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THE CRYSTAL STRUCTURE OF  $(B_9C_2H_{11})Re(CO)_3Cs$

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The Crystal Structure of  $(B_9C_2H_{11})Re(CO)_3Cs^1$

BY ALLAN ZALKIN, TED E. HOPKINS, AND DAVID H. TEMPLETON

The crystal structure of the cesium salt of  $\eta$ -(1)-2,3-dicarbollylrhenium-tricarbonyl,  $(B_9C_2H_{11})Re(CO)_3Cs$ , has been determined from an X-ray diffraction study of a single crystal specimen. The monoclinic cell, space group  $P2_1/c$ , with  $a = 11.435 \text{ \AA}$ ,  $b = 9.516 \text{ \AA}$ ,  $c = 12.730 \text{ \AA}$ , and  $\beta = 92.87^\circ$  contains four formula units. The structure was determined by straightforward crystallographic techniques, and the atomic parameters of all but the hydrogen atoms were refined by a full-matrix least squares procedure. The rhenium atom occupies an apex position of an icosahedron containing boron and carbon, and on the other side occupies the apex of a trigonal pyramid whose base is three carbonyls. In the icosahedron the two carbon atoms are adjacent to each other and to the rhenium.

Introduction

$\eta$ -(1)-2,3-dicarbollylrheniumtricarbonyl was synthesized by Hawthorne and Andrews<sup>2</sup>. The structure work was undertaken to reaffirm the results of our previous study on the dicarbollyliron structure<sup>3</sup>, in  $C_5H_5FeB_9C_2H_{11}$ . In that study there was considerable thermal motion of the cyclopentadienyl ring, and to a lesser extent of the dicarbollyl portion,  $B_9C_2H_{11}$ . This thermal motion, evidenced by large thermal parameters, does not permit the calculation of accurate bond distances. The  $B_9C_2H_{11}Re(CO)_3Cs$  crystal does not suffer these thermal effects as badly, and the resulting structure we believe to be a more accurate description of the dicarbollyl geometry.

The present work confirms the geometry of this compound postulated by Hawthorne and Andrews<sup>2</sup>.

### Experimental

The crystals were sent to us by Dr. M. F. Hawthorne of the Riverside campus of the University of California. A small white crystal,  $\sim 0.25$  mm. long and  $\sim 0.08 \times \sim 0.08$  mm. in cross section, was glued to the end of a pyrex glass fiber. The long direction of the crystal was parallel to the fiber, and is the direction of the  $\underline{b}$  axis. A General Electric XRD-5 X-ray diffraction set up equipped with a Molybdenum X-ray tube (Mo  $K\alpha_1$   $\lambda = 0.70926 \text{ \AA}$ ), a scintillation counter, a pulse height discriminator, and a quarter-circle Eulerian-cradle type goniostat was used. The X-ray tube was operated at 50 KV and 20 ma, and a Zr filter was used on the receiving slit. The crystal was oriented such that the  $\underline{b}$  axis was parallel to the  $\phi$  axis. The cell dimensions were obtained from carefully measured  $2\theta$  ( $\theta$  is the Bragg angle) values of the  $0k0$ ,  $h00$ , and  $00l$  reflections whose  $a_1$  and  $a_2$  components were resolved. The  $\beta$  angle was measured directly from the angle between the  $h00$  and  $00l$  set of reflections.

2452 independent intensities were measured, of which 138 were recorded as zero. A stationary crystal, stationary counter technique using a ten-second count for every reflection was used. The maximum  $2\theta$  angle was  $50^\circ$  ( $\sin\theta/\lambda = 0.595$ ). The maximum observed raw intensity was 7800 counts per second for the  $11\bar{2}$  reflection. The data were corrected for the Lorentz and polarization effects. No corrections were made for either absorption or extinction.

All of the computations were performed on an IBM 7044 computer with a 32 K memory. Our unpublished least squares program minimizes the function  $\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2$ , where  $F_o$  and  $F_c$  are the observed and calculated structure factors, and  $w$  is the weighting factor. All of the reflections were given equal weight. The least squares program has been modified to handle the anomalous dispersion, and these effects were included in the final set of refinements. The atomic scattering factors<sup>4</sup> for neutral Re and Cs<sup>+</sup> were corrected for  $\Delta f'$ , the real part of the anomalous dispersion<sup>5,6</sup>, by the amounts -1.3 and -0.5 electrons respectively. The imaginary components of the anomalous dispersion  $\Delta f''$ , were introduced into the least squares calculations as +7.5 and +2.5 electrons respectively for Re and Cs. Scattering factors for neutral oxygen, carbon, boron and hydrogen were adopted as given in the standard tables<sup>7</sup>. The anisotropic temperature factors used have the form  $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$ .

### Results

Unit Cell and Space Group.-Four formula units of  $(B_9C_2H_{11})Re(CO)_3Cs$  are contained in the monoclinic unit cell in space group  $P2_1/c$  with dimensions:  $a = 11.435 \pm 0.010 \text{ \AA}$ ,  $b = 9.516 \pm 0.005 \text{ \AA}$ ,  $c = 12.730 \pm 0.010 \text{ \AA}$ , and  $\beta = 92.87 \pm 0.04^\circ$ . The errors are estimates. The calculated X-ray density is 2.57 g./cc. The observed extinctions correspond to the space group  $P2_1/c$ . The space group is centric, and each of the atoms occupies the general four fold position,  $\pm (x, y, z; x, 1/2 - y, 1/2 + z)$ .

Determination of the Structure.-The positions of the Cs and Re were easily extracted from the three dimensional Patterson function. These heavy atom positions were refined by least squares using isotropic temperature factors, and after four cycles of refinement yielded an R factor of 0.149 where  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ . Four more cycles using anisotropic temperature factors reduced R to 0.146. A difference Fourier was calculated and the seventeen remaining atoms, excluding hydrogen, appeared as the seventeen largest peaks in the patterns. The parameters of the two heavy atoms with anisotropic temperature factors, and the seventeen lighter atoms with isotropic temperature factors were refined by least squares for two cycles and R decreased to 0.066. Several blunders in punching the data onto the IBM cards and errors in setting the angles were recognized and corrected. Two cycles with the corrected data yielded an R of 0.046. From a study of the interatomic distances and the thermal parameters it was apparent that a boron and a carbon atom were interchanged. This correction improved R very little, but the thermal parameters became more consistent.

A difference function was again calculated and the patterns were studied for hydrogen peaks. Among the 35 peaks whose observed electron density was greater than 0.55 electrons per  $\text{\AA}^3$  at their peaks, 5 were close to Re, 6 were close to Cs, 7 were near the oxygen carbonyls, 10 were peaks in positions that would be suitable hydrogen atom locations, and 7 were peaks in the vicinity of the boron atoms which were either anisotropies or just spurious. The hydrogen atom near B(10) was not found. The ten hydrogen atoms were included in the ensuing refinements with these positions and an isotropic temperature factor of  $4.0 \text{ \AA}^2$ . No attempt was made to refine the hydrogen parameters.

For the final set of refinements, all of the atoms with the exception of the hydrogens were given anisotropic thermal parameters, the imaginary part of the anomalous dispersion for Cs and Re was added, and 10 hydrogen atoms were included but not refined. The final R factor was 0.042. The largest shift of any positional parameter was 0.00002 in the very last cycle. The final results are shown in Table I. Table II lists the observed and calculated structure factors.

Description of Structure.-The  $B_9C_2H_{11}Re(CO)_3$  anion is shown in Figure 1. This structure was postulated by Hawthorne and Andrews<sup>2</sup> and has been confirmed by this work. The anion consists of the dicarbollide portion ( $B_9C_2H_{11}$ ) to which is bonded the rhenium tricarbonyl via  $\pi$ -bonding to the rhenium atom; the rhenium atom occupies the number 1 position in a completed icosahedron involving the dicarbollide portion. A bottom view of the structure is shown in Figure 2; this shows the orientation of the three carbonyls to the icosahedron. In the icosahedron the two carbon atoms are adjacent to each other and the Re atom. Lists of distances and angles are shown in Tables III and IV.

TABLE I.

FINAL POSITIONAL AND THERMAL PARAMETERS<sup>a</sup> IN  $\text{CsB}_9\text{C}_2\text{H}_{11}\text{Re}(\text{CO})_3$ <sup>b</sup>

Atom	$\bar{x}$	$\bar{y}$	$\bar{z}$	$\underline{B}_{11}$	$\underline{B}_{22}$	$\underline{B}_{33}$	$\underline{B}_{12}$	$\underline{B}_{13}$	$\underline{B}_{23}$
Cs	0.2766	0.1909	-0.0065	3.77	4.57	4.65	0.19	0.53	0.08
icosahedron									
Re (1)	-0.1495	0.1406	0.2316	2.09	1.88	2.08	0.14	0.18	0.01
C (2)	-0.232	0.356	0.267	3.4	2.6	2.0	0.3	0.0	-0.2
C (3)	-0.327	0.232	0.279	2.6	2.3	2.2	0.5	0.7	0.3
B (4)	-0.342	0.138	0.164	2.3	1.9	2.8	-0.5	-0.2	-0.1
B (5)	-0.248	0.214	0.075	2.8	2.2	2.6	0.0	0.3	-0.4
B (6)	-0.176	0.358	0.145	3.3	2.2	2.3	-0.2	-0.2	0.3
B (7)	-0.377	0.404	0.269	2.8	3.6	2.2	1.0	0.0	-0.1
B (8)	-0.449	0.263	0.200	2.1	4.0	2.7	0.7	0.6	-0.1
B (9)	-0.401	0.260	0.071	2.5	3.3	3.0	0.3	0.1	-0.7
B (10)	-0.295	0.393	0.060	3.3	3.1	2.9	-0.2	0.8	1.0
B (11)	-0.282	0.483	0.180	3.6	2.9	2.8	1.2	0.2	0.6
B (12)	-0.422	0.425	0.134	3.2	4.2	2.4	0.8	0.0	0.0
carbonyls									
C(1)-CO	-0.043	0.167	0.349	2.7	2.8	3.6	0.5	0.3	0.2
C(2)-CO	-0.021	0.092	0.153	2.4	3.3	3.0	0.4	0.4	0.5
C(3)-CO	-0.168	-0.048	0.275	4.7	2.9	2.8	0.7	0.3	0.2
O(1)-CO	0.024	0.193	0.418	4.3	6.9	4.4	1.4	-2.1	-2.2
O(2)-CO	0.057	0.065	0.102	3.6	5.0	3.6	1.5	0.7	0.3
O(3)-CO	-0.187	-0.162	0.300	7.4	2.4	7.1	-0.1	0.8	1.4

hydrogens <sup>c</sup>			Atom	x	y	z	
H ( 2 )	-0.20	0.40	0.34	H ( 7 )	-0.40	0.46	0.34
H ( 3 )	-0.36	0.20	0.36	H ( 8 )	-0.54	0.28	0.20
H ( 4 )	-0.38	0.04	0.18	H ( 9 )	-0.46	0.20	0.02
H ( 5 )	-0.20	0.18	0.00	H (11)	-0.26	0.60	0.20
H ( 6 )	-0.10	0.42	0.12	H (12)	-0.50	0.48	0.10

<sup>a</sup> Units are  $\text{\AA}^2$ . The anisotropic values  $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$  where  $a_i^*$  is the  $i$ th reciprocal cell length.

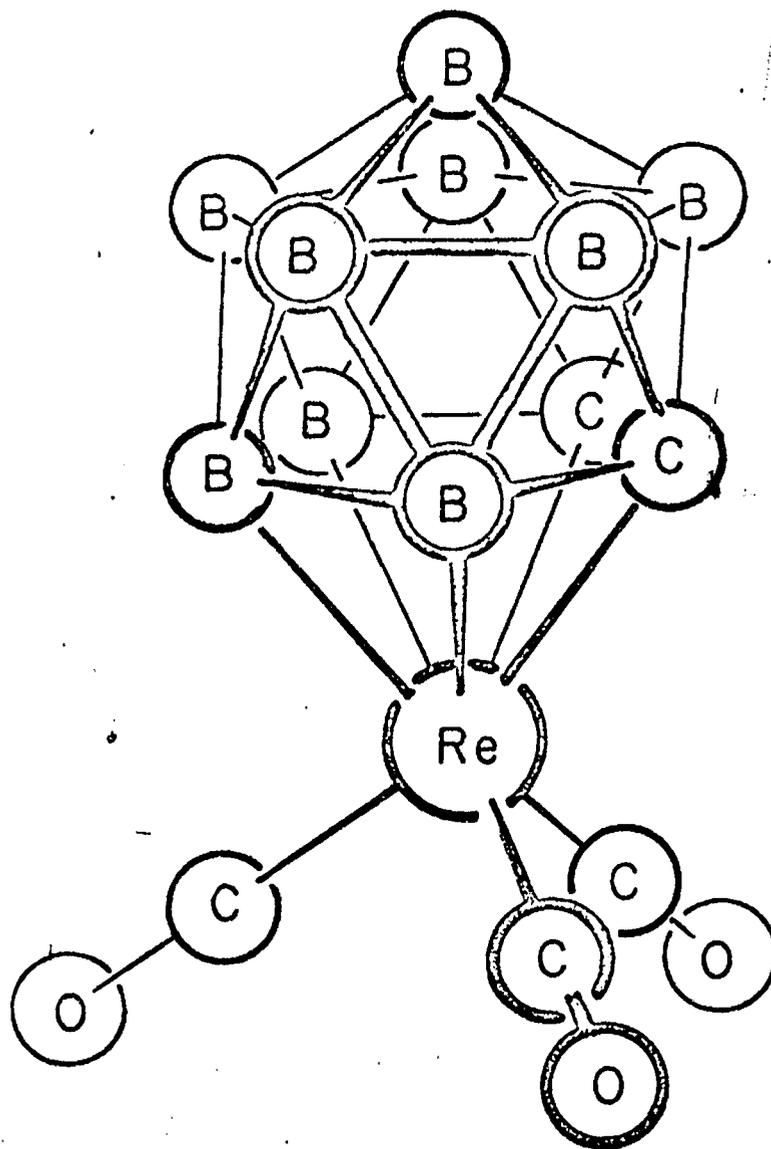
<sup>b</sup> Standard deviations of the positional parameters of Cs and Re are 0.0001 or less, and 0.001 or less for all the other atoms excluding hydrogens.

Standard deviations of the thermal parameters are 0.04 or less for Cs and Re, and 0.7 or less for all the other atoms excluding hydrogens.

<sup>c</sup> Hydrogen positional parameters are those from a difference Fourier and were not refined by least squares. H(10) was not found. The labelling is parallel to the labelling in the icosahedron, i.e. H(5) is the hydrogen to B(5).

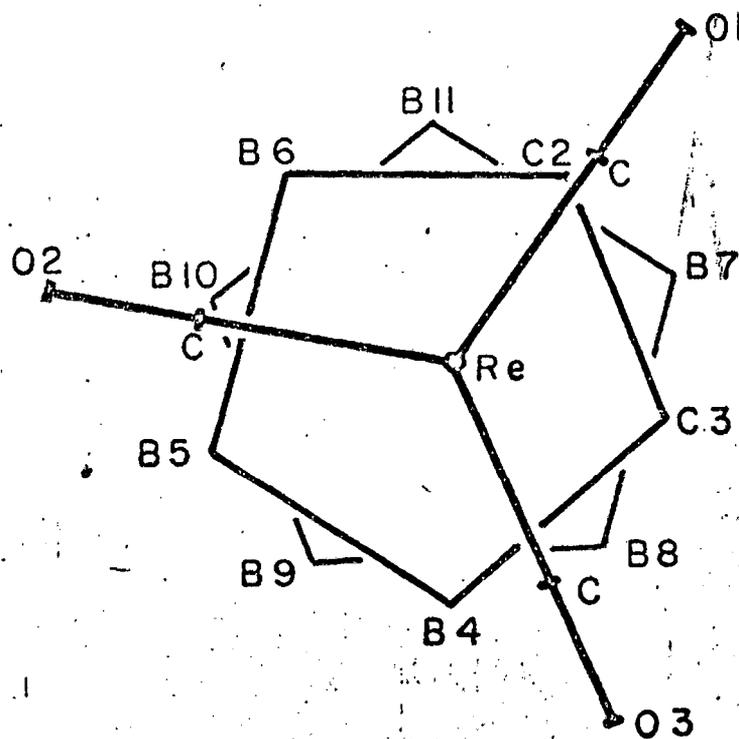


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-13 14 17	-4 9 7	9 30 29	-2 53 54	7 51 44	-8 70 69	-8 70 69	-8 29 23	1 112 111	-4 99 99	-3 74 74	1 16 16
-17 7 4	-5 95 97	8 9 7	-1 55 55	8 117 114	-7 42 80	-7 42 80	-7 44 47	6 32 33	-9 30 30	-2 21 21	2 16 16
-11 65 65	-2 57 57	7 20 21	-0 55 44	6 76 80	-8 33 27	-8 33 27	-8 33 27	5 13 13	-2 20 21	-1 11 11	3 11 11
-10 24 24	-1 147 137	6 11 17	-1 137 139	10 40 41	-5 48 48	-5 48 48	-5 48 48	6 10 10	-10 20 20	-2 10 10	0 0 0
-9 13 10	-C 10 16	5 124 123	2 63 64	11 46 48	-4 48 45	-4 48 45	-4 45 39	7 31 33	-0 47 49	-1 11 11	M=12, 0
-8 4 10	1 101 104	4 37 37	3 70 70	12 75 74	-3 110 120	-3 111 131	-3 79 72	8 0 4	1 11 9	2 27 16	L FOM PCA
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-6 226 228	9 41 38	1 42 42	9 28 28	10 21 20	-1 118 119	-1 118 119	-1 95 9	10 11 11	-2 26 27	-1 11 11	-C 17 10
-5 41 36	4 14 17	1 204 213	4 73 74	5 77 77	-0 40 42	-0 27 25	-0 53 48	6 14 11	4 14 11	M=11, 0	-C 29 19
-4 36 34	9 87 86	7 85 83	7 85 83	8 119 117	-1 116 117	-1 91 93	-1 91 93	5 10 10	5 10 10	L FOM PCA	-C 29 19
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-1 74 74	8 14 13	3 201 210	3 10 10	4 60 67	6 60 67	6 17 21	6 35 34	-9 18 23	8 21 23	-4 31 31	6 33 48
-0 59 42	9 32 33	4 11 4	4 11 4	5 77 75	5 77 75	5 0 4	5 83 84	-8 23 25	9 39 41	-2 171 221	M=12, 1
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3 111 111	M=12, 8	7 144 147	-10 27 15	-4 24 26	6 25 21	8 14 8	-8 0 1	-5 0 3	L FOM PCA	4 47 51	-C 17 10
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-13 27 29	2 20 36	9 69 69	4 29 28	6 32 30	-0 0 0	-9 5 7	5 11 11	9 24 21	3 64 63	-1 46 45	M=12, 7
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1 27 28	-4 46 39	3 127 25	-9 61 60	L FOM PCA	6 25 27	M=12, 7	6 25 27	1 92 89	1 92 89	1 37 36	3 0 10
2 126 131	-4 79 28	4 114 110	-4 114 115	-12 86 89	L FOM PCA	7 15 16	L FOM PCA	2 96 95	2 96 95	2 46 46	4 49 44
3 29 191	-2 181 191	7 75 74	-5 18 17	-10 110 110	L FOM PCA	8 10 15	L FOM PCA	6 11 9	3 0 6	3 104 107	M=12, 5
4 131 132	-0 113 105	6 94 94	-2 35 35	-11 143 143	-10 120 107	-10 120 107	-10 120 107	4 83 84	6 83 84	6 83 84	L FOM PCA
-9 53 54	-9 65 64	6 174 174	-0 25 27	-1 91 92	-1 91 92	-1 91 92	-1 91 92	-1 91 92	-1 91 92	-1 91 92	-C 17 10
-8 74 77	4 126 126	0 84 81	-0 83 84	-0 110 113	-10 113 111	-10 113 111	-10 113 111	-9 96 95	6 65 60	6 35 34	-C 17 10
-7 41 42	6 200 205	1 63 63	1 49 51	1 27 24	-2 72 76	-7 22 21	M=12, 2	-2 10 6	7 0 3	7 92 87	-C 17 10
-6 75 75	8 81 82	2 63 63	2 47 52	2 97 95	-						



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Figure 1. -  $B_9C_2H_{11}Re(CO)_3^-$  ion (hydrogens excluded).



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Figure 2. - Bottom view of  $B_9C_2H_{11}Re(CO)_3$  ion (hydrogens excluded) showing the orientation of the three carbonyls to the icosahedron.

TABLE III.

DISTANCES IN  $\text{CsB}_9\text{C}_2\text{Re}(\text{CO})_3$ .<sup>a</sup>

Atom	Atom	Distance (Å)	Atom	Atom	Distance (Å)
Re ( 1)	- C(1)-CO	1.90	B ( 6)	- B (10)	1.73
	- C(2)-CO	1.88		- B (11)	1.78
	- C(3)-CO	1.90	B ( 7)	- B ( 8)	1.78
	- C ( 2)	2.31		- B (11)	1.77
	- C ( 3)	2.31		- B (12)	1.77
	- B ( 4)	2.32	B ( 8)	- B ( 9)	1.76
	- B ( 5)	2.35		- B (12)	1.79
	- B ( 6)	2.35	B ( 9)	- B (10)	1.76
C ( 2)	- C ( 3)	1.61		- B (12)	1.79
	- B ( 6)	1.71	B (10)	- B (11)	1.76
	- B ( 7)	1.72		- B (12)	1.79
	- B (11)	1.72	B (11)	- B (12)	1.76
C ( 3)	- B ( 4)	1.71	C(1)-CO	- O(1)-CO	1.16 (1.20) <sup>b</sup>
	- B ( 7)	1.71	C(2)-CO	- O(2)-CO	1.16 (1.18) <sup>b</sup>
	- B ( 8)	1.74	C(3)-CO	- O(3)-CO	1.15 (1.19) <sup>b</sup>
B ( 4)	- B ( 5)	1.76	Cs	- O(1)-CO	3.20 <sup>c</sup>
	- B ( 8)	1.78		- O(2)-CO	3.16 <sup>c</sup>
	- B ( 9)	1.77		- O(3)-CO	3.20 <sup>c</sup>
B ( 5)	- B ( 6)	1.81			
	- B ( 9)	1.80			
	- B (10)	1.80			

<sup>a</sup> Estimated standard deviations on the distances involving Cs and Re is ~0.01 Å; all other distances have standard deviations of ~0.02 Å.

<sup>b</sup> Corrected for thermal motion assuming the O rides on the C. This was the only set where the thermal effect was larger than the estimated standard deviations.

<sup>c</sup> Nearest neighbors to the cesium ions. Each oxygen is from a different molecule.

TABLE IV..

ANGLES IN  $B_9C_2H_{11}Re(CO)_3$ 

Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle
O(1)CO	-C(1)CO	-Re(1)	175	C(3)	-C(2)	-B(7)	63	B(11)	-B(7)	-B(12)	60
O(2)CO	-C(2)CO	-Re(1)	178	C(2)	-C(3)	-B(7)	62	B(4)	-B(8)	-B(9)	60
O(3)CO	-C(3)CO	-Re(1)	176	B(6)	-C(2)	-B(11)	63	B(7)	-B(8)	-B(12)	60
C(1)CO	-Re(1)	-C(2)CO	89	B(7)	-C(2)	-B(11)	62	B(9)	-B(8)	-B(12)	61
C(2)CO	-Re(1)	-C(3)CO	92	B(4)	-C(3)	-B(8)	63	B(4)	-B(9)	-B(5)	59
C(3)CO	-Re(1)	-C(1)CO	88	B(7)	-C(3)	-B(8)	62	B(4)	-B(9)	-B(8)	60
C(2)	-Re(1)	-C(3)	41	C(3)	-B(4)	-B(8)	59	B(5)	-B(9)	-B(10)	60
C(3)	-Re(1)	-B(4)	43	C(2)	-B(6)	-B(11)	59	B(8)	-B(9)	-B(12)	60
B(4)	-Re(1)	-B(5)	44	C(2)	-B(7)	-B(11)	59	B(10)	-B(9)	-B(12)	61
B(5)	-Re(1)	-B(6)	45	C(3)	-B(7)	-B(8)	58	B(5)	-B(10)	-B(6)	62
B(6)	-Re(1)	-C(2)	43	C(3)	-B(8)	-B(4)	59	B(5)	-B(10)	-B(9)	61
Re(1)	-C(2)	-C(3)	70	C(3)	-B(8)	-B(7)	60	B(6)	-B(10)	-B(11)	61
Re(1)	-C(2)	-B(6)	70	C(2)	-B(11)	-B(6)	58	B(9)	-B(10)	-B(12)	60
Re(1)	-C(3)	-C(2)	70	C(2)	-B(11)	-B(7)	59	B(11)	-B(10)	-B(12)	60
Re(1)	-C(3)	-B(4)	69	B(5)	-B(4)	-B(9)	61	B(6)	-B(11)	-B(10)	59
Re(1)	-B(4)	-C(3)	68	B(8)	-B(4)	-B(9)	59	B(7)	-B(11)	-B(12)	60
Re(1)	-B(4)	-B(5)	69	B(4)	-B(5)	-B(9)	60	B(10)	-B(11)	-B(12)	61
Re(1)	-B(5)	-B(4)	67	B(6)	-B(5)	-B(10)	58	B(7)	-B(12)	-B(8)	60
Re(1)	-B(5)	-B(6)	68	B(9)	-B(5)	-B(10)	59	B(7)	-B(12)	-B(11)	60
Re(1)	-B(6)	-C(2)	67	B(5)	-B(6)	-B(10)	61	B(8)	-B(12)	-B(9)	59
Re(1)	-B(6)	-B(5)	67	B(10)	-B(6)	-B(11)	60	B(9)	-B(12)	-B(10)	59
C(2)	-B(7)	-C(3)	56	B(8)	-B(7)	-B(12)	60	B(10)	-B(12)	-B(11)	59

The thermal motion of the atoms in the icosahedron in this structure is less than for comparable atoms in the  $C_5H_5FeC_2B_9H_{11}$  structure<sup>3</sup>, and therefore we consider the resulting bond distances an improvement over the previous ones. In  $B_9C_2H_{11}Re(CO)_3$  the average value of 18 B - B bonds, 1.78 Å, is 0.03 Å larger; the average of the 6 C - B bonds, 1.72 Å, is 0.04 Å larger; and the C - C bond, 1.61 Å, is 0.03 Å larger than the comparable values in the  $C_5H_5FeC_2B_9H_{11}$  structure<sup>3</sup>. Such increases are expected since large motions causes the observed distance to be shorter than the true average value.

In the carbonyl portion of the ion, the Re to C to O linkages are almost linear with a slight bend of a few degrees in an outward direction away from the axis of the molecule. At the Re atom the three carbonyl carbons make very nearly right angles with respect to each other. This tricarbonyl structure is quite similar to that reported in hexamethylbenzene-chromium tricarbonyl, thiophenechromium tricarbonyl, and benzenechromium tricarbonyl<sup>8</sup>. The carbonyl oxygens are apparently free to flop around somewhat as their thermal parameters are larger than the carbons to which they are attached. In Table III we have included the thermally adjusted values for the C - O bond distances. These three bonds were the only bonds in the structure where the correction due to thermal motion was larger than the estimated standard deviation of the bond length. The thermal correction is based on a calculation that assumes the oxygens are "riding" on the carbons.

The cesium ion has as its closest neighbors at 3.2 Å, three oxygen atoms of three symmetry unrelated carbonyls from three different anions.

The hydrogen atoms were poorly resolved in this structure determination. One hydrogen atom, H(10), was not resolved at all in the difference function.

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#### References

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