

THE CRYSTAL AND MOLECULAR STRUCTURE OF TETRACARBONYL-(HEXAMETHYLBICYCLO[2.2.0]HEXA-2,5-DIENE)CHROMIUM A TRANSITION METAL COMPLEX OF A SUBSTITUTED DEWAR BENZENE

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SUMMARY

The crystal and molecular structure of tetracarbonyl(hexamethylbicyclo[2.2.0]hexa-2,5-diene)chromium $(\text{CH}_3)_6\text{C}_6\text{Cr}(\text{CO})_4$ has been determined from 804 independent non-zero single-crystal X-ray intensities collected photographically. The structure has been refined by standard Fourier and least-squares techniques to a conventional R value of 0.111 (isotropic temperature factors for the light atoms). The crystals are orthorhombic, spacegroup $Pnma$, $a=12.73(3)$, $b=11.25(2)$, $c=11.57(2)$ Å, $Z=4$. The molecule possesses idealized $mm2$ (C_{2v}) symmetry and can be described as an octahedral complex of chromium in which the ligand occupies two positions *cis* to one another. The Dewar benzene nucleus consists of two fused cyclobutene rings with a dihedral angle of 113° .

The C-C (double-bond) distances in the ligand are 1.36(1) Å, the C-C (bridge) distance is 1.55(2) Å and the remaining C-C (ligand) distances have an average value of 1.53 (2) Å. The steric strain in the molecule causes the Cr-C (ligand) bonding distances to be unusually large *viz.* 2.33 (1) and 2.34 (1) Å.

INTRODUCTION

Hexamethylbicyclo[2.2.0]hexa-2,5-diene forms a number of organometallic complexes of which the tetracarbonylchromium adduct was the first to be reported¹. We undertook the present structural investigation in order to obtain precise structural information of the geometry of the coordinated ligand in the chromium complex and of the metal-ligand bonding distances. A preliminary account of our work has already been published².

EXPERIMENTAL

Single crystals of the complex suitable for diffraction studies were kindly supplied by Professor E. O. Fischer. The yellow crystals are air-stable but proved to be

somewhat sensitive to X-rays so that observations had to be made from two separate crystals.

Crystal data

Tetracarbonyl(hexamethylbicyclo[2.2.0]hexa-2,5-diene)chromium, $(\text{CH}_3)_6\text{C}_6\text{Cr}(\text{CO})_4$, mol.wt. 326.3, diffraction symmetry *mmm*, orthorhombic, $a=12.73(3)$, $b=11.25(2)$, $c=11.57(2)$ Å (determined from zero level precession photographs, Mo- K_α - λ 0.71069 Å), $V=1657(5)$ Å³, $Z=4$, $D_c=1.31$ g·cm⁻³, $D_m=1.29$ g·cm⁻³ (determined by flotation in aqueous K_2HgI_4). Systematic absences: $k+l=2n+1$ for $0kl$ and $h=2n+1$ for $hk0$. Spacegroup: *Pnma* (No. 62³, D_{2h}^{16}) or with the same axial arrangement *Pn2₁a* (No. 33³, C_{2v}^9). The structure has been successfully refined in spacegroup *Pnma* and no deviation from this spacegroup symmetry has been detected during structure refinement.

Data collection

X-ray intensities were estimated from precession photographs taken with Zr-filtered Mo- K_α radiation (λ 0.71069 Å). In the course of the exposures some decomposition was noted since the initially yellow crystals became covered with a white material. No powder lines were associated with this change and repeatedly-taken zero levels, which were used as a monitoring aid, showed no observed change in relative intensities. We do not think therefore that this decomposition adversely affects the validity of the analysis. The levels hkn , $n=0-3$ were collected from a first crystal ($0.3 \times 0.3 \times 0.5$ mm, longest axis parallel to b) and a second ($0.9 \times 0.4 \times 0.4$ mm, longest axis parallel to b) was used for the levels nkl , $n=0, 1$ and for $hk(h-n)$, $n=0, 1$.

The intensities were estimated visually. No absorption corrections were applied since absorption effects were judged to be small for the crystals used ($\mu=7.1$ cm⁻¹ for Mo- K_α radiation). Lorentz and polarisation corrections were applied to the data. After bringing the data onto a common scale⁴ 804 independent nonzero structure-factors were obtained which form the basis of this structure determination.

Solution and refinement

The x and z coordinates of the chromium atom were unambiguously determined from a three-dimensional Patterson synthesis ($x=0.184$, $z=-0.095$) but the y coordinate either must be $1/4$ from symmetry reasons for spacegroup *Pnma* or may be arbitrarily assigned this value with *Pn2₁a*. Although the approximation to the electron density, which resulted from the Fourier synthesis in which the phases were those associated with the chromium atoms alone and which must of necessity therefore show the mirror symmetry fundamental to the spacegroup of higher symmetry, could be interpreted immediately in terms of the structure which we report, we considered arrangements appropriate to spacegroup *Pn2₁a* by the inclusion of atoms at only some of the peaks. All arrangements found and tested by subsequent Fourier refinement were basically insignificantly different from the symmetrical structure inherent with the spacegroup *Pnma* and so this latter spacegroup was used in the remaining calculations.

Seven cycles of isotropic least squares refinement reduced the R value from initially 0.25 to 0.112. During the next two cycles the chromium atom was allowed to refine with anisotropic motion and the resultant R value was then 0.111 and no shift exceeded one half of the corresponding estimated standard deviation as obtained from

TABLE 1 VALUES OF F_o AND F_c FOR $(CH_3)_6C_6Cr(CO)_4$ ^a

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
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^a Values listed in the table are absolute values magnified by 10.

TABLE 2 ATOMIC COORDINATES AND THERMAL PARAMETERS WITH EsD's^a

Atom ^b	x/a	y/b	z/c	B, Å ²
Cr	0.1799(2)	0.25	-0.0959(2)	c
C(1)	0.3449(10)	0.25	0.0630(14)	2.9(2)
C(2)	0.3022(7)	0.3634(8)	0.0062(9)	3.1(2)
C(3)	0.2129(8)	0.3631(8)	0.0704(10)	3.4(2)
C(4)	0.2430(10)	0.25	0.1367(14)	3.3(2)
C(me ₁)	0.4545(13)	0.25	0.1171(17)	4.6(3)
C(me ₂)	0.3597(9)	0.4640(10)	-0.0549(12)	4.8(2)
C(me ₃)	0.1381(10)	0.4631(11)	0.1034(12)	5.2(3)
C(me ₄)	0.2486(14)	0.25	0.2709(18)	5.2(4)
C(10)	0.2946(13)	0.25	-0.1949(16)	4.1(3)
C(11)	0.1266(8)	0.3671(9)	-0.1887(11)	4.1(2)
C(12)	0.0493(11)	0.25	-0.0233(16)	3.6(3)
O(10)	-0.3622(11)	0.25	-0.2621(13)	6.1(3)
O(11)	0.0949(8)	0.4406(8)	-0.2472(9)	6.4(2)
O(12)	-0.0356(10)	0.25	0.0177(13)	6.1(3)

^a EsD's appear in parentheses after each parameter. They are right-adjusted to the last significant digit of the preceding number. ^b Atoms labeled as in Fig. 1. ^c The anisotropic thermal parameter (T) used for the chromium atom was of the form: $T = \exp(-b_{11} \cdot h^2 - b_{22} \cdot k^2 - b_{33} \cdot l^2 - b_{12} \cdot h \cdot k - b_{13} \cdot h \cdot l - b_{23} \cdot k \cdot l)$. The final values are: $b_{11} = 0.00443(14)$, $b_{22} = 0.00557(16)$, $b_{33} = 0.00508(22)$, $b_{13} = -0.00063(17)$, $b_{12} = b_{23} = 0$.

TABLE 3
MOLECULAR GEOMETRY

Bond lengths ^a (Å)			
Cr-C(1)	2.79(2)	C(1)-C(2)	1.54(1)
Cr-C(2)	2.33(1)	C(2)-C(3)	1.36(1)
Cr-C(3)	2.34(1)	C(3)-C(4)	1.53(1)
Cr-C(4)	2.81(2)	C(1)-C(4)	1.55(2)
Cr-C(10)	1.86(2)	C(2)-C(6)	2.55(2)
Cr-C(11)	1.83(1)	C(3)-C(5)	2.55(2)
Cr-C(12)	1.86(2)	C(1)-C(me ₁)	1.53(2)
C(10)-O(10)	1.16(2)	C(2)-C(me ₂)	1.52(2)
C(11)-O(11)	1.14(1)	C(3)-C(me ₃)	1.52(2)
C(12)-O(12)	1.18(2)	C(4)-C(me ₄)	1.55(2)

Bond angles ^a (degrees)			
C(10)-Cr-C(12)	168.6(8)	C(2)-C(1)-C(6)	112.5(7) ^b
C(10)-Cr-C(11)	86.0(5)	C(1)-C(4)-C(3)	86.2(8)
C(11)-Cr-C(12)	86.2(8)	C(2)-C(1)-C(4)	86.5(7)
C(11)-Cr-C(13)	92.1(9) ^b	C(me ₁)-C(1)-C(2)	119.9(6)
Cr-C(10)-O(10)	176.0(15)	C(me ₁)-C(1)-C(4)	122.6(12)
Cr-C(11)-O(11)	178.9(10)	C(me ₄)-C(4)-C(3)	120.7(9) ^b
Cr-C(12)-O(12)	176.9(14)	C(me ₄)-C(4)-C(1)	120.7(12) ^b
C(1)-C(2)-C(3)	93.4(8)	C(me ₂)-C(2)-C(1)	130.3(9) ^b
C(2)-C(3)-C(4)	93.9(9)	C(me ₂)-C(2)-C(3)	131.2(9) ^b
C(3)-C(4)-C(5)	112.1(9) ^b	C(me ₃)-C(3)-C(2)	131.1(9) ^b
		C(me ₃)-C(3)-C(4)	130.1(11)

Torsion angles (°)	
C(4)-C(3)-C(2)-C(1)	0.2
C(4)-C(3)-C(2)-C(me ₂)	156.6
C(1)-C(2)-C(3)-C(me ₃)	-155.8
C(3)-C(2)-C(1)-C(6)	-84.6

Least-squares plane defined by atoms C(1), C(2), C(3), C(4)

Directional cosines of plane normal^c

0.45506 0.55373 0.69736

Distances of atoms from the plane (Å) ·

C(1)	0.000	C(2)	0.000	C(3)	0.000	C(4)	0.000
C(me ₁)	1.070	C(me ₂)	0.468	C(me ₃)	0.455	C(me ₄)	1.119

Vibrational ellipsoid of the chromium atom

RMS displacement along Directional cosines of principal axes^c

principal axes

0.195	0.8304	0.0	-0.5572
0.189	0.0	1.0	0.0
0.181	0.5572	0.0	0.8304 ^c

^a Standard deviations indicated in parentheses refer to the least significant digit(s). ^b The value for this standard deviation is estimated neglecting covariance terms. ^c Directional cosines refer to natural axes.

^d Directional cosines of the twofold axis of the molecule are 0.5301, 0.0 and 0.8479 for comparison.

inversion of the full normal matrix. Analysis of the components, $b_{i\bar{p}}$ of the thermal vibration parameters for the chromium atom showed that the departure from isotropic motion was small (see Table 3). However it is interesting to note that the orien-

tation of the vibrational ellipsoid conforms closely to the overall symmetry of the molecule. The molecular twofold axis is only 2° divergent from the minor principal axis of vibration and the major axis lies in the crystallographic mirror plane.

The weighting scheme used throughout the last four cycles of least squares refinement was chosen so as to give constant mean values for $\Sigma w\Delta F^2$ for all ranges of F_o as well as $\sin^2 \theta/\lambda^2$. A final difference synthesis, based on all atoms except hydrogen, showed nowhere an electron density higher than $0.7 \text{ e} \cdot \text{\AA}^{-3}$. The features could not be interpreted in terms of hydrogen atoms of the methyl groups.* The scattering factors used throughout were those given by Hanson *et al.*⁵ Final observed and calculated structure factors are given in Table 1, positional and thermal parameters are collected in Table 2 and details of the molecular geometry in Table 3. The reasonable values of the temperature factors are a further strong indication that the space-group *Pnma* is correct because even a small deviation from the centric arrangement required by this spacegroup would manifest itself in much higher thermal parameters.

RESULTS AND DISCUSSION

The molecular structure of $(\text{CH}_3)_6\text{C}_6\text{Cr}(\text{CO})_4$ is shown in Fig. 1 and 2. The molecule is highly symmetric, even more so than is imposed by the spacegroup. It has very accurately *mm* (C_{2v}) symmetry whereas only one mirror plane is imposed crystallographically (plane m_1 in Fig. 1). The overall geometry of the molecule can be described in terms of a somewhat distorted coordination octahedron around the central chromium atom with four positions occupied by carbonyl groups and the other two, *cis* to one another, by the bonds C_2-C_3 and C_5-C_6 of the Dewar benzene skeleton, in accord with an earlier suggestion¹.

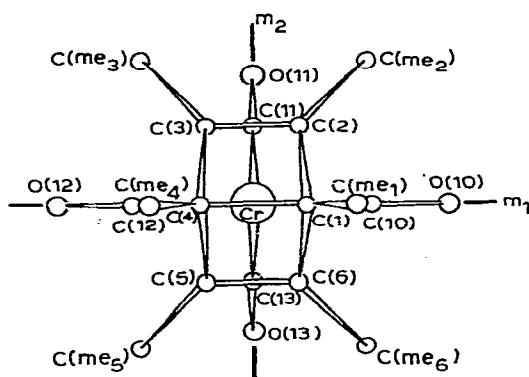


Fig. 1. View of the molecule along the twofold axis.

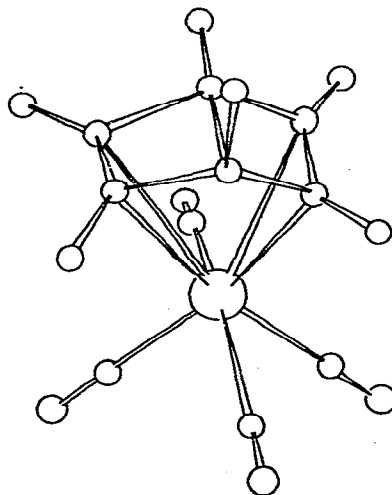


Fig. 2. General view showing the rooflike structure of the Dewar benzene nucleus.

* Programs used in this analysis were those written by the members of the university of Manchester.

The organic ligand

The bond lengths within the ligand fall readily into classes which correspond to the accepted values for single and double bonds even though the geometry around the carbon atoms of the Dewar benzene nucleus is much distorted from ideal tetrahedral or trigonal symmetry (see below). The bond C_2-C_3 ($=C_5-C_6$ by symmetry) is 1.36(1) Å and only marginally greater than the average value⁶, 1.34 Å, for a C-C double bond. The distances C_1-C_2 and C_3-C_4 are identical, 1.53₅ Å, and close to the value expected for a bond between an sp^2 and an sp^3 hybridised carbon atom. The distance between the bridgehead carbons C_1-C_4 is 1.55(2) Å and has thus a value typical of a single bond between two sp^3 hybridised carbon atoms. The rings defined by atoms C_1, C_2, C_3 and C_4 ($=C_1, C_6, C_5, C_4$) are essentially planar (see Table 3) so they are best compared to cyclobutene whilst the Dewar benzene nucleus itself is described as one which involves two fused cyclobutene rings. These rings are inclined at a dihedral angle of 112.8°. An electron diffraction study of cyclobutene¹⁷ gave a double bond distance of 1.33 (4) Å and an average length in the remainder of 1.54(1) Å in excellent agreement with the values reported here. It follows that the angular agreement is equally good. The internal angles at C_2 and C_3 must be somewhat greater than 90° (and are in fact 93.4 and 93.9° respectively) whilst those at C_1 and C_4 are 86.5 and 86.2°. The methyl groups attached to C_2 and C_3 are nearly symmetrical with respect to the adjoining carbon atoms of the ring, but the angles are much greater than the sp^2 values of 120° as follows from the internal angles of 94°. In fact the determined angles are less than the expected value of $(360^\circ - 94^\circ)/2$ due to the fact that the methyl groups are displaced from the plane of the cyclobutene rings by some 0.5 Å to the side *trans* to the chromium atom (see Table 3). The four separately estimated ring-methyl distances vary between 1.52 and 1.55 Å, a variation which is insignificant in the light of the reported standard deviations. The bonds made to atoms C_1 and C_4 are much distorted from tetrahedral and involve two angles less than 90°, one around 112° and three around 120°.

It is interesting to compare the geometry of the ligand with those reported for the platinum and palladium complexes which involve somewhat modified hexamethyl-Dewarbenzene ligands^{7,8,9}. The C-C-distances, where appropriate are generally in agreement with our own. The methyl groups do not appear to be rigidly attached to the bicyclic framework as shown by comparison of their positions in the present structure and in $[\text{Pd}(\text{Acac})(\text{C}_{12}\text{H}_{17})]^\circ$.

The metal to ligand bonds

The Dewar benzene nucleus is symmetrically bonded to the chromium atom. Whereas the geometry of the molecule is similar to that which would be expected for a $\text{Cr}(\text{CO})_4$ derivative of a cyclic unconjugated diene, the bond lengths are found to be longer than would be expected [$(\text{Cr}-C_2)=(\text{Cr}-C_6)$ 2.33, $(\text{Cr}-C_3)=(\text{Cr}-C_5)$ 2.34 Å]. Although no structural information on any adduct of a nonconjugated diene of chromium exists, we would expect the Cr-C-distance to be similar to that found in tricarbonylbenzenechromium (average $\text{Cr}-C_{\text{ligand}}=2.221$ Å)¹⁰ and tricarbonyl(hexamethylbenzene)chromium (average $\text{Cr}-C_{\text{ligand}}=2.233$ Å)¹¹. Our value is 0.1 Å longer than these and indeed longer than the single bond $\text{Cr}^0-C_{sp^2}$ (2.21 Å) as predicted from the value of 1.48 Å for the covalent radius of Cr^0 ¹². It has been pointed out¹³,

that in tricarbonylchromium derivatives of unsymmetrically substituted benzenes, two types of metal carbon distances occur; one around 2.22 and a longer one around 2.32 Å. The present structure is thus far the only example of a complex involving only "long" Cr-C_{ligand}-distances. This observation is readily explicable in terms of nonbonded repulsive interactions between the chromium atom and the bridgehead carbon atoms C₁ and C₄ of the Dewar benzene skeleton.

The distances Cr-C₁ [2.79(2)Å] and Cr-C₄ [2.81(2) Å] are only 0.6 Å longer than a Cr-C-single bond. The observed value of 2.8 Å for the Cr-C nonbonded distance is smaller than the sum of the covalent radius of Cr⁰ (1.48 Å)¹² and the van der Waals radius of carbon (1.5 Å)¹⁴, and must therefore be very much smaller than the sum of the van der Waals radii of chromium and carbon, even though no reliable value for the former is known. It is therefore certain, that repulsive interaction occurs between Cr and the bridgehead carbon atoms C₁ and C₄. The abnormally large Cr-C bonded distances of 2.34 Å thus result from a balance of the bonding interactions at C₂, C₃, C₅, C₆ and the repulsive forces at C₁ and C₄. For this explanation to be valid it is necessary to assume that the conformation of the Dewar benzene nucleus is very stable, since a reduction of the dihedral angle between the two fourmembered rings of the bicyclic system from 113° to 102°, with the nonbonding contacts Cr-C₁ and Cr-C₄ remaining the same, would reduce the distance between the chromium and the bonded atoms C₂, C₃, C₅, C₆ from 2.34 Å to the "normal" value of 2.2 Å. There is indeed enough experimental evidence for the rigidity of the Dewar benzene framework. It is observed that the dihedral angle is nearly equal for all Dewar benzene complexes whose structures have thus far been determined. In Pd(Acac)(C₁₂H₁₇)⁹, where only one double bond of the ligand is part of the coordinating system this angle is 112°. In [PtCl(C₁₂H₁₇)]₂^{7,8}, where the two double bonds of the ligand are coordinated with one metal atom and a methylene carbon of the dehydro hexamethyl Dewar benzene is σ-bonded to the other, the dihedral angle is found to be 111°*. Since in this latter compound the two double bonds of the ligand are involved in coordination, the steric situation is close to that described for the chromium complex. It follows that abnormally long carbon-platinum-bonding distances should be found. It is indeed observed^{7,8} that while one double bond makes normal contacts to the metal atom [Pt-C 2.17(2) Å, 2.18(2) Å] the other shows abnormally long Pt-C-distances [Pt-C 2.31(2), 2.36(2) Å]. The bridgehead carbons are still rather close to the platinum [Pt-C 2.72(2), 2.69(2) Å] and any closer approach of the ligand would enhance the repulsive interactions. Since the metal atom is unsymmetrically substituted in this compound, the bond lengthening effect is also unsymmetrical and the trans effect of the various ligands may be invoked to explain the direction of this asymmetry⁸.

Metal to carbon monoxides bonds

The values found for the Cr-C and C-O distances are not unusual. They are shorter than those found in hexacarbonylchromium itself¹⁶ as is normal when a ligand with poor acceptor qualities is co-ordinated, but not as short as has been found

* A value of 117.7° was found for the dihedral angle in perfluorobicyclo[2.2.0]hexa-2,5-diene from an electron diffraction study. It has been shown however that this value is rather sensitive to the assumptions made in this structure determination¹⁵ and thus it may not be appropriate to compare it with the results quoted above.

in some triene complexes. The minor variations which occur in the Cr-C and C-O bond lengths are not significant in the light of the reported standard deviations. The Cr-C-O bonds are essentially linear. The angle subtended at the chromium atom by the carbonyl groups *trans* to the Dewar benzene ligand is slightly greater than 90°, though perhaps not significantly so. All the remaining angles are rather more significantly changed to give an average value of 86°. This results in the two apical carbonyl groups, relative to the equatorial plane defined as that which contains the bonds to the organic ligand, making an angle of 169° to one another.

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