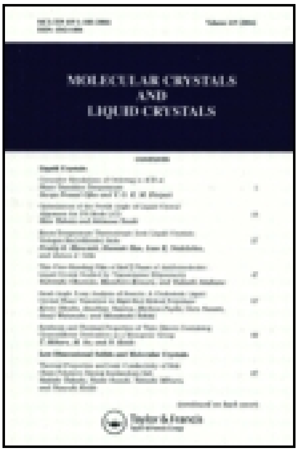

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Disorder in the Crystal Structures of Hexakis(dimethylsilyl)benzene and its Tricarbonyl Chromium, Molybdenum, and Tungsten Complexes

Bart Kahr [a], Jeffrey M. Chance [a b] & Kurt Mislow [a]

[a] Department of Chemistry, Princeton University, Princeton, NJ, 08544

[b] Department of Chemistry, Vassar College, Poughkeepsie, NY, 12601

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Disorder in the Crystal Structures of Hexakis(dimethylsilyl)benzene and its Tricarbonyl Chromium, Molybdenum, and Tungsten Complexes

BART KAHR,† JEFFREY M. CHANCE,‡ and KURT MISLOW
Department of Chemistry, Princeton University, Princeton, NJ 08544

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The crystal structures of hexakis(dimethylsilyl)benzene (**1**) and its tricarbonyl tungsten (**2**), molybdenum (**3**) and chromium (**4**) complexes were determined by X-ray diffraction. Compound **1** crystallizes in the monoclinic system, space group $P2_1/c$ with a = 11.196(5)Å, b = 19.675(9)Å, c = 24.447(8)Å, Z = 8, at 175K. The metal complexes **2**, **3**, **4** are isomorphic; the compounds exhibit trigonal modifications (**2t**, **3t**, **4t**), space group $R3$ or $R\bar{3}$, Z = 6. Crystal data: (**2t**) a = 19.044(5)Å, c = 14.343(4)Å, at 193 K; (**3t**) a = 19.056(4)Å, c = 14.633(5)Å, at 298 K; (**4t**) a = 19.047(5)Å, c = 14.144(5)Å, at 193 K. The metal complexes were dimorphic; compounds **2** and **3** exhibit monoclinic modifications (**2m**, **3m**), space group $P2_1$, Z = 2. Crystal data: (**2m**) a = 11.059(4)Å, b = 13.885(4)Å, c = 11.140(3)Å, β = 114.79(3)°, at 225 K; (**3m**) a = 11.020(6)Å, b = 13.838(4)Å, c = 11.099(4)Å, β = 114.54(3)°, at 193 K. Each of the five structures that were solved and refined (**1**, **2m**, **2t**, **3m**, **4t**) exhibit an orientational disorder. The extent of the disordering, measured as the refined occupancy of the minor species, varies for independent molecules within the same asymmetric unit in **1**, and between isomorphic structures in the trigonal and monoclinic series of **2**, **3**, and **4**. The disorder was accommodated differently in the trigonal and monoclinic modifications. The metal tricarbonyl units adopt a staggered conformation with respect to the side chains. Substantial out-of-plane deviations (>0.2 Å) of the dimethylsilyl groups were observed in all the structures and arene bond alternations were measured in the metal complexes.

1. INTRODUCTION

Hexaisopropylbenzene (HIB) is the prototype of a class of stereochemically unusual hexasubstituted benzenes in which the interdigitation of the side chains enforces a rigid conformation.[1] X-ray crystallography has confirmed this statically-geared arrangement in HIB[2] as well as in hexakis(dichloromethyl)benzene (HCB),[3] and in hexakis(dimethylamino)benzene (HAB).[4] In this report we present the crystal

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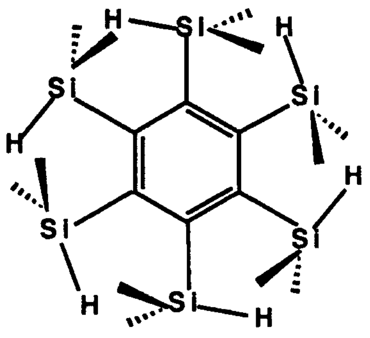
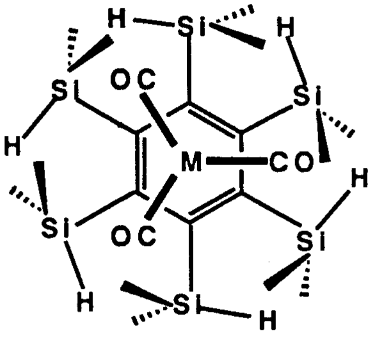
†Address correspondence to: Department of Chemistry, Purdue University, West Lafayette, IN 49707.

‡Department of Chemistry, Vassar College, Poughkeepsie, NY 12601.

structure of hexakis(dimethylsilyl)benzene (**1**), another member of this series that adopts the gear-locked conformation.



1



2 M=W
3 M=Mo
4 M=Cr

Additionally, we report the synthesis of the tricarbonyl tungsten (**2**), molybdenum (**3**), and chromium[5] (**4**) complexes of hexakis(dimethylsilyl)benzene and the characterization of five crystalline forms of these compounds. Detailed refinements of four of these structures revealed that isomorphic monoclinic modifications of the tungsten and molybdenum complexes were disordered, with heterochiral molecules sharing lattice sites by virtue of the superposition of arene rings. Isomorphic trigonal modifications of the tungsten and chromium complexes were also disordered, with heterochiral molecules sharing lattice sites; however the impossible superposition of major and minor orientations at adjacent lattice sites indicated twinning of large domains.

2. CRYSTAL STRUCTURES

Hexakis(dimethylsilyl)benzene (**1**) was prepared according to the procedure of Brennan and Gilman.[6] The compound crystallized from heptane in the monoclinic space group $P2_1/c$ with $Z = 8$. Two independent molecules I and II adopt general positions in the lattice with $a = 11.196(5)$ Å, $b = 19.675(9)$ Å, $c = 24.447(8)$ Å, and $\beta = 94.66(3)°$. Crystallographic data for **1** and all other structures to be described are summarized in Table I.

Figure 1 shows a stereoview of the packing of the major orientations of **1** along the b axis. The parallel packing of the arenes is consistent with an observed orientational disorder in which rings are flipped over at lattice sites such that enantiotopic faces are exchanged. We had previously observed that of the isosteric molecules HIB, HCB, and HAB, the latter compound was unique in that it showed no orientational disordering in the lattice and it adopted an edge-to-face packing motif.[3] The disorder in **1** resembles that in HIB and HCB. Six minor silicon positions were resolved in the Fourier difference map. Table II gives the atomic positional

TABLE I

Crystal data for **1**, **2**, **3**, and **4**

Compound	**1**	**4t**	**3m**	**3t**	**2m**	**2t**
Formula	$C_{18}H_{42}Si_6$	$C_{21}H_{42}CrO_3Si_6$	$C_{21}H_{42}MoO_3Si_6$		$C_{21}H_{42}O_3Si_6W$	
Temperature	175 K	193 K	193 K	298 K	225 K	193 K
Crystal System	monoclinic	trigonal	monoclinic	trigonal	monoclinic	trigonal
Lattice Constants:						
a, Å	11.196 (5)	19.047(5)	11.020(6)	19.056(4)	11.059(4)	19.044(5)
b, Å	19.675(9)	19.047(5)	13.838(4)	19.056(4)	13.885(4)	19.044(5)
c, Å	24.447(8)	14.144(5)	11.099(4)	14.633(5)	11.140(3)	14.343(4)
α, deg	90	90	90	90		90
β, deg	94.66 (3)	90	114.54(3)	90	114.79(3)	90
γ, deg	90	120	90	120	90	120
V Å^3	5368(4)	4442(2)	1531(1)	4601(2)	1558 (1)	4504(2)
Space Group	$P2_1/c$	$R\bar{3}$	$P2_1$		$P2_1$	$R3$
Z	8	6	2	6	2	6
MW g/mol	427.1	563.2	607.1	607.1	695.0	695.0
d_{calcd} g/cm^3	1.06	1.26	1.32	1.31	1.48	1.54
F(000)	1872	1800	636	1938	700	2100
μ_{calcd} (MoKα)	3.1 cm^{-1}	6.6 cm^{-1}	6.7 cm^{-1}	6.9 cm^{-1}	41.8 cm^{-1}	43.2 cm^{-1}
Solvent	Heptane	CH_2Cl_2/MeOH	Hexane	Hexane	Hexane	Hexane
Crystal Size (mm)	.15x.20x.25	.14x.20x.38	.11x.30x.50	.14x.14x.70	.39x.41x.41	.26x.50x.50
Habit	prism	rhombohedron	polyhedral	hexagonal prism	polyhedral	rhombohedron
2θ Range	3°-50°	3°-50°	3°-50°		3°-50°	3°-50°
Reflections Msd.	$h,k \geq 0$	$k,l \geq 0$ $-h+k+l = 3n$	$h,k \geq 0$		$k,l \geq 0$	$k,l \geq 0$ $-h+k+l = 3n$
Data Collected	10664	2814	2970		3024	2858
Unique Data	9407	1821	2812		2865	1722
Obsd $\lvert F_o \rvert > 3\sigma(F_o)$	6446	1532	2676		2758	1562
Absorption Corr.	Psi-scans	Psi-scans	Psi-scans		Psi-scans	analytical
R, Rw	0.076, 0.060	0.075, 0.065	0.034, 0.035		0.037, 0.039	0.043, 0.051
Parameters	480	114	304		304	166
Residuals e/Å^3	0.5	1.2	0.4		2.3	0.9

parameters along with the labeling scheme for molecules I and II. Table III gives the anisotropic thermal parameters.

The principal difference between the independent molecules I and II in the asymmetric unit is the extent to which they share unit occupancy with their respective orientational isomers. The ratios of major to minor orientations are 6.0:1 and 25.2:1, respectively. The observed geometries of the two orientational isomers

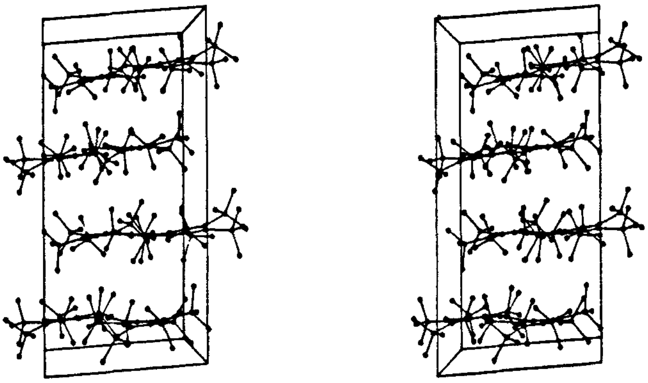


FIGURE 1 Stereoview of the unit cell of **1** along the *b* axis showing the parallel arene packing scheme. Only molecules in major orientations are shown for clarity. Methyl hydrogen atoms are deleted for clarity.

were averaged because the atomic positions of all non-silicon atoms were not crystallographically resolved and geometric differences between I and II were therefore ascribed to population differences.

In the comparable studies of HIB, the distorted, averaged geometry was corrected by partitioning the structure into discrete contributions with the use of a simple geometric algorithm.[2] This procedure did not produce reasonable results for HCB. In that case, the geometries of the major and minor orientational isomers were deconvoluted experimentally by refining the structure under the constraints of isotropic temperature factors for the aromatic carbon atoms.[3] For **1**, a third procedure was used, neglect of the minor contribution. Given that the percent contribution of the minor isomer (4%) for molecule II is small, the average geometry must be a good approximation of the geometry of the molecule.

This approximation can be shown to be sensible. The crystallographic parameters most sensitive to distortion due to disorder in HIB and its analogues were the C_{ar}—C_{ar}—C_m angles. For molecule I of **1**, the angles syn to the methyl groups have an average value of 125.1(3)° whereas the corresponding value for molecule II is 124.2(3)°. Since the difference in this value on decreasing the contribution of the minor isomer from 14% to 4% is only ca.1°, the residual error in molecule II for this parameter must be only a fraction of a degree, well within the experimental error for the determination of the atomic positions. The modest thermal ellipsoids for the aromatic carbon atoms attest to the smaller artifactual geometric distortions from the minor orientations as compared to HIB and HCB. Also, the long C_{ar}—Si bond lengths should contribute to a reduction in the angle ϕ, the offset of the benzene hexagons in the major and minor orientations.[7]

The structure of **1** is evaluated with this understanding. All metric values in the following discussion refer to the major orientational isomer of molecule II. These values are in reasonable agreement with those previously obtained by the empirical-force-field method.[5] The computed values are listed in parentheses. The average C_{ar}—Si bond length is 1.91(1)Å (1.928 Å). The average C_m—Si bond length is

1.87(1)Å (1.843 Å). The observation of longer bonds between methyl carbon atoms and silicon than between phenyl carbon atoms and silicon has precedent.[8] The average C_{ar}—C_{ar} bond length, 1.42(1)Å (1.415 Å), agrees with the value of 1.416 Å[9] for HIB, 1.402(2) for HCB, and 1.40(1) for HAB. The C_{ar}—C_{ar}—Si values are 124.2(3)° (120.4°) and 115.7(3)° (119.6°) for the syn and anti angles with respect to the methyls.

One aspect of the structure of **1** that was not predicted by the computations[5] is its surprising non-planarity. The average absolute deviation of the silicon atoms from the mean arene plane is 0.25 Å; torsion angles between ortho substituents are as large as 24° and −22° for Si(11)-C(11)-C(12)-Si(12) and Si(12)-C(12)-C(7)-Si(7), respectively. Assuming that out-of-plane distortions and large homomerization barriers are both consequences of steric crowding, this arrangement is inconsistent with the fact that **1** has a smaller rotational barrier to homomerization than its smaller analogues.[5] As a result of these large torsions, **1** diverges considerably from idealized C_{6h} symmetry, in contrast to HIB, HCB, and HAB. Figure 2 shows stereoviews parallel to the mean arene plane of molecule II that highlights the skewed arrangement of the side chains.

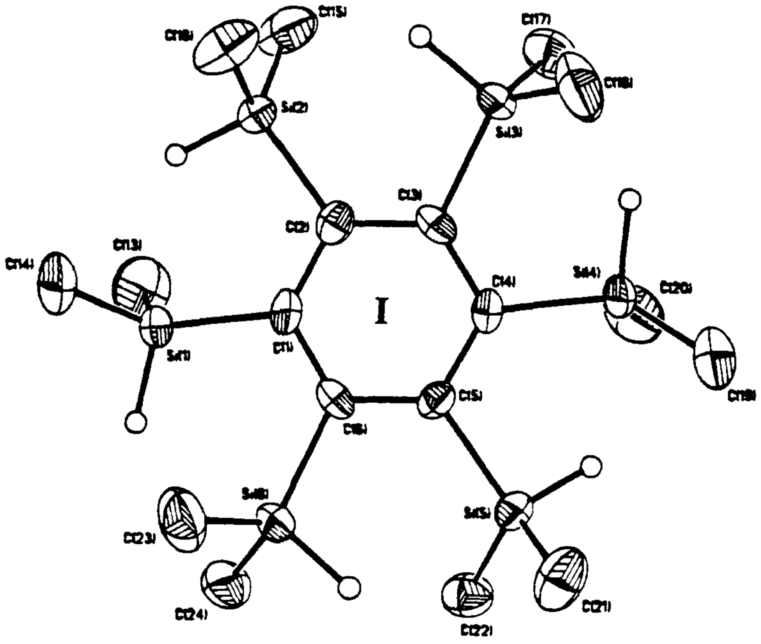
Hexakis(dimethylsilyl)benzenetricarbonyl Group 6 metal complexes. The group of crystalline chromium, molybdenum, and tungsten tricarbonyl complexes of hexakis(dimethylsilyl)benzene (**1**) was characterized by a dimorphism. The tungsten complex (**2**) co-crystallized in both a monoclinic (**2m**) and trigonal (**2t**) modification from hexane. The modifications were distinguished microscopically; crystals from a given batch were partitioned according to their morphology. Crystals of the molybdenum complex (**3**) are isomorphous to the monoclinic and trigonal tungsten complex crystals, yet each form was obtained only in separate crystallizations. Crystals of the chromium complex (**4**) are isomorphous to the trigonal crystals of **2** and **3**. All attempts to grow the unrepresented member of this family of crystals, the monoclinic version of **4**, by seeding, epitaxy, or sublimation were unsuccessful.

Both the monoclinic and trigonal crystals exhibit a two-fold orientational disorder. The disorder is of a very different nature for the crystals of the two systems and will be described independently in the sections which follow. All remarks concerning molecular geometries will refer to the major orientational isomers in the crystal. Detailed analyses of the geometry of these disordered structures is not warranted. This is unfortunate since, to the best of our knowledge, these are the only X-ray investigations of a complete series of group 6 transition metal tricarbonyl complexes of the same arene. However, there are several selected parameters that we believe may be reasonably described either because they include well defined atoms or planes or because they highlight features that are observed in the structures, irrespective of the nature of the orientational disorder.

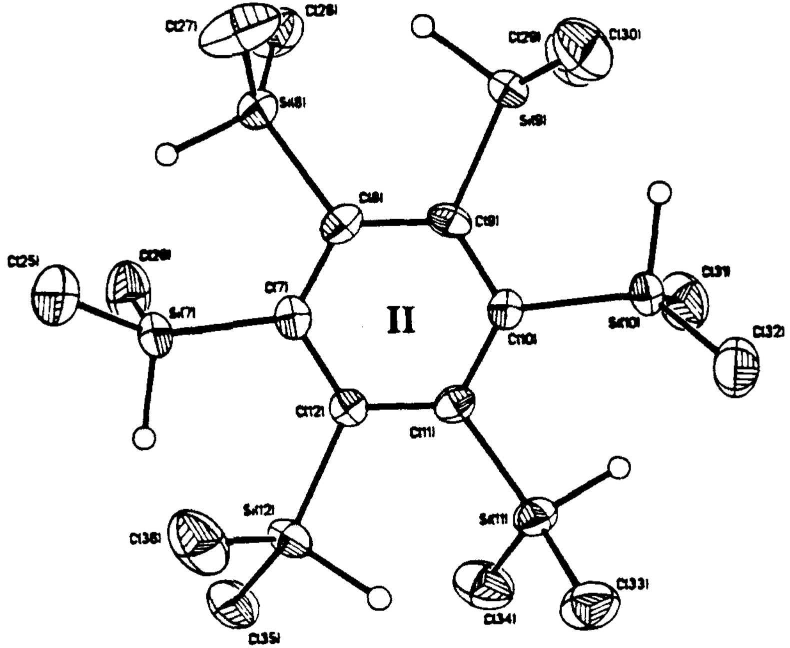
Hexakis(dimethylsilyl)benzenetricarbonyltungsten (**2**). Hexane solutions of **2** deposited golden polyhedra. Microscopic examination revealed two morphologies, rhombohedra (**2t**) and a polyhedral form with many minor facets (**2m**). The latter type indexed as monoclinic with a = 11.059(4)Å, b = 13.885(4)Å, c = 11.140(3)Å, and β = 114.79(3)°. The crystals belong to the space group $P2_1$ with Z = 2. While the crystals are chiral with a single molecule occupying a general position, they are not enantiomerically pure. This is the consequence of the type of orientational

TABLE II

Atomic positional parameters (Å × 10^4) for **1**



	x	y	z
C(1)	4930(4)	402(3)	-1266(2)
C(2)	5807(4)	927(2)	-1260(2)
C(3)	7032(4)	741(2)	-1261(2)
C(4)	7370(4)	58(2)	-1321(2)
C(5)	6496(4)	-469(2)	-1268(2)
C(6)	5289(4)	-285(2)	-1220(2)
Si(1)	3243(1)	532(1)	-1388(1)
Si(21)	3549(11)	1020(7)	-1402(5)
Si(2)	5193(2)	1824(1)	-1235(1)
Si(22)	6045(10)	1903(5)	-1132(4)
Si(3)	8140(2)	1474(1)	-1140(1)
Si(23)	8694(9)	1102(6)	-1215(4)
Si(4)	9000(1)	-80(1)	-1466(1)
Si(24)	8638(9)	-527(5)	-1575(4)
Si(5)	7078(2)	-1372(1)	-1334(1)
Si(25)	6373(10)	-1452(6)	-1130(5)
Si(6)	4284(1)	-998(1)	-990(1)
Si(26)	3659(10)	-644(6)	-1129(4)
C(13)	2796(5)	859(4)	-2090(3)
C(14)	2483(5)	975(3)	-827(3)
C(15)	5655(6)	2433(3)	-1760(2)
C(16)	5290(5)	2218(3)	-545(2)
C(17)	8897(5)	1774(3)	-1756(3)
C(18)	9184(5)	1364(3)	-514(2)
C(19)	9957(5)	-638(3)	-1004(3)
C(20)	9113(5)	-254(3)	-2215(3)
C(21)	7562(5)	-1798(3)	-667(2)
C(22)	6140(5)	-1960(3)	-1781(2)
C(23)	3526(5)	-757(3)	-365(2)
C(24)	3227(4)	-1413(3)	-1530(2)



C(7)	145(4)	287(2)	3763(2)
C(8)	1266(4)	507(2)	3709(2)
C(9)	2325(4)	197(2)	3716(2)
C(10)	2237(4)	-518(2)	3736(2)
C(11)	1109(4)	-831(2)	3802(2)
C(12)	84(4)	-421(2)	3851(2)
Si(7)	-1365(1)	746(1)	3689(1)
Si(27)	-810(17)	1134(11)	3635(8)
Si(8)	1241(1)	1569(1)	3660(1)
Si(28)	2122(17)	1512(11)	3717(9)
Si(9)	3798(1)	686(1)	3703(1)
Si(29)	4153(20)	257(13)	3744(11)
Si(10)	3702(1)	-997(1)	3679(1)
Si(30)	3133(19)	-1340(13)	3590(10)
Si(11)	1062(1)	-1793(1)	3736(1)
Si(31)	398(21)	-1673(14)	3923(11)
Si(12)	-1256(1)	-863(1)	4136(1)
Si(32)	-1614(22)	-455(15)	3991(12)
C(25)	-1685(5)	1342(3)	4257(2)
C(26)	-1740(5)	1091(3)	2985(2)
C(27)	1843(6)	2007(3)	4306(2)
C(28)	1771(5)	1964(3)	3030(2)
C(29)	4588(5)	582(3)	3064(2)
C(30)	4810(5)	630(3)	4351(2)
C(31)	3922(5)	-1327(3)	2979(2)
C(32)	4115(4)	-1630(3)	4223(2)
C(33)	1199(5)	-2315(3)	4382(2)
C(34)	-166(5)	-2107(3)	3251(2)
C(35)	-2605(4)	-1086(3)	3660(2)
C(36)	-1712(5)	-432(3)	4766(2)

TABLE III

Anisotropic thermal parameters (Å^2 × 10^3) for **1**

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
		MOLECULE I				
C(1)	23(2)	40(2)	30(2)	-3(2)	5(2)	6(2)
C(2)	35(2)	36(2)	26(2)	-2(2)	7(2)	6(2)
C(3)	27(2)	37(2)	28(2)	-4(2)	2(2)	-13(2)
C(4)	22(2)	38(2)	30(2)	1(2)	3(2)	7(2)
C(5)	32(2)	24(2)	30(2)	0(2)	7(2)	6(2)
C(6)	24(2)	37(2)	28(2)	-1(2)	2(2)	-10(2)
Si(1)	22(1)	37(1)	74(1)	1(1)	2(1)	2(1)
Si(2)	32(1)	26(1)	53(1)	-2(1)	2(1)	2(1)
Si(3)	27(1)	32(1)	79(1)	-13(1)	13(1)	-8(1)
Si(4)	24(1)	37(1)	61(1)	-7(1)	14(1)	2(1)
Si(5)	34(1)	27(1)	47(1)	-2(1)	10(1)	5(1)
Si(6)	28(1)	35(1)	48(1)	9(1)	8(1)	-5(1)
C(13)	63(3)	87(3)	106(3)	29(3)	-28(3)	15(3)
C(14)	49(3)	72(3)	163(3)	-26(3)	52(3)	3(2)
C(15)	94(3)	41(3)	75(3)	2(2)	21(3)	8(2)
C(16)	91(3)	44(3)	70(3)	-11(2)	11(3)	17(2)
C(17)	58(3)	57(3)	120(3)	27(3)	20(3)	-14(2)
C(18)	32(2)	101(3)	78(3)	-42(3)	6(2)	-10(2)
C(19)	34(2)	78(3)	137(3)	15(3)	-6(3)	3(2)
C(20)	77(3)	89(3)	79(3)	-31(3)	36(2)	-17(3)
C(21)	63(3)	65(3)	46(2)	9(2)	6(2)	22(2)
C(22)	61(3)	41(2)	47(2)	-4(2)	12(2)	-3(2)
C(23)	43(2)	81(3)	71(3)	25(3)	20(2)	3(2)
C(24)	39(2)	52(3)	88(3)	5(2)	-14(2)	-10(2)
		MOLECULE II				
C(7)	26(2)	33(2)	23(2)	-3(2)	0(2)	3(2)
C(8)	40(2)	22(2)	26(2)	-1(2)	-0(2)	2(2)
C(9)	26(2)	33(2)	23(2)	4(2)	5(2)	-8(2)
C(10)	25(2)	27(2)	27(2)	-1(2)	1(2)	4(2)
C(11)	34(2)	24(2)	22(2)	2(2)	2(2)	-1(2)
Si(7)	26(1)	36(1)	47(1)	2(1)	8(1)	7(1)
Si(8)	35(1)	27(1)	51(1)	5(1)	9(1)	1(1)
Si(9)	23(1)	32(1)	74(1)	6(1)	7(1)	-3(1)
Si(10)	24(1)	33(1)	52(1)	-2(1)	5(1)	5(1)
Si(11)	39(1)	25(1)	42(1)	-3(1)	6(1)	-3(1)
Si(12)	25(1)	39(1)	48(1)	7(1)	8(1)	-5(1)
C(25)	57(3)	52(3)	75(3)	-9(2)	21(2)	9(2)
C(26)	54(2)	76(3)	54(3)	14(2)	3(2)	25(2)
C(27)	116(3)	40(3)	61(3)	-4(2)	9(3)	-24(3)
C(28)	77(3)	39(2)	64(3)	18(2)	10(2)	-2(2)
C(29)	45(2)	82(3)	94(3)	41(3)	30(2)	-0(2)
C(30)	42(2)	76(3)	92(3)	-8(3)	-17(2)	-3(2)
C(31)	51(2)	71(3)	64(3)	-17(2)	17(2)	7(2)
C(32)	45(2)	49(3)	64(3)	-4(2)	-5(2)	11(2)
C(33)	66(3)	40(2)	54(3)	4(2)	25(2)	-3(2)
C(34)	59(3)	64(3)	61(3)	-13(2)	11(2)	-19(2)
C(35)	25(2)	63(3)	88(3)	6(3)	-9(2)	-9(2)
C(36)	52(2)	86(3)	46(2)	11(2)	20(2)	2(2)

The anisotropic temperature factor exponent takes the form:
$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$

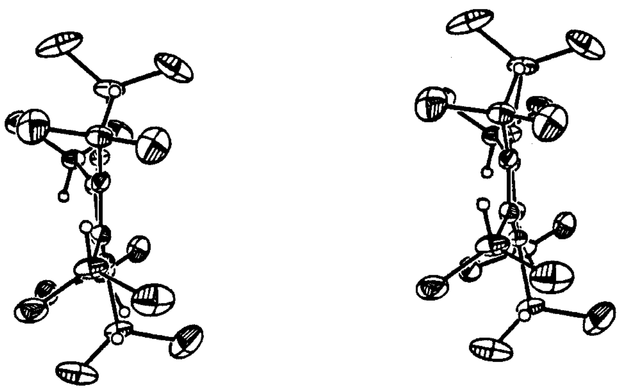


FIGURE 2 The ORTEP figure for molecule II in **1** viewed parallel to the mean plane of the ring and emphasizing the skewed arrangement of the side chains. Methyl hydrogen atoms are deleted for clarity.

disorder seen in crystals of **1**. Lattice sites are occupied by molecules of either handedness. The observation of minor silicon positions in the Fourier difference maps is analogous to the situation observed for **1**, HIB, and for HCB. Only average $W(CO)_3$ positions are observed in the complex. The ratio of major to minor orientations in the crystal is 5.9:1. Figure 3 shows a stereoview of the unit cell packing of the major orientational isomer of **2m** along *b*. Table IV gives the atomic positional parameters for **2m** along with the labeling scheme. Table V lists the anisotropic thermal parameters.

The trigonal crystals (**2t**) indexed along hexagonal axes with a = 19.044(5)Å, c = 14.343(4)Å. The structure was solved and refined in $R3$ with Z = 6. Figure 4 shows the unit cell packing of **2t** along *c* and clearly displays the trigonal symmetry. There are a pair of independent molecules of opposite handedness aligned along the three-fold axis.[10] Figure 5 shows a stereoview normal to this axis of the two independent molecules I and II. Table VI gives the atomic positional parameters for **2t** along with the labeling scheme. Table VII lists the anisotropic thermal parameters.

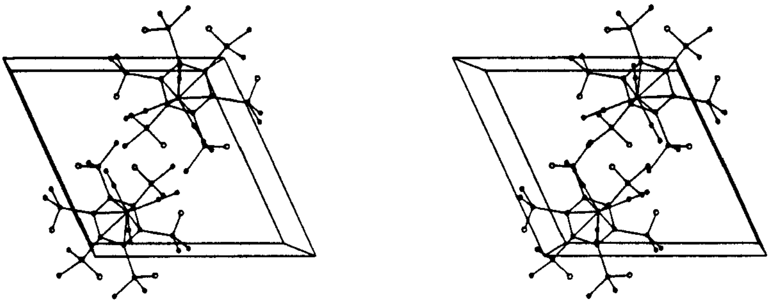
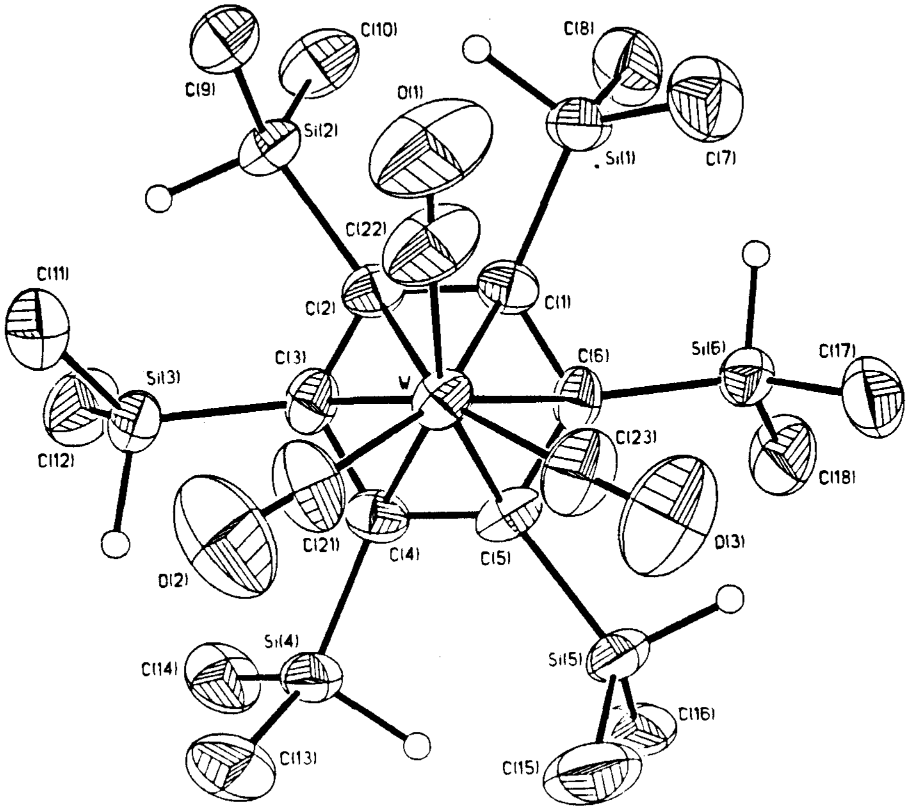


FIGURE 3 The unit cell packing of the major orientational isomer of **2m**, viewed along *b*. Methyl hydrogen atoms are deleted for clarity.

TABLE IV

Atomic positional parameters (Å × 10^4) for **2m**



	x	y	z
W	11876(1)	1670	2607(1)
Si(1)	10466(3)	139(3)	4436(3)
Si(11)	9488(19)	136(13)	3674(18)
Si(2)	13435(3)	-675(2)	4613(3)
Si(21)	12749(17)	-429(13)	4940(17)
Si(3)	14404(3)	-17(3)	2244(3)
Si(31)	14350(16)	-470(12)	2992(16)
Si(4)	12103(3)	864(3)	-674(3)
Si(41)	13050(21)	814(15)	121(21)
Si(5)	9179(3)	1649(4)	-800(3)
Si(51)	9803(17)	1445(10)	-1141(17)
Si(6)	8139(3)	804(2)	1475(3)
Si(61)	8124(18)	1263(14)	762(19)
C(1)	10825(9)	285(6)	2883(8)
C(2)	12180(9)	36(7)	3077(9)
C(3)	12622(9)	216(7)	2105(10)
C(4)	11760(9)	668(6)	865(9)

TABLE IV (*continued*)

	x	y	z
C(5)	10436(9)	920(7)	663(9)
C(6)	9933(8)	719(7)	1670(9)
C(7)	9768(14)	1219(11)	4883(15)
C(8)	9515(13)	-987(10)	4464(16)
C(9)	14421(11)	39(10)	6150(10)
C(10)	12721(14)	-1779(10)	4981(14)
C(11)	15777(11)	472(12)	3769(13)
C(12)	14641(14)	-1319(11)	1845(14)
C(13)	13173(14)	1915(9)	-674(14)
C(14)	12633(13)	-249(11)	-1212(11)
C(15)	9792(16)	2797(11)	-1165(14)
C(16)	8223(11)	899(13)	-2368(10)
C(17)	7481(13)	2023(10)	1657(14)
C(18)	6992(11)	156(12)	6(13)
C(21)	13331(11)	2432(10)	2509(12)
O(1)	12965(12)	2341(8)	5532(9)
C(22)	12604(13)	2088(9)	4464(11)
O(2)	14194(12)	2882(9)	2496(13)
C(23)	10920(12)	2901(7)	2241(12)
O(3)	10337(11)	3625(7)	2041(12)

The rhombohedral crystals (**2t**) also exhibit a twofold orientational disorder in which a pair of heterochiral molecules occupy a lattice site. But, unlike the monoclinic modification (**2m**) where the arene rings assume distinguishable sites and the $W(CO)_3$ units achieve superposition within the limits of resolution, in the average unit cell of **2t** the $W(CO)_3$ group sits either above or below a single resolved hexakis(dimethylsilyl)benzene.

Superposition of discrete $W(CO)_3$ groups in **2t** is evident in the exaggerated thermal parameters for the carbonyl carbon and oxygen atoms. They may be compared with the same parameters in **2m**. The ratio of populations of major to minor tungsten atoms is 5.1:1. Thus, as for the ligand (**1**), there are four isomers in the crystal; two of one hand and two of the other (Figure 6). None of the four are related by symmetry in *R*3.

While it is probably unusual for symmetry-independent molecules of a substance to lie along the same symmetry axis, we found no evidence of an additional symmetry element that related any pair of isomers. There exists a pseudo-inversion center at the ring centroid that relates the atomic positions of the major and minor isomers of a given arene, but a crystallographic inversion center requires equal occupancies. Refinement diverged under the constraints of centrosymmetry. Furthermore, the E-statistics indicated the acentric structure. The space group *R*32 requires twofold rotation axes through the carbonyl oxygens and in the plane defined by them. This operation would equivalence homochiral molecules but would also require equal occupancies in nominally major and minor sites. Refine-

TABLE V

Anisotropic thermal parameters (Å² × 10³) for **2m**

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W	35(1)	33(1)	38(1)	-1(1)	8(1)	-3(1)
Si(1)	52(2)	52(2)	37(1)	4(1)	19(1)	-0(1)
Si(2)	42(2)	51(2)	36(1)	6(1)	4(1)	3(1)
Si(3)	35(1)	62(2)	44(2)	2(1)	12(1)	6(1)
Si(4)	43(2)	69(2)	34(1)	10(1)	13(1)	-4(1)
Si(5)	43(1)	60(2)	41(1)	19(2)	8(1)	7(2)
Si(6)	33(1)	54(2)	46(2)	5(1)	12(1)	0(1)
C(1)	48(5)	38(4)	37(4)	-3(3)	20(4)	-3(4)
C(2)	47(5)	39(4)	32(4)	-3(4)	12(4)	-1(4)
C(3)	30(4)	45(5)	49(5)	-3(4)	8(4)	-6(4)
C(4)	48(5)	38(4)	40(4)	0(4)	20(4)	-9(4)
C(5)	46(5)	38(4)	36(5)	7(3)	3(4)	-0(4)
C(6)	25(4)	43(4)	49(5)	-3(4)	11(4)	-4(3)
C(7)	69(8)	86(8)	69(8)	-25(7)	29(6)	2(7)
C(8)	64(7)	79(9)	105(10)	26(8)	49(7)	-8(6)
C(9)	47(5)	81(8)	44(5)	-6(5)	7(4)	-4(5)
C(10)	82(8)	58(7)	69(7)	18(6)	17(6)	10(6)
C(11)	47(6)	97(10)	73(8)	3(7)	26(6)	-0(6)
C(12)	85(9)	71(8)	79(8)	1(7)	27(7)	27(7)
C(13)	89(8)	76(11)	91(8)	30(7)	46(7)	-17(7)
C(14)	79(8)	99(10)	50(6)	-21(6)	33(6)	-13(7)
C(15)	96(9)	85(10)	72(8)	40(7)	25(7)	2(8)
C(16)	60(7)	117(12)	28(5)	10(6)	5(5)	-13(6)
C(17)	67(7)	70(7)	94(9)	12(6)	51(7)	18(5)
C(18)	41(5)	108(11)	72(8)	-10(7)	8(5)	-9(6)
C(21)	49(5)	55(7)	86(8)	-15(5)	35(6)	-27(5)
O(1)	123(9)	93(8)	56(5)	-33(5)	-6(5)	-1(6)
C(22)	82(8)	61(6)	44(6)	-18(5)	-1(5)	2(6)
O(2)	100(7)	104(9)	145(10)	-35(7)	73(7)	-54(7)
C(23)	67(7)	26(5)	83(8)	4(4)	27(6)	14(4)
O(3)	95(7)	50(5)	130(9)	-6(5)	24(6)	14(5)

The anisotropic temperature factor exponent takes the form:
$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$

ment diverged in *R*32. A glide plane would relate heterochiral molecules and would not require a 1:1 disorder. However, there were many strong reflections of the type *hhOl* where $l = 2n + 1$. Beside lacking these requisite absences the structure was not refined in the space group *R*3*c*.[11]

The different types of disorder in the monoclinic and rhombohedral structures imply different kinds of packing defects. The disorder in the monoclinic structure is consistent with an uninterrupted lattice. Some fraction of the sites merely contain a complex molecule of the opposite hand. The volume requirements for the packing of either isomer are similar. In the rhombohedral lattice adjacent packing (along *c*) of both major and minor orientations would result in a severe carbonyl clashing. Perhaps ordered domains predominate, these joined at vacancies. There was no photographic evidence of pronounced diffuse scattering or a superlattice. The crystals were optically homogeneous between crossed nicols.

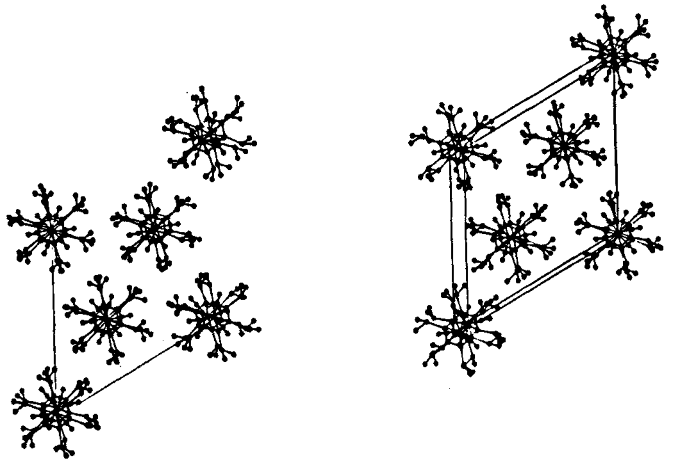


FIGURE 4 Unit cell packing of **2t** along *c* clearly displaying the trigonal symmetry. Only major orientation isomers are shown for clarity. Methyl hydrogen are deleted for clarity.

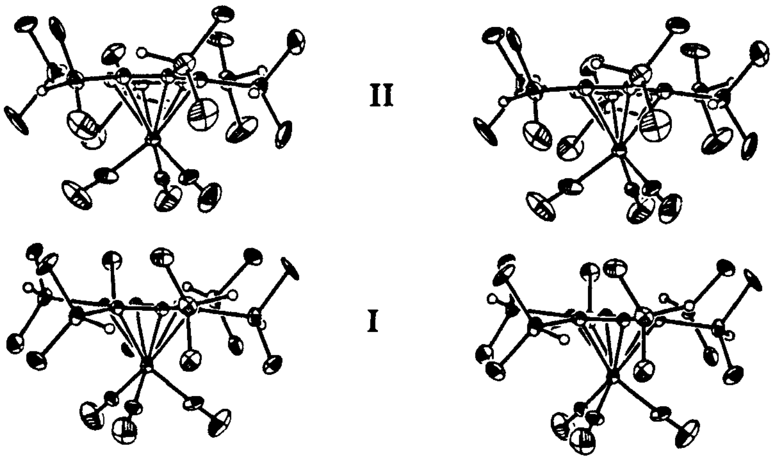
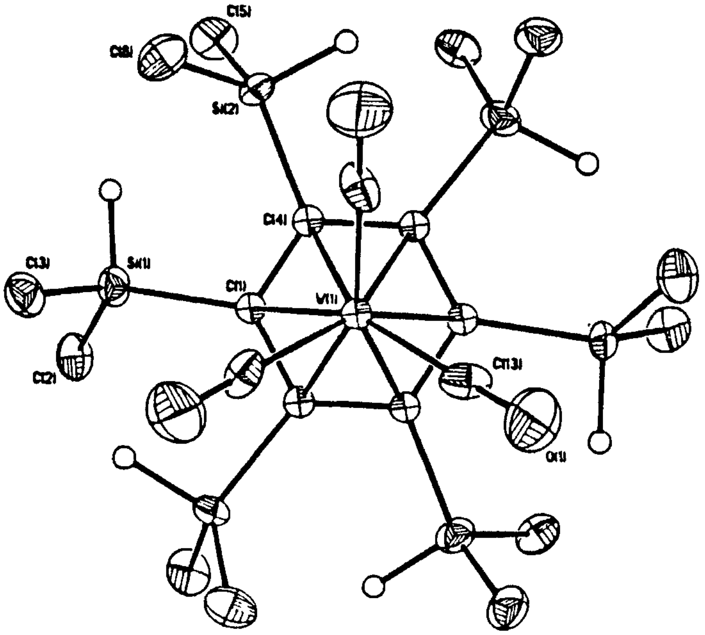


FIGURE 5 Stereoview of the two independent molecules I and II in **2t**. View is normal to the three-fold axis *c*. Methyl hydrogens are deleted for clarity.

The disorder in both structures vitiated a detailed description and comparison of the molecular geometries. We can only say with certainty that the carbonyl tripods in both structures adopt a staggered conformation with respect to the side chains. The only other reported X-ray structure of a tungsten tricarbonyl complex of a benzene derivative is that of 1,3,5-trimethylbenzenetricarbonyltungsten.[12] It adopts an eclipsed conformation with respect to the methyl groups which is consistent with symmetrically trisubstituted chromium and molybdenum tricarbonyl complexes.[13] For 1,3,5-trimethylbenzenetricarbonyltungsten, the crystallographers constrained the aromatic ring as a regular hexagon with normal benzene bond

TABLE VI

Atomic positional parameters (Å × 10^4) for **2t**



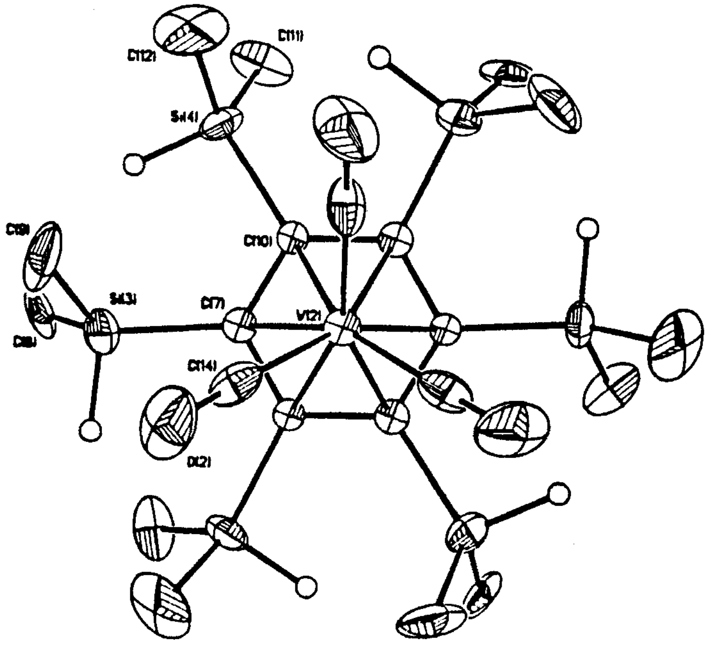


TABLE VI (*continued*)

	x	y	z
W(1)	0	0	1333
W(2)	0	0	6338(1)
W(3)	0	0	3829(8)
W(4)	0	0	-1142(9)
Si(1)	492(2)	-1465(2)	2781(3)
Si(2)	1950(2)	486(2)	2495(3)
Si(3)	1893(2)	300(2)	7484(3)
Si(4)	1585(2)	1893(2)	7811(3)
C(1)	160	-663	2639
C(2)	-57(6)	-2196(6)	3778(7)
C(3)	495(9)	-1990(7)	1705(10)
C(4)	823	160	2639
C(5)	2542(7)	491(7)	3572(10)
C(6)	2204(7)	35(8)	1521(9)
C(7)	823	160	7659
C(8)	2556(6)	575(7)	8484(9)
C(9)	2455(8)	963(9)	6493(11)
C(10)	664	823	7659
C(11)	1515(10)	2465(8)	8831(9)
C(12)	1999(13)	2589(11)	6728(15)
C(13)	-600(7)	334(7)	517(8)
C(14)	609(7)	-295(7)	5513(8)
O(1)	-933(6)	534(5)	73(8)
O(2)	958(6)	-490(7)	5063(8)

lengths of 1.395 Å. The average bond length in **2m** is 1.44(1)Å. There is considerable bond variation and alternation in this ring: the average length of the bonds eclipsed by the carbonyls is 1.46(1)Å and the average length of those staggered is 1.42(1)Å. Hall and coworkers studied the interruption of conjugation in arenetricarbonylchromium complexes in some detail.[14] This phenomenon seems exaggerated in the monoclinic structure of **2m**.

In **2t** the C_{ar}—C_{ar} lengths were fixed at 1.44(1)Å, the average value of the corresponding lengths in the monoclinic structure. When this constraint was relaxed, gross arene bond alternations (~0.4 Å) were observed. This could be interpreted as an artifact of correlation resulting from the blocked-diagonal least squares procedure; however it is also consistent with the monoclinic structure where each of the six arene bond lengths was explicitly refined.[15]

The distance from the mean aromatic plane in 1,3,5-trimethylbenzenetricarbonyltungsten is 1.886 Å. The corresponding distances in **2m** and **2t** are 1.84 Å and 1.88 Å, respectively. As in the free ligand **1**, the silicon atoms in both structures of **2** deviate from the mean arene plane by average absolute values of 0.20 Å and 0.22 Å. These deviations are alternately plus and minus in the tungsten complexes, whereas the deviations in **1** are helter-skelter. Surprisingly, complexation of the bulky $W(CO)_3$ to the already crowded arene does not cause greater out-of-plane

TABLE VII

Anisotropic thermal parameters ($Å^2 \times 10^3$) for **2t**

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W(1)	17(1)	17(1)	19(1)	0	0	8(1)
W(2)	25(1)	25(1)	16(1)	0	0	12(1)
W(3)	23(2)	23(2)	2(2)	0	0	11(1)
W(4)	10(2)	10(2)	36(3)	0	0	5(1)
Si(1)	33(2)	24(2)	33(2)	2(1)	-4(2)	18(1)
Si(2)	17(1)	28(2)	32(2)	1(1)	-1(1)	13(1)
Si(3)	32(2)	45(2)	34(2)	-2(2)	5(1)	23(2)
Si(4)	29(2)	20(2)	42(2)	4(1)	-4(2)	2(1)
C(2)	46(5)	31(5)	29(5)	9(4)	-0(4)	24(4)
C(3)	38(6)	23(5)	39(6)	7(5)	6(5)	14(4)
C(5)	30(5)	43(6)	42(7)	1(5)	-28(5)	16(5)
C(6)	37(6)	52(6)	31(6)	-1(5)	11(5)	26(5)
C(8)	37(5)	65(6)	56(7)	-27(5)	-6(5)	40(5)
C(9)	22(5)	76(8)	74(8)	-13(7)	18(5)	10(5)
C(11)	96(8)	53(6)	22(6)	-9(5)	-11(6)	49(6)
C(12)	107(9)	63(8)	82(9)	61(7)	54(8)	42(7)
C(13)	20(5)	34(6)	21(5)	7(5)	-3(4)	6(4)
C(14)	36(6)	27(5)	21(5)	3(4)	9(5)	2(5)
O(1)	62(6)	59(5)	76(6)	10(5)	-24(5)	35(4)
O(2)	48(5)	84(7)	79(7)	-35(5)	19(5)	22(5)

The anisotropic temperature factor exponent takes the form: $-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$

deviations of the arene substituents than in the uncomplexed arene **1**. As in **1**, the average Car—Si bond length (1.93(1)Å) is longer than the average C_m—Si (1.87(1)Å) bond length in both **2m** and **2t**.

Hexakis(dimethylsilyl)benzenetricarbonylmolybdenum (**3**). Hexane solutions of hexakis(dimethylsilyl)benzenetricarbonylmolybdenum (**3**) precipitated only monoclinic (**3m**: *a* = 11.020(6)Å, *b* = 13.838(4)Å, *c* = 11.099(4)Å, β = 114.54(3)°, *Z* = 2 at 193K) or only trigonal (**3t**: *a* = 19.056(4)Å, *c* = 14.633(5)Å, *Z* = 6 at 298K) crystals that are isomorphous with their tungsten analogues **2m** and **2t**. A complete structure was determined for the monoclinic crystal only.

Like its monoclinic tungsten isomorph, **3m** exhibits an orientational disorder with a ratio of major or minor orientational isomers of 4.3:1. The arene bond lengths show considerable alternation. The average length of the bonds that eclipse the carbonyls is 1.46 Å and the average length of the staggered bonds is 1.42 Å. Alternation was observed for the arene bond lengths of hexamethylbenzenetricarbonylmolybdenum[16] (1.405(5)Å, 1.441(9)Å) but not for hexaethylbenzenetricarbonylmolybdenum.[17]

Parameters in **3m** whose values are consistent with those of **2m** are the mean metal-arene distance (1.85 Å), the average C_{ar}—Si distance (1.92 Å), and the average C_{ar}—Si distance (1.86 Å). The silicon atoms in **3m** deviate alternately above and below the mean arene plane by an average absolute distance of 0.21 Å. Labeling schemes, fractional coordinates, bond lengths, and bond angles are provided in the supplementary material.

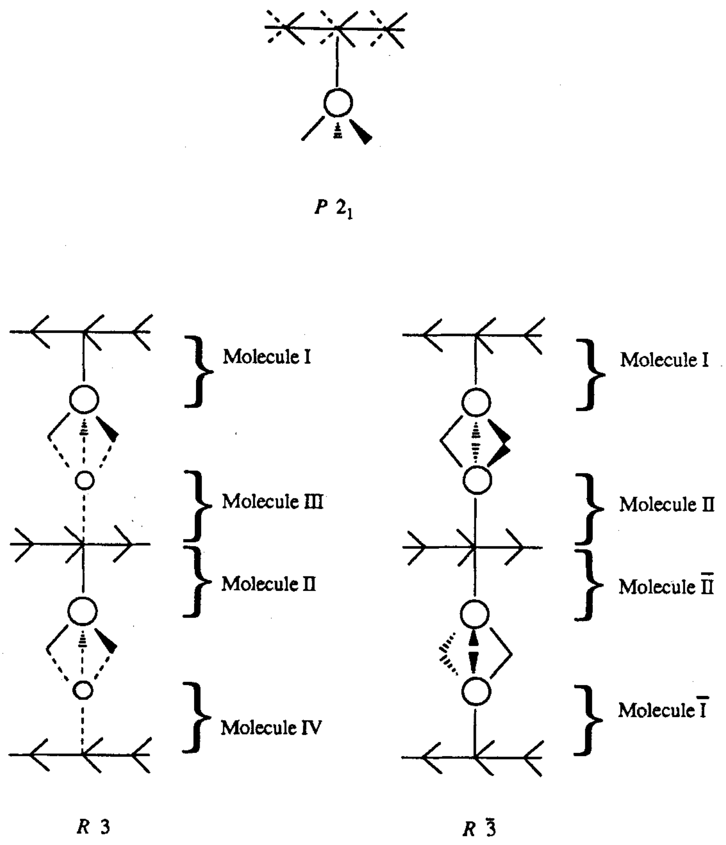


FIGURE 6 A schematic diagram of the disorder in the monoclinic (top) and rhombohedral (bottom) modifications of metal tricarbonyl (Cr, Mo, W) complexes of hexakis(dimethylsilyl)benzene viewed along the arene plane in each case. Open circles represent the metal atoms. The orientation of the side chains in the hexakis(dimethyl)silylbenzene rings is indicated by the multiply headed arrows. Top: In the monoclinic modification the disorder is similar to that found in the free arene (**1**). Rings with opposite disposition of the dimethylsilyl groups occupy the same lattice sites. The averaged metal tricarbonyl appendage is not resolved. Minor arene position are indicated by dashed lines. Bottom left: In $R3$ (represented by **2t**), there are four independent molecules stacked along the threefold axis. There are major and minor tungsten positions on either face of each arene ring. The carbonyl oxygens of major and minor orientations coincide. Bottom right: In $\bar{3}$ (represented by **4t**) a center of symmetry is introduced by the equal populations of the different orientations. There are consequently only two independent heterochiral molecules stacked along the threefold axis and these are related to their enantiomers by the centers of symmetry at the centers of the arene rings.

Hexakis(dimethylsilyl)benzenetricarbonylchromium (**4**). Crystals of hexakis(dimethylsilyl)benzenetricarbonylchromium (**4t**) are isomorphous to the rhombohedral crystals of the tungsten complex (**2t**). The cell constants are $a = 19.047(5)$Å, $c = 14.144(5)$Å with $Z = 6$. The only significant difference between the two structures is that the ratio of major to minor orientational isomers in the chromium structure is smaller. This permitted refinement in either $R3$ or $R\bar{3}$. The distinction in this instance was subtle. We settled on $R\bar{3}$ since the higher symmetry structure contains less information and it is a more conservative choice: when diffraction data to not provide a clear choice between a centrosymmetric or noncentrosymmetric structure the centrosymmetric option is safer, even if a disordered structure results.[18] In our case we are merely distinguishing between a more or less disordered structure. By analogy with **2t**, **4t** it probably nearly centrosymmetric, but it cannot be distinguished as such. However, unlike **2t**, the E-statistics are consistent with the centrosymmetric structure.

The consequence of centrosymmetry is to center the arene rings at Wyckoff *a* and *b*, sites of local S_6 symmetry. The major and minor orientations of $R\bar{3}$ are not constrained to have 0.50 populations.

In $R\bar{3}$, the C_{ar}—C_{ar} distance is 1.44 Å, the same as the average values in **2** and **3**. The approach of the chromium atom to the mean arene plane is closer at 1.69 Å. The average Cr-C_{ar} (2.22 Å) is also smaller than in the hexaethylbenzene analogue 2.345 Å. Similar bond lengths are associated with silicon in **4t** as in **3** and **2**; C_{ar}—Si (1.92 Å) and C_m—Si (1.86 Å). The average absolute deviation of the silicon atoms from the mean arene plane in **4t** is 0.24 Å. Centrosymmetry requires that this deviation be alternately above and below the ring plane.

Refinement in $R\bar{3}$ with arene rings constrained as regular hexagons with 1.44 Å Car—Car bond lengths led to a ratio of site occupancies of the major and minor orientational isomers of 2.3:1. In this space group R and R_w converged at 0.053, 0.058 with one persistent non-positive atom. The reflections $hh\bar{0}l$ were also significant for **3** thus ruling out the possibility of $R3c$ or $R\bar{3}c$. Refinement diverged in $R32$.

3. EXPERIMENTAL

3.1 Synthesis

Hexakis(dimethylsilyl)benzene (**1**) was synthesized according to the procedure of Brennan and Gilman.[4] The tungsten, molybdenum, and chromium tricarbonyl complexes (**2**, **3**, **4**) were synthesized by a modification of the procedure described by Mance.[19] The appropriate metal hexacarbonyl was refluxed under argon with **1** in a mixture of dry heptane, glyme, and diglyme (1:1:6). Workup of the reaction mixtures was conducted open to the air and consisted of dilution of the dark suspensions with hot toluene to insure complete dissolution of the complexes, followed by filtration through celite. The solvents and excess metal hexacarbonyl were then removed by using a rotary evaporator at 10^{-1} torr. The resulting yellow solids were triturated with pentane to give the pure metal tricarbonyl complexes as chunky yellow solids.

Hexakis(dimethylsilyl)benzenetricarbonyltungsten (**2**). Tungsten hexacarbonyl (4.13 g, 0.0117 mol) and **1** (5.00 g, 0.0117 mol) reacted as above, however longer reaction times (48 hrs) were required. The yield of pure **2** was poor (~1%); mp 271–272°C dec; IR (CH_2Cl_2) 1885, 1960 cm^{-1} (CO), 2190 cm^{-1} (Si-H); ^1H NMR (toluene-d_8) d 0.55 (brs, CH_3), 4.65 (septet, J = 3.5 Hz, SiH); ^{13}C-NMR (toluene-d_8) d 0.77, 3.44 (CH_3), 111.29 (Car), 210.13 (CO); mass spectrum (high resolution) *m/z* 694.1225 (694.1259 calcd for $C_{21}H_{42}O_3Si_6{}^{184}W$).

Hexakis(dimethylsilyl)benzenetricarbonylmolybdenum (**3**). Molybdenum hexacarbonyl (7.44 g, 0.0278 mol) and **1** (7.40 g, 0.0175 mol) gave pure **3** (0.0156 mol, 89%), mp 268–269°C dec; IR (CH_2Cl_2); 1885, 1960 cm^{-1} (CO), 2190 cm^{-1} (Si-H). ^{1}H-NMR (toluene-d_8) d 0.55 (brs, CH_3), 4.65 (septet, J = 3.6 Hz, SiH); ^{13}C-NMR (toluene d_8) d 0.68, 3.09 (CH_3), 116.48 (Car), 220.89(CO); mass spectrum (high resolution) *m/z* 608.0804 (608.0804 clacd for $C_{21}H_{42}O_3Si_6{}^{98}Mo$).

Hexakis(dimethylsilyl)benzenetricarbonylchromium (**4**). Chromium hexacarbonyl (6.70 g, 0.0305 mol) and **1** (8.13 g, 0.0191 mol) reacted in above manner gave pure **1** (7.08 g, 0.0126 mol, 66%), mp 266–277°C dec. (lit.[5] mp 265–266°C).

3.2 X-ray Crystallography

All intensities were collected on a Nicolet R3m four-circle diffractometer equipped with a nitrogen-flow cooling device. In all cases graphite monochromated MoKα (λ = 0.71069 Å) radiation was applied. Structures were solved and refined using the SHELXTL software. Crystallographic data are listed in Table I.

Hexakis(dimethylsilyl)benzene (**1**). Crystals of **1** suitable for X-ray analysis were obtained by slow evaporation from heptane at room temperature. The structure was solved by direct methods in the space group $P2_1$ and the center of symmetry was subsequently located. Nonhydrogen atoms, except minor silicon atoms, were refined anisotropically by using a blocked-cascade least-squares procedure. Hydrogen atoms were included at ideal positions (Si—H = 1.4 Å, C—H = 0.96, C-Si-H = 109.5°). The silyl hydrogen atoms were included only for the major orientation and weighted accordingly. All hydrogens were varied with a riding model. Population coefficients p_{I} and p_{II} were refined for the major silicon atoms in molecules I and II under the constraint that $p_{\mathrm{I}} + p_{\mathrm{I}}' = 1$ and $p_{\mathrm{II}} + p_{\mathrm{II}}' = 1$. Their final values were 0.857(1) and 0.942(1), respectively. R and R_w factors converged at 0.076 and 0.060, respectively.

Hexakis(dimethylsilyl)benzenetricarbonyltungsten (**2**). Crystals of **2m** and **2t** were grown from hexane at refrigerator temperatures. The structure of **2m** was determined by substituting the solution of its molybdenum isomorph (see below). Refinement and treatment of thermal parameters was as for **1** (see above). A population coefficient was refined for the silicon atoms. The final value was 0.854(2). R and R_w factors converged at 0.037 and 0.039, respectively.

The structure of **2t** was solved by substituting the solution of the chromium isomorph (see below). Carbonyl carbon and oxygen atoms corresponding to minor orientations were not located in the final difference map. Refinement and treatment of thermal parameters was as for **1** (see above). A population coefficient p was refined for the silicon atoms. The final value was 0.835(2). R and R_w factors converged at 0.043 and 0.051, respectively.

Hexakis(dimethylsilyl)benzenetricarbonylmolybdenum (**3**). Crystals of **3t** were grown from hexane at refrigerator temperatures. The structure was solved by the Patterson heavy-atom method in $P2_1$. Refinement and treatment of thermal parameters was as for **1**. The final refined population coefficient for the silicon atoms was 0.812(2). R and R_w factors converged 0.034 and 0.035, respectively. Crystals of **3m** were grown from hexanes at room temperature. The irregularly shaped monoclinic crystals were picked from a batch which contained mostly rhombohedra. The crystal were indexed at room temperature.

Hexakis(dimethylsilyl)tricarbonylchromium (**4**). The crystal of **4m** chosen for X-ray measurements was grown from methylene chloride/methanol. Refinement and treatment of thermal parameters was as for **1** (see above). The structure was solved by the Patterson heavy-atom method in $R3$. A population coefficient p was restricted by the space group symmetry to be 0.50 in $R\bar{3}$. R and R_w factors after refinement were 0.043 and 0.051, respectively.

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Supplementary Material Available: Observed and calculated structure factors (**1**, **2m**, **2t**, **3m**, **4t**), atomic positional parameters (**3m**, **4t**), bond lengths (**1**, **2m**, **2t**, **3m**, **4t**), bond angles (**1**, **2m**, **2t**, **3m**, **4t**), anisotropic thermal parameters (**3m**, **4t**) and figures with labeling schemes (**3m**, **4t**) are available by contacting Gordon & Breach, 5301 Tacony Street, Drawer 330, Phila., PA 19137. Please mark your envelope "attention MCLC Supplementary Materials."

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11. A least-squares fit of the geometries of I and II was performed using a routine in the *Uranus86* package of programs. We thank Simon K. Kearsley for the use of these routines. Cartesian coordinates of molecule II were first inverted. The centroids of each molecule were places at the origin and a rotation matrix was computed to bring paired atoms into register. The largest deviation was between C3 and C12 (0.243 Å).
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