department of Chemistry, University of Manchester, Manchester 13*)

ALTHOUGH both organic and organometallic derivatives of Dewar benzene have been prepared, so far no detailed structural information has been reported. Of the organometallic π-complexes, tetracarbonyl(hexamethylbicyclo[2,2,0]hexa-2,5-diene)chromium (I)[1] and dichloro(hexamethylbicyclo[2,2,0]hexa-2,5-diene)palladium,[2–4] (I) is the better choice for *X*-ray analysis since the lighter metal should yield a more precise description of the ligand and also the stability of the compound is reputedly greater.

Crystals of (I)† had cell dimensions $a = 12{\cdot}73$, $b = 11{\cdot}25$, and $c = 11{\cdot}57$ Å, orthorhombic, space group either *Pnma* (No. 62, D_{2h}^{16}) or $Pna2_1$ (No. 33, C_{2v}^{9}) by systematic absences, $D_m = 1{\cdot}29$ by flotation, $D_c = 1{\cdot}31$, $U = 1657$ Å^3, and $Z = 4$. Although the crystals gradually decomposed in the *X*-ray beam, it was possible to measure some 804 independent, non-zero reflexions from two crystals by the precession method. The intensities, recorded with Mo-K_α radiation, were estimated visually.

If the space group is *Pnma*, the molecule must exhibit at least mirror symmetry since it cannot be centrosymmetric. The lower space group places no restriction on molecular shape. The structure was solved by Patterson and Fourier methods and although we have continually considered both space groups we have been able to refine the structure to $R = 11\%$ (with isotropic temperature factors) within the symmetry of *Pnma*. Since the isotropic temperature factors for all the atoms are very reasonable it seems that this is correct.

The main features of the molecular structure are shown in the Figure. The molecule has, very accurately, *mm* (C_{2v}) symmetry where only one mirror plane is crystallographically imposed (m_1 in the Figure). Of the four carbonyl groups, two lie in the plane m_1 and the others are related by it. The former are bent slightly away from the organic ligand to give the C–Cr–C angle 169°. All the Cr–C–O bonds are linear, within experimental error, and of equal length, 1·85 Å. The four carbon atoms C(1—4) are accurately coplanar and the two symmetry-related planes so defined are inclined at a dihedral angle of 113°. In contrast with C(2)–C(3) (1·36 Å), the other seven independent carbon–carbon bond lengths lie within one standard deviation (0·02 Å) of their mean

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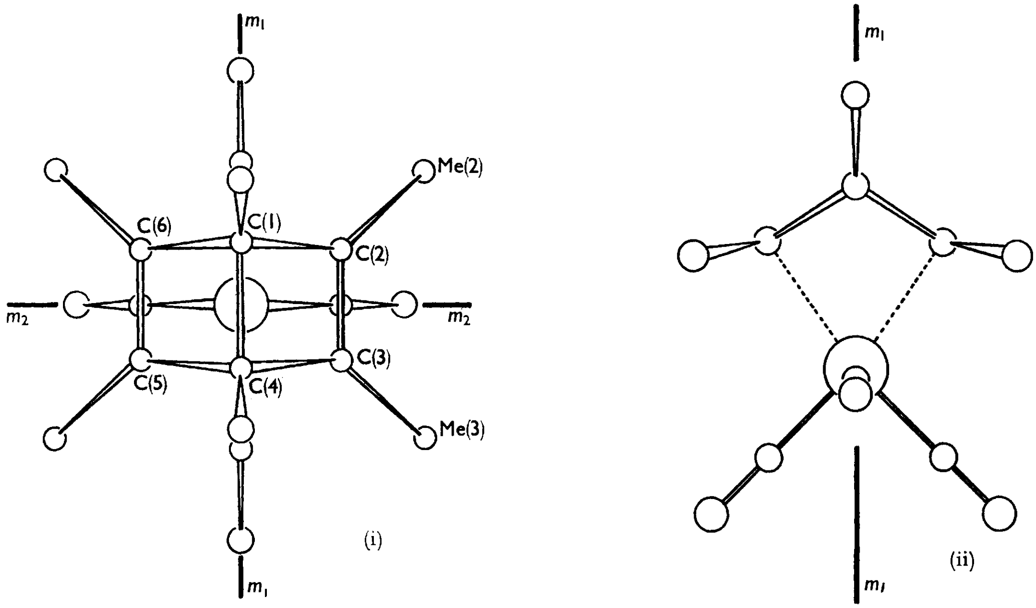
† We thank Professor E. O. Fischer for providing us with a sample.



FIGURE

Views of molecule (i) *parallel with and* (ii) *perpendicular to the two-fold axis.*

value, $1{\cdot}53_5$ Å. These values correspond closely with the normally accepted values for double and single bonds respectively. The mid-points of C(2)–C(3) and C(5)–C(6) subtend an angle of 69·4° at the chromium atom.

The conformation of the Dewar benzene nucleus is described by the torsion angles listed in the Table. None of the methyl substituents are coplanar with the Dewar benzene carbon atoms. Those attached to C(2,3,5,6) lie nearly 0·5Å from the cyclobutene planes. We expect that the structure of the free ligand will not be very different from our findings since the n.m.r. peaks for the complexed methyl protons, which occur at τ 8·26 and 9·1 in the ratio 2 : 1, are only slightly changed from those of the free ligand at τ 8·45 and 8·94.[1] The geometry of the complex is similar to that proposed,[1] with the two bonds C(2)–C(3) and C(5)–C(6) occupying *cis*-positions of a somewhat distorted co-ordination octahedron. The Cr–C(2,3,5,6) distance is 2·33 Å; the (non-bonded) Cr–C(1,4) distance is 2·80 Å.

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TABLE

Torsion angles

Atoms	*Angle°*	*Atoms*	*Angle°*
C(1)–C(2)–C(3)–C(4)	0·2	C(2)–C(3)–C(4)–C(5)	−84·6
C(1)–C(2)–C(3)–Me(3)	156·6	C(4)–C(3)–C(2)–Me(2)	−155·8

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