predicts a bond of order unity to be 0.18 Å shorter than one of order 0.5. If we represent nonbridging bonds in $(RhF_5)_4$ as electron-pair bonds, then, if the Pauling equation is valid, the bridging M-F bonds must be single electron bonds. Now, this F-bridging situation is reminiscent of the Cl bridging in Al_2Cl_6 and the CH_3 bridging in $Al_2(CH_3)_6$. The geometries of Al_2Cl_6 and $Al_2(CH_3)_6$ are similar[23,24] and in each case the bridging ligand-Al interatomic distance is greater than the nonbridging, the actual values being: Al-Cl, bridging = 2.21 Å, nonbridging = 2.06 Å; Al-CH_3, bridging = 2.24 Å, nonbridging = 2.00 Å. The bridge bonding in $Al_2(CH_3)_6$ is usually discussed[24] in terms of three-center two-electron bonding. A similar bonding model appears to be appropriate for the halogen-bridging cases discussed here. As has already been pointed out, however, the M-F-M bridging is not the same for all of the transition metal pentafluorides.

The near-hexagonal close packing of the fluorine atoms in RhF_5 indicates that the M-F-M angle of ~135° seen in this structure must be as acute as any such bridging angle could become, without further lengthening of the bridging bonds relative to the nonbridging. It is notable that in AuF_3 polymer,[25] the Au-F-Au bridge angle is 116°, but the gold atom coordination, in F atoms, is four in a square, not octahedral.

The adoption of the RhF_5 type structure by those pentafluorides at the right-hand end of each transition series suggests that the bridge bonding in this type has a greater measure of covalency than in the other structure types. This is because the increasing nuclear charge in the series Nb → Rh and Ta → Pt is not screened by the formally nonbonding d electrons (which occupy the dt_{2g} orbitals). Evidently, in VF_5 and its structural relatives, the covalency constraint on the M-F-M bridging is great enough to render the better packed NbF_5 type structure energetically less desirable but, yet, not great enough to produce the RhF_5 type. On the basis of this rationalization, the NbF_5 type structure comes closest to representation as an ionic assembly $(MF_4{}^+F^-)_4$. Of the transition metal pentafluorides it is, therefore, more likely that those of the NbF_5 type should form $MF_4{}^+$ salts with excellent F^- acceptors such as SbF_5 and Edwards[26] has already presented evidence for the salt $NbF_4{}^+SbF_6{}^-$.

It remains to be seen whether AuF_5, PdF_5, and MnF_5 can be obtained as crystalline solids. There is no certainty that these pentafluorides would be fluorine-bridged polymers and not monomers (like AsF_5 and PF_5) but if bridging does occur, the RhF_5 type structure appears to be the most likely one to be adopted.

Acknowledgments. This work was sponsored under the auspices of the U. S. Atomic Energy Commission. One of us (A. T.) thanks CRNS for fellowship support.

Registry No. $(RhF_5)_4$, 41517-05-9.

Supplementary Material Available. Table II, which gives a listing of observed and calculated structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2640.

---

[23] "Tables of Interatomic Distances and Configurations in Molecules and Ions," *Chem. Soc. Spec. Publ.*, No. 11 (1958).

[24] R. E. Rundle, *Rec. Chem. Progr.*, 23, 195 (1962).

[25] F. W. B. Einstein, P. R. Rao, J. Trotter, and N. Bartlett, *J. Chem. Soc. A*, 478 (1967).

[26] A. J. Edwards, *Chem. Commun.*, 820 (1970).

Contribution from Gibbs Chemical Laboratory,
Harvard University, Cambridge, Massachusetts 02138

Thermal Rearrangements of Icosahedral Carboranes. Molecular and Crystal Structure of 5,12-Dichloro-1,7-dimethyl-1,7-dicarba-*closo*-dodecaborane(12)

HASKELL V. HART and W. N. LIPSCOMB*

Received March 5, 1973

Thermal rearrangement of 9,12-dichloro-*C,C'*-dimethyl-*o*-carborane at 420° yields 5,12-dichloro-*C,C'*-dimethyl-*m*-carborane as the major product, in addition to a large number of the possible 15 other meta isomers. This major product is the only one expected from the cuboctahedral intermediate mechanism. Other products may result from triangle rotations in this intermediate and possibly from other less important mechanisms. This major product is orthorhombic, in the space group $Pmn2_1$, and has two molecules in a unit cell having dimensions of $a = 7.725$, $b = 10.181$, and $c = 8.079$ Å. The value of $R_F = \Sigma \| k|F_o| - |F_c| \| / \Sigma k|F_o|$ is 0.078 for 460 observed diffraction maxima.

Earlier studies[1,2] of thermal rearrangements of monohalocarboranes $(B_{10}H_9XC_2H_2)$ have supported the original proposal[3] that the major transformation proceeds through a cuboctahedral intermediate (Figure 1). Products in addition to those produced by this mechanism are believed[1,2] to arise principally from triangle rotations occurring only during the lifetime of this intermediate. It is not yet known whether apparent preference for rotation of triangles which are furthest from C atoms occurs because of electronic or steric effects. Nevertheless, electronic effects are known[2] in the final equilibria for different halogens, and preferred collisional effects have been proposed[2] for triangles in which one B atom is attached to Cl. Also, further study is required in order to decide whether rotation of a pentagonal cap,[4,5] or of a

---

[1] H. D. Kaesz, R. Bau, H. A. Beall, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 89, 4218 (1967).

[2] H. V. Hart and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 91, 771 (1969).

[3] A. Kaczmarczyk, R. D. Dobrott, and W. N. Lipscomb, *Proc. Nat. Acad. Sci. U. S.*, 48, 729 (1962).

[4] D. Grafstein and J. Dvorak, *Inorg. Chem.*, 2, 1128 (1963).

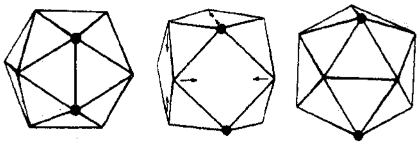

Figure 1. Transformation of *o*- to *m*-carborane through the cuboctahedral intermediate.

triangle,[6] in the icosahedron itself may also contribute to the occurrence of minor products, even though it has been shown[1,2] that these alternative mechanisms are not the major processes.

In the present study we ambitiously set out to isolate and isomerize the 16 ortho, 16 meta, and 5 para isomers of dichlorocarborane, starting with 9,12-Cl_2-*o*-$B_{10}H_8C_2(CH_3)_2$. At present we are far short of this objective, but we do show below that the principal product of the isomerization of this starting material is 5,12-Cl_2-*m*-$B_{10}H_8C_2(CH_3)_2$. The numbering scheme is shown in Figure 2, where C atoms are 1 and 2 for *o*-, 1 and 7 for *m*-, and 1 and 12 for *p*-carboranes.

Experimental Section

Rearrangements. All *C,C'*-dimethyl,[7] chloro,[8] bromo,[9] and iodo[10] derivatives were prepared by standard procedures from *o*-$B_{10}H_{10}C_2H_2$[11] and *m*-$B_{10}H_{10}C_2H_2$.[11] Yields were comparable to those reported elsewhere.

Samples for isomerization were weighed in glass tubes which were subsequently sealed under vacuum. The sealed tubes were placed in a furnace at 420° for the desired time, removed and quickly cooled, and later cracked open for chromatographic analysis.

Isomerization products so obtained were dissolved in acetonitrile and chromatographed on an F & M 720 temperature-programmed gas chromatograph. The best separation of isomers was obtained on an 8-ft Carbowax 20M column operating between 150 and 250°. The various ortho intermediate rearrangement products of 9,12-Cl_2-*o*-$B_{10}H_8C_2H_2$ and 9,12-Br_2-*o*-$B_{10}H_8C_2H_2$ did not pass through the Carbowax column and were poorly resolved on other columns. However, intermediate ortho and all final meta rearrangement products of 9,12-Cl_2-*o*-$B_{10}H_8C_2(CH_3)_2$ were resolved by the use of a 0.25-in. diameter column for standard analytical work and a 0.5-in. diameter column for preparative separations (Figure 3). Peak areas on the chromatograms were measured with a Keuffel and Esser 4236M compensating polar planimeter.

^{11}B Nmr Spectra. All 80.53-MHz ^{11}B nmr spectra were obtained on a spectrometer built by Drs. F. A. L. Anet and C. Bradley and operated by Dr. Richard J. Wiersema at UCLA.

^{1}H Nmr Spectra. All 60-MHz ^{1}H nmr spectra were obtained on a Varian T-60 spectrometer.

Crystal Structure. The major meta isomer (product 5, Figure 3) was recrystallized from heptane by slow cooling from 20 to 4°. Needle-like crystals several millimeters long resulted. From these, one was cut to 0.04 × 0.06 × 0.56 mm and mounted inside a glass capillary which was sealed to avoid sublimation. Weissenberg and precession photographs taken with Cu Kα radiation indicated D_{2h} Laue symmetry. Extinction of $h0l$ reflections when $h + l = 2n + 1$ is consistent with space groups $Pmn2_1$ (No. 31) and $Pmnm$ (No. 59 transposed). The orthorhombic unit cell parameters $a = 7.725 \pm 0.001$, $b = 10.181 \pm 0.001$, and $c = 8.079 \pm 0.002$ Å were determined from a least-squares fit of optimized angular measurements of the positions of 11 reflections made with the use of a Picker automated diffractometer. A density of 1.26 g/cm^3 was measured by the floatation method and was identical, within experimental error, with the calculated density of 1.261 g/cm^3 assuming two molecules per unit cell.

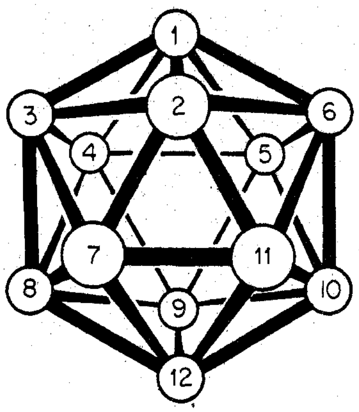

Figure 2. Numbering convention for icosahedral structures.

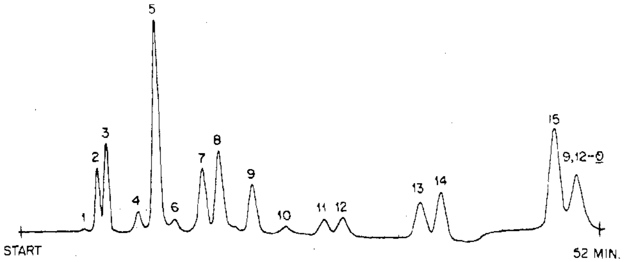

Figure 3. Vapor-phase chromatogram of the quenched reaction mixture of 9,12-Cl_2-*o*-$B_{10}H_8C_2(CH_3)_2$ after 4 hr at 420°. The chromatographic sample was started at 150°, increased 2° per min, and ended at 52 min. The solvent peak due to CH_3CN has been eliminated.

Intensity data to $2\theta = 120°$ were taken by the use of the Picker automated diffractometer with the crystal maintained at 4° by the use of a refrigerated air stream. A 2θ scan of 1°/min was employed and background counts were taken for 10 sec before and after the scan. The scan interval was 2°. The incident X-ray beam of Ni-filtered Cu Kα radiation passed through a 1-mm collimator at a take-off angle of 4°, and the diffracted beam passed through a 2-mm collimator to the detector. After every 25 reflections, two check reflections were measured, and no significant variation in the intensities was found. Two symmetry-equivalent sets of reflections were collected for a total of 1130 reflections. After correcting for background and applying Lorentz and polarization factors, 233 of these were rejected because of background asymmetry (a factor of 5 or more) or negative net counts. Symmetry-equivalent pairs were averaged to yield 540 unique reflections of which 80 were given zero weight in the refinement because both symmetry-equivalent reflections differed from the average by more than 25%. In general, the rejected and zero weight reflections were the very weakest ("unobservable"). An overall correlation value of

$$R_I = \sum_{hkl} |I_{hkl} - \bar{I}_{hkl}| / \sum_{hkl} \bar{I}_{hkl} = 0.032$$

was obtained for the 460 reflections in the refinement. No absorption correction was applied because the calculated absorption coefficient, $\mu = 42.1$ cm^{-1}, is sufficiently small for a crystal of the size noted above. A scale factor and an overall temperature factor were obtained by Wilson's method. The scale factor was subsequently refined.

A three-dimensional Patterson map contained a Harker plane at $z = 1/2$ which uniquely determined the space group as $Pmn2_1$ (acentric) and led to the choice of a and c axes. The molecule was, therefore, required to lie on the mirror plane at $x = 0$. An intramolecular Cl–Cl vector was located in the Patterson map, and coordinates of both chlorine atoms were determined. The z coordinate of one was arbitrarily assigned the value of zero because the origin location along z is arbitrary in space group $Pmn2_1$. A structure-factor calculation based on the coordinates of the chlorine atoms and Wilson plot temperature and scale factors yielded

$$R_F = \sum_{hkl} |kF_o - |F_c|| / \sum_{hkl} kF_o = 0.47$$

---

(5) L. I. Zakharkin and V. N. Kalinen, *Dokl. Akad. Nauk SSSR*, 169, 590 (1966).

(6) E. L. Muetterties and W. N. Knoth, "Polyhedral Boranes," Marcel Dekker, New York, N. Y., 1968, p 70.

(7) T. L. Heying, *et al.*, *Inorg. Chem.*, 2, 1097 (1963).

(8) L. I. Zakharkin and V. N. Kalinin, *Dokl. Akad. Nauk SSSR*, 169, 590 (1966).

(9) H. D. Smith, T. A. Knowles, and H. Schroeder, *Inorg. Chem.*, 4, 107 (1965).

(10) L. I. Zakharkin and V. N. Kalinin, *Dokl. Akad. Nauk SSSR*, 170, 92 (1966).

(11) Obtained from Olin Mathieson Chemical Corp., New Haven, Conn.

for the 460 nonzero weight reflections. Three cycles of Fourier refinement yielded the coordinates of all atoms (except hydrogen) and $R_F = 0.23$. A final electron density map showed all atoms unshifted from their positions in the previous map and showed no extra peaks.

A full-matrix isotropic refinement failed to converge. The chlorine atoms were refined isotropically with coordinates, thermal parameters, and the scale factor in three separate blocks for three cycles of half-shifts after which $R_F = 0.19$. Next, the boron and carbon atoms were refined isotropically with the coordinates, thermal parameters, and the scale factor in separate blocks for three cycles of half-shifts after which $R_F = 0.15$. A full-matrix isotropic refinement of all parameters then gave $R_F = 0.12$ after three cycles of half-shifts. Three cycles of anisotropic refinement with three separate blocks for coordinates, thermal parameters, and the scale factor and half-shifts gave $R_F = 0.085$. A difference Fourier then revealed the positions of the four hydrogens bonded to boron. With the hydrogen atoms included $R_F = 0.079$. A final block-diagonal refinement with all the parameters of each Cl, B, or C atom in one block converged to $R_F = 0.078$ and

$$R_{wF^2} = \sum_{hkl} w(k^2F_o^{\,2} - |F_c|^2)^2 / \sum_{hkl} w(kF_o)^4 = 0.021$$

after one cycle of half-shifts. The hydrogen isotropic thermal parameters were not refined. A weighting scheme of $w = 1/F_o^{\,2}$ for F_o greater than $4F_{\min}$ and $w = 1/4F_oF_{\min}$ for F_o less than $4F_{\min}$ (the Hughes scheme for counter data) was used in all refinements. The function minimized in all cases was $\Sigma_{hkl} w(k^2F_o^{\,2} - |F_c|^2)^2$.

A final difference Fourier showed no peaks greater than 1.14 e/Å^3 or less than −0.36 e/Å^3. Boron and carbon atom residuals were between 0.23 and 0.55 e/Å^3 and chlorine residuals were 1.00 and 1.14 e/Å^3. The six methyl hydrogen atoms were never located, probably because of rotation about the C–C bond.

Results and Discussion

Crystal Structure. Atomic parameters are given in Table I, and bond distances are in Tables II and III. Structure factors have been recorded elsewhere.[12] The final value of $R = \Sigma|k|F_o| - |F_c||/\Sigma k|F_o|$ is 0.078 for 460 observed reflections. This crystal structure (Figure 4) has a molecular mirror plane coincident with the crystallographic mirror plane at $x = 0$. Atoms C(1), C(7), C(1′), C(7′), B(5), Cl(5′), B(12), and Cl(12′) are on this mirror plane. Within one molecule, atom pairs B(2) and B(3), B(4) and B(6), B(8) and B(11), and B(9) and B(10) are related by the mirror plane. The molecular structure with 50% probability ellipsoids calculated from the final thermal parameters is shown in Figure 5. The positions of the cage carbon atoms are determined by the external methyl carbon atoms to which they are bound. The chlorine atoms are, therefore, bonded to boron atoms B(5) and B(12) in the conventional numbering system for icosahedral cages. Noncrystallographically equivalent bond distances are listed in Table II. In Table III the bond distances are averaged to the probable C_{2v} molecular symmetry. In all but two cases the symmetry-equivalent pairs were within one standard deviation of the average, thus confirming the distorted icosahedral cage structure of C_{2v} symmetry found previously but with larger standard deviations in m-$B_{10}Cl_{10}C_2H_2$[13] and 9,10-Br_2-m-$B_{10}H_8C_2H_2$.[14] Average bond distances, B–Cl = 1.81 Å, B–C = 1.72 Å, and B–B = 1.79 Å, are in excellent agreement with those found in these earlier studies. Closest H–H intermolecular contacts of 2.79, 2.99, and 3.00 Å agree very well with previously reported values for similar compounds.[15,16]

Table I. Final Atomic Parameters[a]

Atomic Positions in Fractions of a Unit Cell Edge

Atom	x	y	z
Cl(12′)	0 (0)[b]	0.5960 (4)	0 (0)[b]
Cl(5′)	0 (0)[b]	0.0761 (4)	0.3530 (7)
C(1)	0 (0)[b]	0.1022 (14)	−0.0182 (24)
B(2)	0.1193 (17)	0.1906 (12)	−0.1630 (17)
B(5)	0 (0)[b]	0.1784 (16)	0.1691 (26)
B(6)	0.1903 (16)	0.1779 (11)	0.0418 (15)
C(7)	0 (0)[b]	0.3335 (14)	−0.1811 (20)
B(10)	0.1189 (16)	0.3236 (11)	0.1508 (19)
B(11)	0.1873 (18)	0.3325 (11)	−0.0641 (17)
B(12)	0 (0)[b]	0.4189 (16)	0.0057 (28)
C(1′)	0 (0)[b]	−0.0522 (15)	−0.0409 (22)
C(7′)	0 (0)[b]	0.4050 (17)	−0.3472 (22)
H(2′)	0.185 (14)	0.138 (9)	−0.247 (12)
H(6′)	0.306 (14)	0.109 (10)	0.103 (13)
H(10′)	0.188 (14)	0.346 (10)	0.269 (13)
H(11′)	0.313 (13)	0.388 (10)	−0.075 (13)

Anisotropic Thermal Parameters (×10^4)[c]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl(12′)	209 (9)	52 (3)	181 (8)	0 (0)[b]	0 (0)[b]	16 (12)
Cl(5′)	181 (8)	87 (4)	132 (6)	0 (0)[b]	0 (0)[b]	75 (10)
C(1)	132 (27)	60 (13)	167 (28)	0 (0)[b]	0 (0)[b]	66 (38)
B(2)	104 (21)	72 (11)	119 (21)	16 (31)	13 (46)	−28 (32)
B(5)	137 (29)	72 (15)	89 (21)	0 (0)[b]	0 (0)[b]	35 (34)
B(6)	99 (21)	67 (10)	116 (19)	29 (29)	9 (37)	7 (25)
C(7)	137 (30)	70 (15)	128 (28)	0 (0)[b]	0 (0)[b]	−18 (34)
B(10)	113 (22)	64 (11)	129 (22)	−62 (32)	−40 (45)	−1 (29)
B(11)	137 (26)	54 (11)	114 (18)	8 (30)	3 (44)	−53 (24)
B(12)	197 (36)	87 (17)	161 (30)	0 (0)[b]	0 (0)[b]	33 (48)
C(1′)	187 (34)	60 (15)	169 (35)	0 (0)[b]	0 (0)[b]	−25 (38)
C(7′)	298 (42)	107 (17)	114 (22)	0 (0)[b]	0 (0)[b]	139 (33)

Isotropic Thermal Parameters[d]

Atom	B[e]	Atom	B[e]
H(2′)	3.5	H(10′)	3.5
H(6′)	3.5	H(11′)	3.5

[a] Standard deviations are indicated in parentheses, *e.g.*, 0.5960 (4) = 0.5960 ± 0.0004. [b] Not refined. [c] Anisotropic thermal parameters are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$. [d] The isotropic thermal parameter is of the form $\exp[-B \sin^2 \theta/\lambda^2]$. [e] From the Wilson plot, unrefined.

Table II. Bond Distances[a-c]

Bond	Dist, Å	Bond	Dist, Å
C(1)–B(2)	1.74 (2)	B(6)–B(11)	1.79 (2)
C(1)–B(5)	1.70 (3)	B(6)–H(6′)	1.24 (11)
C(1)–B(6)	1.73 (1)	C(7)–B(11)	1.73 (2)
C(1)–C(1′)	1.58 (2)	C(7)–B(12)	1.74 (3)
B(2)–B(3)	1.81 (2)	C(7)–C(7′)	1.53 (2)
B(2)–B(6)	1.75 (2)	B(10)–B(9)	1.84 (2)
B(2)–C(7)	1.71 (2)	B(10)–B(11)	1.82 (2)
B(2)–B(11)	1.73 (2)	B(10)–B(12)	1.78 (2)
B(2)–H(2′)	1.02 (10)	B(10)–H(10′)	1.12 (10)
B(5)–B(6)	1.79 (2)	B(11)–B(12)	1.78 (2)
B(5)–B(10)	1.75 (2)	B(11)–H(11′)	1.13 (10)
B(5)–Cl(5′)	1.81 (2)	B(12)–Cl(12′)	1.80 (2)
B(6)–B(10)	1.81 (2)		

[a] Standard deviations are indicated in parentheses, *e.g.*, 1.74 (2) = 1.74 ± 0.02, and were calculated from the standard deviations in x, y, and z in Table I. [b] Hydrogens have the same number (with prime added) as the boron to which they are bonded. [c] Other bond distances are related by the crystallographic (and molecular) mirror plane.

Isomerizations. At present we discuss only a few limited aspects of products and mechanisms of these complex isomerizations. A definitive account will have to await a complete identification of all products.

Percentage yields of prominent meta isomers arising from 9,12-Cl_2-o-$B_{10}H_8C_2(CH_3)_2$, 9,12-Cl_2-o-$B_{10}H_8C_2H_2$, and 9,12-Br_2-o-$B_{10}H_8C_2H_2$ are shown in Table IV. Percentages from

---

(12) See paragraph at end of paper regarding supplementary material.

(13) J. A. Potenza and W. N. Lipscomb, *Proc. Nat. Acad. Sci. U. S.*, 56, 1917 (1966).

(14) H. A. Beall and W. N. Lipscomb, *Inorg. Chem.*, 6, 874 (1967).

(15) H. V. Hart and W. N. Lipscomb, *Inorg. Chem.*, 7, 1070 (1968).

(16) T. F. Koetzle, F. E. Scarbrough, and W. N. Lipscomb, *Inorg. Chem.*, 7, 1076 (1968).

Table III. Bond Distances Averaged to C_{2v} Symmetry

Bond type	No. averaged[b]	Dist, Å[a]
B-Cl	2 (2)	1.81 (1)
C(1)-B(2)	2 (4)	1.72 (1)
C(1)-B(5)	2 (2)	1.72 (2)
C(1)-B(6)	2 (4)	1.73 (1)
C(1)-C(1')	2 (2)	1.56 (2)
B(2)-B(3)	1 (1)	1.81 (2)
B(2)-B(6)	2 (4)	1.74 (1)
B(5)-B(6)	2 (4)	1.79 (1)
B(5)-B(10)	2 (4)	1.76 (1)
B(6)-B(10)	2 (4)	1.81 (1)
B(6)-B(11)	1 (2)	1.79 (2)
B(10)-B(9)	1 (1)	1.84 (2)

[a] Standard deviations are indicated in parentheses, *e.g.*, 1.81 (1) = 1.81 ± 0.01, and were calculated from the standard deviations in Table II or taken directly from Table II when the number averaged was one. [b] The number in parentheses is the total number of such distances in a molecule of C_{2v} symmetry.

Table IV. Final Percentage Yields of Meta Isomers at 420°

	Starting material	Time, hr	Meta isomer no.[a,b] 2	3	4	5	7	8
A.	9,12-Cl_2-$(CH_3)_2$-*o*-	24	15	27	8	30	9	11
B.	9,12-Cl_2-*o*-	8	10	8	3	56	10	14
	9,12-Cl_2-*o*-	24	11	9	4	51	9	16
C.	9,12-Br_2-*o*-	8	7	4	4	53	13	19
	9,12-Br_2-*o*-	24	7	6	2	52	13	20

[a] The numbering of isomers is in order of increasing vpc retention time. Isomers **1** and **6** appeared in trace amounts and could not be isolated or characterized. Isomer **10**, which appeared in trace amounts, has retention times like those of 9,10-Cl_2-*m*-$B_{10}H_8C_2(CH_3)_2$ in series A and 9,10-Cl_2-*m*-$B_{10}H_8C_2H_2$ in series B. [b] Isomer **3** fraction of series A also contains an appreciable amount of a second isomer having the same retention time.

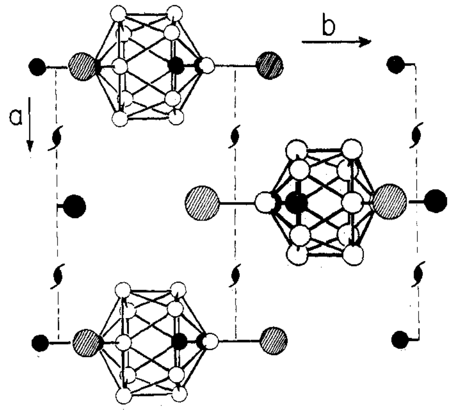

Figure 4. Crystal structure of 5,12-Cl_2-*m*-$B_{10}H_8C_2(CH_3)_2$ as seen in the *hk*0 projection. Open circles are boron atoms, solid circles are carbon atoms, and diagonally shaded circles are chlorine atoms. Hydrogen atoms have been eliminated for clarity.

the latter two are so similar that they suggest a common mechanism for these rearrangements. Perhaps with caution about the relative identities of meta isomers **2** and **3** for the *C,C'*-dimethyl derivative (Table IV), we believe that the identities of meta products from all three of these compounds are in correspondence to their retention times. In particular, meta isomer **5**, identified above as 5,12-Cl_2-*m*-$B_{10}H_8C_2(CH_3)_2$ in the first series of Table IV, is produced in largest yield from each of these starting materials.

Interconversion among meta isomers was tested by heating separately samples of 9,10-Br_2-*m*-$B_{10}H_8C_2H_2$, 9,10-Cl_2-*m*-$B_{10}H_8C_2H_2$, and 9,10-Cl_2-*m*-$B_{10}H_8C_2(CH_3)_2$. No rearrangement occurred at 420° over 24 hr for any of these samples. Also, it is unlikely that intermolecular exchange of Br or Cl occurs during these rearrangements. For example, no mass spectroscopic evidence could be found for monobromo products after heating a mixture of *m*-$B_{10}H_{10}C_2H_2$ and 9,10-Br_2-*m*-$B_{10}H_8C_2H_2$ for 24 hr at 420°. Also, neither chlorine nor methyl monosubstituted products were found when a mixture of *m*-$B_{10}H_{10}C_2H_2$ and 9,10-Cl_2-*m*-$B_{10}H_8C_2(CH_3)_2$ was subjected to this same experiment. Mass spectroscopic examination of the mixture of meta isomers from 9,12-Cl_2-*o*-$B_{10}H_8C_2(CH_3)_2$ (Table IV) also showed no monochloro derivatives. Intermolecular exchange of iodine atoms between carborane frameworks has, however, been observed previously.[17]

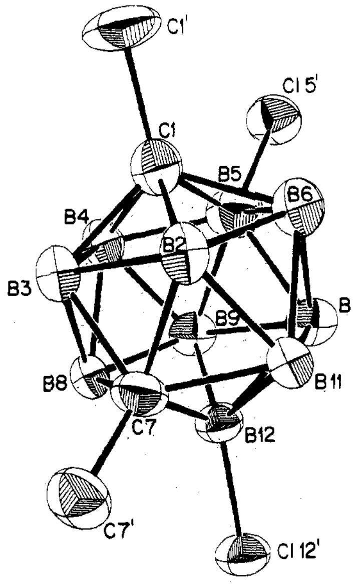

Figure 5. Molecular structure of 5,12-Cl_2-*m*-$B_{10}H_8C_2H_2$ with 50% probability thermal ellipsoids. Conventional atom numbers (ref 13) are preceded by the symbol of the element, B, C, or Cl. Hydrogen atoms have been eliminated for clarity.

Previous work[1] has shown that ortho to ortho isomerizations occur in icosahedral monohalocarboranes. We therefore investigated whether the major isomer **5** arises directly from the starting 9,12-dihalo-*o*-carborane or from the intermediate ortho products. Only from 9,12-Cl_2-*o*-$B_{10}H_8C_2(CH_3)_2$, among starting materials of Table IV, were we able to separate ortho isomers by vpc. Those ortho isomers which appeared in quantity (**9**, **11-15** of Figure 3) were isolated by preparative vpc and then subjected to thermal rearrangement at 420°. Percentage yields of meta isomers (Table V) indicate clearly that isomer **5** is produced in relatively small amounts. We therefore believe that the 5,12-dihalo-*m*-carboranes of Table IV (isomer **5**) arise principally from the starting materials and not from a quasi-steady state among ortho intermediates.

Identification of products is quite incomplete. Crystal structures establish the molecular configurations of 5,12-Cl_2-*m*-$B_{10}H_8C_2(CH_3)_2$ (this study), 9,12-Br_2-*o*-$B_{10}H_8C_2H_2$,[18] and 9,10-Br_2-*m*-$B_{10}H_8C_2H_2$.[15] Nuclear magnetic resonance ^{11}B spectra at 80.53 MHz of 5,12-Cl_2-*m*-$B_{10}H_8C_2(CH_3)_2$, 9,12-Cl_2-*o*-$B_{10}H_8C_2(CH_3)_2$, and 9,10-Cl_2-*m*-$B_{10}H_8C_2(CH_3)_2$ all show magnetic equivalences consistent with the C_{2v} symmetry expected for each of these three molecules. Moreover, preparative procedures are similar to those used for the corresponding dibromocarboranes. Also, 9,12-Cl_2-*o*-

---

(17) L. I. Zakharkin and V. N. Kalinin, *Zh. Obshch. Khim.*, **36**, 362 (1966); *Izv. Akad. Nauk SSSR., Ser. Khim.*, 607 (1969).

(18) J. A. Potenza and W. N. Lipscomb, *Inorg. Chem.*, **5**, 1471 (1966).

Table V. Yields for Various Cl_2-*o*-$B_{10}H_8C_2(CH_3)_2$ Isomers after 24 hr at 420° [a]

Ortho isomer no.	Meta isomer no.					
	2	3	4	5	7	8
9	24	31	14	11	8	12
11[b]	29	40	12	12	3	4
12[b]	27	38	11	17	4	3
13	26	37	12	14	8	3
14	23	37	9	17	11	4
15	21	32	6	17	12	12

[a] For the relation of numbering to the vpc, see Figure 3. [b] Some ortho isomers remain after 24 hr at 420°.

$B_{10}H_8C_2(CH_3)_2$ was prepared by methylation of 9,12-Cl_2-*o*-$B_{10}H_8C_2H_2$, and we also showed magnetic equivalences of C_{2v} symmetry in the ^{11}B nmr spectra of 9,12-Cl_2-*o*-$B_{10}H_8C_2H_2$, 9,10-Cl_2-*m*-$B_{10}H_8C_2H_2$, and 5,12-Cl_2-*m*-$B_{10}H_8C_2H_2$.

Preparative procedures also established two other relationships. Methylation of meta isomer **5** from the 9,12-Cl_2-*o*-$B_{10}H_8C_2H_2$ yields a dimethyl derivative which gives identical vpc and 60-MHz ^1H nmr spectrum with those properties of 5,12-*m*-$B_{10}H_8C_2(CH_3)_2$. Also, Friedel-Crafts chlorination of 5-Cl-*m*-$B_{10}H_9C_2H_2$ yields a product which has vpc behavior and 60-MHz ^1H nmr spectrum identical with isomer **8** from the starting material 9,12-Cl_2-*o*-$B_{10}H_8C_2H_2$. Inasmuch as this halogenation reaction has, so far, always placed Cl at the 9 (or equivalent 10 position in the 5-Cl-*m*-$B_{10}H_8C_2H_2$) position in previous studies,[14] we believe that this product is 5,9-Cl_2-*m*-$B_{10}H_8C_2H_2$, a tentative identification of isomer **8** of this series.

The ^{11}B nmr spectra[19] at 80.53 MHz were run on 9,10-Cl_2-*m*-$B_{10}H_8C_2H_2$, 5,12-Cl_2-*m*-$B_{10}H_8C_2H_2$, 9,12-Cl_2-*o*-$B_{10}H_8C_2H_2$, the three corresponding *C,C'*-dimethyl derivatives, on meta isomers **2-5** (included above), **7**, and **8**, and on ortho isomers **9**, **14**, and **15**. Analysis, based upon the assumption of a nearly constant downfield shift when B-H is converted to B-Cl, together with the assignments from the compounds whose structures are based upon crystallographic studies yields the following results. The assignment of ^{11}B nmr peaks in *m*-$B_{10}H_{10}C_2H_2$ is confirmed: these earlier assignments[14,20,21] are B(2), B(3) at 35.4 ppm; B(4), B(6), B(8), B(11) at 31.7 ppm; B(9), B(10) at 29.1 ppm; and B(5), B(12) at 25.1 ppm relative to $B(OCH_3)_3$. Assignments were made of isomers as shown in Table VI, which also shows an analysis indicating a tendency for the shift to be almost systematic for the position of substitution, largely independent of the position of the other Cl atom in the molecule. The test is not complete, since no ortho isomers were observed for which Cl is in position 3 or 6, and, of course, only a small number of the 16 ortho and 16 meta isomers were isolated in these experiments. Thermal isomerizations (at 420°) were made on these ortho isomers which were isolated, but the identification of only a small number of ortho products made most of the results ambiguous. The two unambiguous results are that 9,12-Cl_2-*o*-$B_{10}H_8C_2(CH_3)_2$ yields only 8,9-Cl_2-*o*-$B_{10}H_8C_2(CH_3)_2$ and that this product yields a mixture of only two compounds [9,12-Cl_2-*o*-$B_{10}H_8C_2(CH_3)_2$ and 4,9-Cl_2-*o*-$B_{10}H_8C_2(CH_3)_2$] in the initial stages of isomerization.

Table VI. Chemical Shifts of Boron Atoms Bonded to Chlorine

Isomer no.	Isomer[a]	Position	δ,[b] (ppm)	
	9,10-Cl_2-*m*-	9,10	−0.5	Av −0.3
7	4,9-Cl_2-*m*-	9	0.0	
8	5,9-Cl_2-*m*-	9	−0.5	
8	5,9-Cl_2-*m*-	5	−0.5	Av −1.2
5	5,12-Cl_2-*m*-	5	−1.9	
7	4,9-Cl_2-*m*-	4	+2.7	Av +2.3
4	4,11-Cl_2-*m*-	4,11	+2.4	
3	2,4-Cl_2-*m*-	4	+1.9	
2	2,6-Cl_2-*m*-	6	+2.1	
2	2,6-Cl_2-*m*-	2	+4.5	Av +4.6
3	2,4-Cl_2-*m*-	2	+4.6	
	9,12-Cl_2-*o*-	9,12	−5.7	Av −5.3
15	8,9-Cl_2-*o*-	9	−5.1	
14	4,9-Cl_2-*o*-	9	−5.0	
15	8,9-Cl_2-*o*-	8	0.0	Av +0.4
9	4,8-Cl_2-*o*-	8	0.9	
14	4.9-Cl_2-*o*-	4	+1.8	Av +2.3
9	4,8-Cl_2-*o*-	4	+2.8	

[a] The formula is abbreviated, *e.g.*, 9,10-Cl_2-*m*- = 9,10-Cl_2-*m*-$B_{10}H_8C_2(CH_3)_2$. [b] Relative to BF_3OEt_2 = 0.0. In order to convert to the $B(OCH_3)_3$ standard, add 18.2 ppm.

Table VII. Possible Ortho to Meta Conversions of Dihalocarboranes by the Cuboctahedral Pathway[a]

Dichloro-*o*-carborane		Dichloro-*m*-carborane
3,4 = 3,7 = 5,6 = 6,11[b]	→	2,6 = 2,11 = 3,4 = 3,8
3,5 = 3,11 = 4,6 = 6,7	→	2,4 = 2,8 = 3,6 = 3,11
3,6	→	2,3
3,8 = 6,10	→	2,10 = 3,9
3,9 = 3,12 = 6,9 = 6,12	→	2,5 = 2,12 = 3,5 = 3,12
3,10 = 6,8	→	2,9 = 3,10
4,5 = 7,11	→	4,6 = 8,11
4,7 = 5,11	→	4,8 = 6,11
4,8 = 5,10 = 7,8 = 10,11	→	4,9 = 6,10 = 8,9 = 10,11
4,9 = 5,9 = 7,12 = 11,12	→	4,5 = 5,6 = 8,12 = 10,12
4,10 = 5,8 = 7,10 = 8,11	→	4,10 = 6,9 = 8,10 = 9,11
4,11 = 5,7	→	4,11 = 6,8
4,12 = 5,12 = 7,9 = 9,11	→	4,12 = 5,8 = 5,11 = 6,12
8,9 = 8,12 = 9,10 = 10,12	→	5,9 = 5,10 = 9,12 = 10,12
8,10	→	9,10
9,12	→	5,12

[a] Each dihalo-*o*-carborane yields a *single* dihalo-*m*-carborane *via* a cuboctahedron intermediate in a single step (see footnote, Table VIII). [b] Symmetry-equivalent isomer designations follow the conventional designation of halogen positions.

Table VIII. Possible Ortho to Ortho Conversions of Dihalocarboranes by the Cuboctahedral Pathway[a]

3,4	→	3,4; 3,8; 4,5; 3,5
3,5	→	4,7; 3,4; 4,10; 3,6
3,6	→	3,5; 3,5; 3,5; 3,5
3,8	→	4,8; 3,4; 4,8; 3,4
3,9	→	4,12; 3,9; 4,9; 3,9
3,10	→	4,11; 3,10; 4,11; 3,10
4,5	→	3,4; 4,8; 4,8; 3,4
4,7	→	3,5; 4,10; 3,5; 4,10
4,8	→	3,8; 4,8; 4,10; 4,5
4,9	→	3,9; 8,9; 4,9; 4,9
4,10	→	3,5; 8,10; 4,7; 4,8
4,11	→	3,10; 3,10; 4,11; 4,11
4,12	→	3,9; 8,9; 4,12; 4,12
8,9	→	8,9; 4,12; 8,9; 4,9
8,10	→	4,10; 4,10; 4,10; 4,10
9,12	→	9,12; 9,12; 9,12; 9,12

[a] On the right are the four dihalo-*o*-carboranes produced from four of the five unique cuboctahedron intermediates obtained from the dihalo-*o*-carboranes on the left in a single step. The fifth unique cuboctahedron intermediate yields the dihalo-*m*-carborane listed in Table VII.

Mechanisms. The major meta product 5,12-Cl_2-*m*-$B_{10}H_8C_2(CH_3)_2$ from 9,12-Cl_2-*o*-$B_{10}H_8C_2(CH_3)_2$ arises in a

---

(19) These spectra are available in the Ph.D. Thesis of H. V. Hart, Harvard University, 1972.

(20) G. D. Vickers, H. Schroeder, H. Agahigian, and E. A. Pier, *Inorg. Chem.*, 5, 693 (1966).

(21) G. R. Eaton and W. N. Lipscomb, "Nmr Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1966, pp 377-378.

single step through the cuboctahedral pathway (Table VII). The one-step rotation of a pentagonal pyramid predicts the 9,10-meta isomer, while the rotation of a triangle in the icosahedron predicts the 5,9 isomer.

A second unique experimental result is that the initial ortho product from 9,12-Cl$_2$-*o*-B$_{10}$H$_8$C$_2$(CH$_3$)$_2$ is 8,9-Cl$_2$-*o*-B$_{10}$H$_8$C$_2$(CH$_3$)$_2$. This result does not arise from the simple cuboctahedral mechanism (Table VIII)[3] but is the unique product obtained by triangle rotation of a B$_3$ unit not attached to C *in the cuboctahedral intermediate.* This type of rotation was given preference in our earlier studies of ortho-ortho isomerizations of monohalocarboranes.[1] The one-step rotation of a pentagonal pyramid yields the 4,9-, the 8,9-, and the 8,10-ortho isomers in ratios of 2:2:1, respectively; and the triangle rotation in the icosahedron predicts the 8,9- and the 4,12-ortho isomers in a 2:1 ratio.

Rearrangement of 8,9-Cl$_2$-*o*-B$_{10}$H$_8$C$_2$(CH$_3$)$_2$, shown experimentally to yield the 9,12- and the 4,9-ortho derivatives, should also have yielded the 4,12-ortho product by the cuboctahedral mechanism (Table VIII). This and other more preliminary results suggest that the simple statistical application of these geometrical mechanisms will prove inadequate when detailed kinetic data are available. It has already been shown that there is an effect of substituent (Cl or F) on the final equilibrium of *m*- and *p*-carboranes. Other evidence for electronic effects, and also steric effects, is expected. Finally, we would not, at this stage, exclude minor contributions of other mechanisms than the cuboctahedral pathway, as modified by triangle rotation in this intermediate, in these interesting isomerization reactions.

Acknowledgment. We thank the Office of Naval Research and the National Institutes of Health for support of this research. We are also much indebted to Richard J. Wiersema of the University of California at Los Angeles for the ^{11}B nmr spectra.

Registry No. 9,10-Cl$_2$-*m*-B$_{10}$H$_8$C$_2$(CH$_3$)$_2$, 23810-46-0; 2,6-Cl$_2$-*m*-B$_{10}$H$_8$C$_2$(CH$_3$)$_2$, 41184-44-5; 2,4-Cl$_2$-*m*-B$_{10}$H$_8$C$_2$(CH$_3$)$_2$, 41184-45-6; 4,11-Cl$_2$-*m*-B$_{10}$H$_8$C$_2$(CH$_3$)$_2$, 41184-46-7; 5,12-Cl$_2$-*m*-B$_{10}$H$_8$C$_2$(CH$_3$)$_2$, 41267-46-3; 9,12-Cl$_2$-*o*-B$_{10}$H$_8$C$_2$(CH$_3$)$_2$, 41184-47-8; 4,9-Cl$_2$-*m*-B$_{10}$H$_8$C$_2$(CH$_3$)$_2$, 41184-48-9; 5,9-Cl$_2$-*m*-B$_{10}$H$_8$C$_2$(CH$_3$)$_2$, 41267-47-4; 4,8-Cl$_2$-*o*-B$_{10}$H$_8$C$_2$(CH$_3$)$_2$, 41184-49-0; 8,9-Cl$_2$-B$_{10}$H$_8$C$_2$(CH$_3$)$_2$, 41184-50-3; 4,9-Cl$_2$-*o*-B$_{10}$H$_8$C$_2$(CH$_3$)$_2$, 41184-51-4; boron-11, 14798-13-1.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2644.

Contribution from the Department of Chemistry, Tulane
University, New Orleans, Louisiana 70118

Crystal and Molecular Structure of Chloroaquobis(trimethylarsine)tetrakis(trifluoromethyl)rhodiacyclopentadiene, RhCl(H$_2$O)(As(CH$_3$)$_3$)$_2$C$_4$(CF$_3$)$_4$[1]

JOEL T. MAGUE

Received April 5, 1973

The structure of chloroaquobis(trimethylarsine)tetrakis(trifluoromethyl)rhodiacyclopentadiene, RhCl(H$_2$O)As(CH$_3$)$_3$)$_2$C$_4$(CF$_3$)$_4$, has been determined from three-dimensional X-ray data collected by counter methods. The final conventional and weighted *R* factors obtained from a block-diagonal least-squares refinement for 1689 reflections are 0.063 and 0.060, respectively. The material crystallizes in the orthorhombic system with space group $P2_12_12_1$ and a unit cell of dimensions $a = 11.580$ (1), $b = 20.034$ (1), and $c = 10.158$ (1) Å. There are four molecules in the unit cell and the crystal consists of the packing of these monomeric molecules with no unusual intermolecular contacts. The coordination about rhodium is in the form of a distorted octahedron with the Cl atom, the O atom of the water molecule, and the 1 and 4 C atoms of the C$_4$(CF$_3$)$_4$ moiety approximately defining a plane and the arsenic atoms disposed above and below it. Both the Rh–Cl (2.448 (5) Å) and Rh–O (2.241 (12) Å) distances are significantly longer than anticipated due to a strong trans influence exerted by the fluorocarbon moiety. The Rh–C distances of 2.047 (16) and 1.998 (16) Å are different to a marginally significant extent which is believed to be real while the C–C distances in the metallocyclopentadiene ring suggest the π bonding to be largely localized. Semiempirical molecular orbital calculations on a model for this complex suggest that the asymmetric ring geometry observed represents the geometry of minimum energy.

Introduction

In the course of our studies on the interaction of fluoroacetylenes with low-valent transition metal complexes, we investigated the decarbonylation of the six-coordinate metallocycle Rh(CO)Cl(As(CH$_3$)$_3$)$_2$C$_4$(CF$_3$)$_4$.[2] The material obtained was not the expected five-coordinate metallocycle RhCl(As(CH$_3$)$_3$)$_2$C$_4$(CF$_3$)$_4$, analogous to RhCl(Sb(C$_6$H$_5$)$_3$)$_2$C$_4$(CF$_3$)$_4$ whose structure has been determined previously,[3] but initally appeared from infrared data to contain a molecule of formic acid. Since the production of formic acid from carbon monoxide in the coordination sphere of rhodium would be a novel process, the determination of the crystal structure of the material was undertaken to ascertain the nature of the sixth ligand. Unfortunately, the material did not prove to contain formic acid but rather is the aquo derivative of the five-coordinate metallocycle. Nevertheless, the com-

(1) Supported by the National Science Foundation (Grant No. GP-8066) and the Gulf Research and Development Co.

(2) J. T. Mague, M. O. Nutt, and E. H. Gause, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., April 1971, No. INOR 133.

(3) J. T. Mague, *Inorg. Chem.*, **9**, 1610 (1970).