electronegativities[29] E of the X (Y) atoms. For PF_3 and PCl_3, where the atom X is missing, the electronegativities are regarded as zero. Regular curves are obtained for the bond angles (Figure 5) and also for the bond lengths (Figure 6). In addition, the equatorial P–F and P–Cl bond lengths in PF_5 and PCl_5 apparently fit in the curves if they are, rather arbitrarily, plotted against $^1/_2E$(F) and $^1/_2E$(Cl), respectively.

Acknowledgment.—The authors wish to thank Professor L. S. Bartell for his valuable comments on the manuscript.

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[29] H. O. Pritchard and H. A. Skinner, *Chem. Rev.*, **55**, 745 (1955).

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The Molecular Structures of 1,2-, 1,7-, and 1,12-Dicarba-*closo*-dodecaborane(12), $B_{10}C_2H_{12}$[1]

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Received January 23, 1970

The molecular structures of 1,2-, 1,7-, and 1,12-dicarba-*closo*-dodecaborane(12), $B_{10}C_2H_{12}$, *o*-, *m*-, and *p*-carborane, respectively, have been determined from electron diffraction studies of their vapors. Each structure is a slightly distorted icosahedron. The structure of *p*-carborane with D_{5d} symmetry was characterized most precisely with the following parameter values: B–C = 1.710 ± 0.011 Å, B2–B3 = 1.792 ± 0.007 Å, B2–B7 = 1.772 ± 0.013 Å, B–H = 1.22 ± 0.02 Å, and C–H = 1.15 ± 0.09 Å. Each error limit is the geometric mean of 3 times the least-squares standard deviation and 3 times an estimated 0.1% standard deviation in the scale factor. A "diameter" along the C···C axis is about 10% shorter than a "diameter" along a B···B axis. *o*- and *m*-carborane have much lower symmetry, C_{2v}, and unique structures could not be determined. In *o*-carborane, C–C = 1.65 ± 0.05 Å, B–C (av) = 1.711 ± 0.014 Å, and B–B(av) = 1.793 ± 0.010 Å. In *m*-carborane, B–C(av) = 1.726 ± 0.010 Å and B–B(av) = 1.805 ± 0.008 Å. The B–B bond lengths in the icosahedral carboranes suggest the trend that B–B bonds nearer carbon atoms are longer.

Introduction

Three isomers of the icosahedral carborane[2] $B_{10}C_2H_{12}$ are known.[3-6] The isomers, 1,2-, 1,7-, and 1,12-dicarba-*closo*-dodecaborane(12), will be called *o*-, *m*-, and *p*-carborane, respectively. Crystal structures of a variety of derivatives of *o*- and *m*-carborane have been determined. In each the structure of the boron carbon cage is a slightly distorted icosahedron. Since the carboranes are nearly spherical, crystals of the compounds are disordered with a statistical population of borons and carbons at each site. Even in crystals of many of the substituted carboranes there is some disorder. Therefore, not much precise structural information is known. Russian electron diffraction workers have reported results on *o*-[7] and *m*-carborane,[8] *C,C'*-dimethyl-*o*-carborane,[9] and a *C,C'*- and a *B,B'*-diiodo-*m*-carborane.[10] These reports confirm the icosahedral structures of the ortho and meta isomers and report average bond lengths. We undertook electron diffraction studies of the three unsubstituted carboranes to determine the structure of *p*-carborane, to characterize the distortions from icosahedral symmetry, and to deduce structural relationships among the isomers.

Experimental Section and Data Analysis

Samples of the three carborane isomers were purified by preparative vapor phase chromatography and were obtained from Dr. H. A. Schroeder of Olin Corp. The electron diffraction patterns were recorded on the University of Oslo apparatus with a nozzle temperature of 70°. Exposures were taken at two nozzle to plate distances, 48 and 19 cm, which covered the scattering ranges $1.5 \leq s \leq 20$ Å^{-1} and $7 \leq s \leq 45$ Å^{-1}, respectively. The electron wavelength was 0.064606 Å. Four plates from each range were studies for each compound. These were photometered and converted into molecular scattering intensity curves by correcting for nonlinearity of response of the photographic emulsion, for plate flatness, and for the shape of the rotating sector and by subtracting a background intensity.[11] The intensity and background values are given in Tables IA and IB. A theoretical intensity curve was calculated according to

$$sM(s) = \sum_{i}\sum_{\substack{j \\ (i>j)}} A_{ij} \exp(-l_{ij}^2 s^2/2) \sin (s r_{ij})/r_{ij}$$

where $A_{ij} = Z_iZ_j/(1 - F_B/Z_B)^2$. Z_i and F_i are the atomic

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[1] R. K. Bohn and M. D. Bohn, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

[2] R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 3489 (1962).

[3] T. L. Heying, J. W. Ager, S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, *Inorg. Chem.*, **2**, 1089 (1963).

[4] M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. S. Cohen, *ibid.*, **2**, 1111 (1963).

[5] D. Grafstein and J. Dvorak, *ibid.*, **2**, 1128 (1963).

[6] S. Papetti and T. L. Heying, *J. Amer. Chem. Soc.*, **86**, 2295 (1964).

[7] L. V. Vilkov, V. S. Mastryukov, P. A. Akishin, and A. F. Zhigach, *Zh. Strukt. Khim.*, **6**, 447 (1965); L. V. Vilkov, V. S. Mastryukov, A. F. Zhigach, and V. N. Siryatskaya, *ibid.*, **7**, 5 (1966).

[8] V. S. Mastryukov, L. V. Vilkov, A. F. Zhigach, and V. N. Siryatskaya, *ibid.*, **10**, 136 (1969).

[9] L. V. Vilkov, V. S. Mastryukov, A. F. Zhigach, and V. N. Siryatskaya, *ibid.*, **8**, 3 (1967).

[10] V. S. Mastryukov, A. F. Zhigach, and V. N. Siryatskaya, *Acta Crystallogr., Sect. A*, **25**, S165 (1969).

[11] The reduction of the data is discussed in detail by O. Bastiansen and P. N. Skancke, *Advan. Chem. Phys.*, **3**, 323 (1961).

TABLE IA

INTENSITY AND BACKGROUND DATA (48 CM) FOR *p*-, *o*-, AND *m*-CARBORANE

	Para		Ortho		Meta			Para		Ortho		Meta	
s	I	B	I	B	I	B	*s*	I	B	I	B	I	B
1.25			18.0	6.0			10.75	-75.4	-24.8	13.5	25.3	22.1	28.7
1.50	-19.1	10.0	-1.8	8.5	-2.3	11.6	11.00	0.0	-24.8	32.8	24.4	45.4	27.4
1.75	-56.8	2.7	-9.1	8.9	-8.3	11.5	11.25	76.3	-24.8	59.4	23.4	67.1	26.1
2.00	-78.8	-3.3	-13.4	10.5	-10.9	13.1	11.50	124.1	-24.8	66.1	22.3	77.4	24.8
2.25	-73.8	-8.7	-8.2	11.5	-7.2	13.7	11.75	125.1	-25.3	63.4	21.1	69.3	23.5
2.50	-71.0	-13.6	-4.3	12.9	-3.5	14.9	12.00	85.1	-25.2	48.7	19.8	49.4	22.1
2.75	-65.4	-16.8	-0.4	14.1	-1.0	15.8	12.25	21.8	-25.2	26.9	18.5	25.6	20.6
3.00	-71.0	-19.8	0.0	15.7	0.0	17.1	12.50	-41.4	-25.8	7.5	17.1	6.0	19.3
3.25	-79.4	-22.3	-0.3	17.2	-0.7	18.4	12.75	-85.4	-25.3	-4.6	15.7	-7.3	17.8
3.50	-85.5	-24.3	-0.6	18.8	-0.4	19.7	13.00	-102.8	-25.3	-10.1	14.1	-10.7	16.3
3.75	-81.6	-26.4	3.3	20.6	4.4	21.0	13.25	-101.6	-24.8	-9.0	12.6	-8.2	14.9
4.00	-54.3	-27.0	14.3	22.1	17.8	22.5	13.50	-90.0	-24.3	-4.3	11.0	-4.4	13.4
4.25	0.0	-28.1	32.1	23.5	38.5	23.9	13.75	-76.3	-23.8	-0.4	9.4	-0.9	11.9
4.50	65.9	-28.8	53.6	25.0	60.3	25.4	14.00	-60.5	-22.8	2.0	7.8	1.6	10.4
4.75	117.9	-29.6	69.7	26.4	76.5	27.1	14.25	-41.1	-21.8	5.2	6.3	3.8	8.7
5.00	137.5	-29.5	75.3	27.3	79.2	28.4	14.50	-17.9	-20.3	7.7	5.0	8.3	7.0
5.25	99.0	-29.6	64.0	28.4	64.6	29.9	14.75	5.2	-18.8	10.5	3.6	13.7	5.4
5.50	12.0	-29.6	37.1	29.2	33.5	31.2	15.00	34.0	-16.8	15.0	2.3	21.2	3.7
5.75	-111.2	-29.3	6.5	30.0	-2.1	32.5	15.25	52.5	-14.9	18.5	1.1	24.9	1.9
6.00	-192.4	-28.2	-21.0	30.4	-24.4	33.7	15.50	57.1	-12.4	18.2	0.0	24.1	0.0
6.25	-222.9	-27.8	-25.7	31.0	-26.9	34.8	15.75	48.4	-9.9	13.7	-1.0	18.4	-1.6
6.50	-180.3	-26.8	-12.8	31.2	-8.4	35.6	16.00	23.7	-6.4	5.3	-2.0	5.5	-3.1
6.75	-93.4	-25.8	14.1	31.4	23.3	36.4	16.25	-3.7	-3.5	-6.1	-2.9	-11.2	-4.6
7.00	-2.7	-25.3	40.4	31.6	50.0	36.9	16.50	-29.6	0.5	-18.2	-3.8	-22.3	-5.9
7.25	59.7	-24.9	58.8	31.6	69.6	37.2	16.75	-49.0	4.5	-24.8	-4.7	-31.2	-7.2
7.50	88.0	-24.3	67.4	31.7	76.8	37.3	17.00	-59.7	8.9	-26.8	-5.6	-33.8	-8.3
7.75	90.1	-24.4	66.1	31.6	75.2	37.3	17.25	-53.2	13.9	-23.9	-6.2	-28.9	-9.5
8.00	77.0	-23.8	61.0	31.4	68.6	37.1	17.50	-31.4	18.8	-17.0	-6.8	-19.5	-10.6
8.25	52.1	-23.4	50.5	31.2	58.3	36.9	17.75	0.0	24.8	-8.0	-7.5	-7.0	-11.6
8.50	18.2	-21.3	42.0	30.8	46.0	36.5	18.00	37.3	30.2	0.0	-8.1	0.0	-12.5
8.75	-20.8	-21.3	31.3	30.4	33.3	36.0	18.25	67.5	35.7	5.0	-8.7	3.7	-13.3
9.00	-50.5	-23.3	20.7	29.9	22.7	35.5	18.50	87.0	40.7	6.3	-9.4	0.4	-14.1
9.25	-71.3	-23.8	14.7	29.3	15.7	34.8	18.75	95.4	45.6	4.6	-10.0	-5.1	-14.9
9.50	-85.1	-23.8	10.0	28.9	9.7	34.0	19.00	92.7	50.6	-0.1	-10.6	-10.8	-15.6
9.75	-100.1	-21.8	4.9	28.3	4.3	33.1	19.25	88.4	55.5	-2.6	-11.2	-15.9	-16.2
10.00	-115.4	-23.0	0.0	27.7	0.0	32.2	19.50	71.2	59.6	-6.2	-11.8	-20.2	-16.7
10.25	-131.1	-24.3	-3.2	27.0	0.0	31.1	19.75	58.4	63.5				
10.25	-124.0	-24.8	0.2	26.2	4.7	29.9							

TABLE IB

INTENSITY AND BACKGROUND DATA (19 CM) FOR *p*-, *o*-, AND *m*-CARBORANE

	Para		Ortho		Meta			Para		Ortho		Meta	
s	I	B	I	B	I	B	*s*	I	B	I	B	I	B
3.00			-276.9	-233.2			24.00	-143.9	-106.4	-3.9	9.9	-85.3	-49.7
3.25			-270.4	-223.2			24.25	-162.1	-111.5	-3.4	7.0	-80.7	-55.7
3.50			-261.4	-211.0			24.50	-157.4	-115.0	-5.0	4.0	-75.7	-61.7
3.75			-239.1	-200.7			24.75	-151.2	-118.6	-1.7	1.5	-70.7	-66.7
4.00			-203.7	-189.0			25.00	-137.0	-121.6	0.0	-2.0	-66.8	-73.3
4.25			-150.6	-176.2			25.25	-124.2	-123.6	2.4	-4.5	-64.3	-78.8
4.50			-93.6	-162.8			25.50	-104.5	-125.7	3.8	-8.0	-63.3	-85.3
4.75			-45.4	-149.9			25.75	-84.7	-127.2	7.2	-11.0	-65.7	-91.8
5.00			-17.7	-134.6			26.00	-68.5	-128.7	6.0	-14.0	-67.6	-97.8
5.25			-33.6	-121.5			26.25	-71.8	-129.7	-5.7	-17.5	-76.3	-103.8
5.50			-79.2	-105.7	-217.9	-197.5	26.50	-87.7	-130.7	-18.1	-20.9	-102.2	-110.7
5.75			-153.1	-93.2	-360.3	-185.5	26.75	-114.1	-131.2	-28.1	-24.0	-129.0	-117.3
6.00			-203.1	-79.3	-429.6	-160.5	27.00	-142.4	-132.2	-38.3	-27.9	-148.4	-123.7
6.25			-206.8	-65.5	-403.0	-143.9	27.25	-173.4	-132.7	-44.9	-31.4	-160.9	-129.7
6.50			-164.7	-53.6	-292.7	-121.1	27.50	-177.5	-133.1	-50.1	-34.9	-161.8	-135.6
6.75			-77.0	-41.7	-134.3	-109.3	27.75	-175.1	-133.6	-49.6	-38.9	-157.3	-141.6
7.00	142.9	7.9	0.0	-30.8	0.0	-92.4	28.00	-158.3	-134.5	-49.9	-42.8	-153.1	-147.4
7.25	241.0	10.9	53.7	-19.9	85.6	-77.6	28.25	-146.5	-134.6	-48.9	-46.4	-151.6	-152.5
7.50	286.8	13.4	83.7	-10.9	122.7	-61.6	28.50	-126.7	-135.1	-49.0	-49.8	-145.8	-157.0
7.75	275.2	15.9	89.3	-2.0	118.5	-46.7	28.75	-120.6	-135.7	-52.7	-53.9	-145.9	-161.6
8.00	232.8	18.4	81.4	7.0	89.7	-31.8	29.00	-119.2	-136.2	-54.9	-56.9	-146.3	-165.6
8.25	146.9	20.9	65.9	14.9	60.6	-16.9	29.25	-116.2	-136.2	-57.9	-60.9	-150.1	-169.6
8.50	77.4	23.8	45.6	21.8	18.1	-4.0	29.50	-119.3	-136.7	-62.0	-63.9	-154.7	-173.6
8.75	0.0	26.8	24.8	28.3	-25.5	11.9	29.75	-127.3	-136.8	-63.8	-66.9	-166.7	-176.7
9.00	-52.0	29.8	6.3	34.2	-48.9	25.8	30.00	-122.5	-136.7	-67.5	-69.4	-180.4	-179.7
9.25	-97.3	33.2	-5.0	39.2	-64.3	40.7	30.25	-124.5	-136.8	-70.8	-71.9	-186.5	-181.8
9.50	-121.8	36.2	-14.1	44.1	-78.0	52.6	30.50	-126.7	-136.8	-69.1	-73.9	-193.1	-183.7
9.75	-149.1	37.2	-21.7	48.6	-89.1	62.5	30.75	-136.7	-136.3	-71.2	-75.4	-195.2	-184.7
10.00	-176.9	42.6	-26.6	52.5	-96.1	72.4	31.00	-142.5	-135.7	-75.4	-76.4	-195.9	-185.6
10.25	-187.3	46.1	-28.2	56.0	-84.3	80.3	31.25	-155.4	-135.2	-77.8	-77.3	-194.0	-186.1
10.50	-127.7	49.1	-11.3	59.5	-7.1	89.2	31.50	-161.5	-134.7	-78.1	-77.8	-196.7	-186.1
10.75	2.5	52.6	35.6	62.5	106.7	96.2	31.75	-159.2	-133.2	-75.0	-78.8	-198.2	-185.5
11.00	181.8	55.5	99.8	65.4	237.4	103.0	32.00	-150.7	-132.2	-76.7	-78.8	-190.1	-184.5
11.25	336.0	59.5	161.1	68.4	332.7	109.0	32.25	-137.2	-130.7	-78.7	-79.8	-186.2	-183.5
11.50	411.6	62.9	193.8	70.3	363.6	115.9	32.50	-125.4	-128.7	-78.3	-79.8	-183.1	-182.6
11.75	386.1	65.4	185.2	72.8	330.6	120.9	32.75	-112.4	-125.7	-77.1	-80.3	-177.4	-181.1
12.00	276.3	67.3	145.2	74.8	226.7	125.2	33.00	-104.8	-122.8	-79.4	-81.4	-176.5	-179.7
12.25	126.5	69.3	93.4	76.2	124.1	129.7	33.25	-102.1	-120.1	-83.6	-83.1	-180.2	-179.2
12.50	1.6	70.3	47.0	77.8	42.1	132.7	33.50	-100.3	-116.8	-86.9	-84.4	-174.9	-177.2
12.75	-83.6	70.9	17.1	79.3	5.7	135.8	33.75	-99.8	-113.9	-94.0	-85.9	-168.5	-175.8
13.00	-111.1	70.3	8.8	80.2	7.4	136.7	34.00	-106.1	-109.8	-96.8	-87.9	-166.4	-174.3
13.25	-102.4	69.3	17.5	81.2	27.1	138.1	34.25	-108.3	-105.8	-97.3	-89.9	-163.5	-172.7
13.50	-81.6	67.4	31.9	81.7	47.3	138.7	34.50	-108.1	-101.4	-98.5	-91.9	-161.2	-170.8
13.75	-56.1	65.4	45.4	82.3	70.7	138.8	34.75	-99.9	-94.9	-101.2	-93.9	-162.8	-168.9
14.00	-22.2	62.4	62.2	82.7	96.6	137.6	35.00	-95.6	-91.9	-90.2	-96.9	-164.3	-167.3
14.25	15.7	59.5	75.2	82.8	124.5	135.8	35.25	-85.8	-85.9	-97.9	-99.4	-158.8	-165.3
14.50	69.6	55.5	88.0	83.2	159.9	133.7	35.50	-87.0	-79.9	-97.9	-101.8	-154.4	-163.2
14.75	122.8	52.1	101.0	83.3	194.6	131.5	35.75	-77.3	-73.9	-97.9	-103.9	-154.3	-160.8
15.00	180.1	48.0	116.0	83.2	230.0	128.8	36.00	-71.9	-66.9	-97.0	-105.8	-152.3	-158.7
15.25	207.3	44.6	127.3	82.7	244.5	125.8	36.25	-72.8	-59.9	-97.8	-106.9	-151.9	-156.2
15.50	197.3	41.1	127.2	82.3	229.9	122.9	36.50	-62.2	-51.9	-101.8	-108.3	-154.1	-153.8
15.75	151.7	37.6	117.4	81.7	187.6	119.9	36.75	-40.6	-42.9	-103.5	-109.8	-156.5	-150.7
16.00	77.7	33.7	95.6	80.7	119.6	116.4	37.00	-21.7	-35.0	-105.9	-110.4	-157.3	-147.3
16.25	0.0	29.7	69.0	79.3	59.6	113.5	37.25	-16.9	-25.0	-109.9	-110.9	-154.7	-141.8
16.50	-72.5	25.8	42.2	78.3	-1.2	110.0	37.50	-3.3	-16.0	-113.2	-110.4	-143.4	-133.8
16.75	-119.7	22.3	28.5	76.7	-24.1	106.9	37.75	4.7	-7.0	-115.3	-109.9	-134.2	-123.9
17.00	-143.4	18.8	18.6	75.3	-11.2	103.6	38.00	0.0	2.0	-114.7	-108.9	-114.5	-112.9
17.25	-124.5	14.9	29.9	73.6	36.2	99.7	38.25	15.4	12.0	-111.2	-106.3	-100.2	-101.3
17.50	-70.9	11.4	53.2	71.9	95.7	96.2	38.50	24.4	22.0	-107.7	-103.9	-84.2	-88.9
17.75	-8.6	7.9	77.3	70.4	143.4	92.2	38.75	29.5	32.0	-102.9	-100.4	-74.9	-75.9
18.00	53.0	4.0	95.1	68.4	170.4	88.3	39.00	42.1	42.0	-98.9	-95.9	-64.8	-62.9
18.25	95.8	0.0	103.9	66.4	174.2	84.3	39.25	63.0	51.9	-92.9	-91.9	-37.3	-48.9
18.50	119.8	-4.0	103.9	64.5	158.5	79.9	39.50	69.7	61.9	-86.9	-86.9	-24.0	-36.0
18.75	118.9	-7.4	96.7	62.5	130.7	72.4	39.75	74.1	71.9	-79.5	-81.9	-13.9	-21.0
19.00	90.2	-11.9	81.6	60.5	101.3	71.4	40.00	85.8	80.9	-74.0	-76.9	0.0	-5.0
19.25	50.7	-15.9	67.2	58.5	71.7	66.4	40.25	80.1	88.9	-68.2	-72.0	7.5	11.0
19.50	3.8	-19.9	52.0	56.6	41.3	61.5	40.50	92.5	98.9	-62.6	-66.9	24.3	26.0
19.75	-51.5	-23.8	41.6	53.6	19.3	56.6	40.75	93.7	108.9	-55.9	-62.0	37.6	41.0
20.00	-94.6	-28.3	31.2	51.6	0.0	51.1	41.00	111.9	118.9	-51.6	-56.4	62.0	56.9
20.25	-125.7	-32.8	21.3	48.7	-19.7	45.7	41.25	125.7	129.9	-40.3	-50.9	79.9	70.9
20.50	-138.7	-37.3	17.5	46.7	-24.9	39.8	41.50	150.5	141.9	-35.1	-44.5	88.0	86.9
20.75	-133.8	-41.8	17.4	44.8	-23.9	34.3	41.75	155.1	155.8	-27.5	-37.0	94.9	101.9
21.00	-118.6	-46.8	22.8	41.8	-11.0	28.4	42.00	166.4	170.9	-25.6	-31.5	103.7	117.9
21.25	-90.1	-51.8	29.4	39.4	14.0	22.4	42.25	181.7	186.8	-22.6	-24.5	129.6	134.9
21.50	-58.6	-56.8	39.4	36.9	43.8	15.9	42.50	208.2	204.8	-19.6	-16.5	161.9	152.9
21.75	-23.8	-61.8	51.4	34.4	71.3	10.0	42.75	231.0	226.8	-12.1	-8.5	166.5	170.8
22.00	9.8	-66.8	58.3	31.4	85.8	3.0	43.00	253.3	249.8	0.0	0.0	178.9	187.8
22.25	21.4	-71.8	58.4	28.9	77.3	-3.5	43.25	285.0	275.7	5.3	8.5	192.7	204.8
22.50	15.4	-76.8	51.1	25.9	47.7	-10.0	43.50	314.3	299.7	10.0	17.5		
22.75	-11.5	-81.8	36.0	23.4	-1.4	-17.0	43.75	336.7	325.7	18.2	28.0		
23.00	-53.2	-87.2	23.1	20.9	-33.6	-23.4	44.00	350.4	352.6	28.4	39.0		
23.25	-100.0	-92.7	7.0	17.9	-65.1	-29.9	44.25	386.1	379.4	39.9	52.9		
23.50	-137.3	-97.6	-1.1	15.4	-75.3	-36.4	44.50	417.7	412.6	55.2	65.9		
23.75	-160.3	-102.5	-3.4	12.9	-84.2	-42.8	44.75	441.9	439.7	107.6	79.9		

number and form factor,[12] respectively, of atom i, l_{ij} is the root-mean-square amplitude of vibration, and r_{ij} is the interatomic distance. This curve was fitted to the experimental intensity curve by a least-squares method based on a program written by Dr. Hans Seip.[13] The variable parameters are the interatomic distances and the amplitudes of vibration. Independent parameters were selected for each compound and the interatomic distances were calculated from them according to the symmetry of the model structure. Experimental and theoretical radial distribution functions were obtained by calculating Fourier transforms of the intensity curves.

Results

***p*-Carborane.**—The least-squares refinement of the molecular scattering intensity curve of *p*-carborane (Figure 1) was carried out assuming D_{5d} symmetry. Six parameters define the structure: the C1–B2, B2–B3, B2–B7, C–H, and B–H distances and the H–B2–B7 angle. The 28 different interatomic distances were calculated from these. Shrinkage effects were neglected. The least-squares refinement procedure rapidly converged to give the values listed in Table II. Since a diagonal weight matrix was used in the least-squares

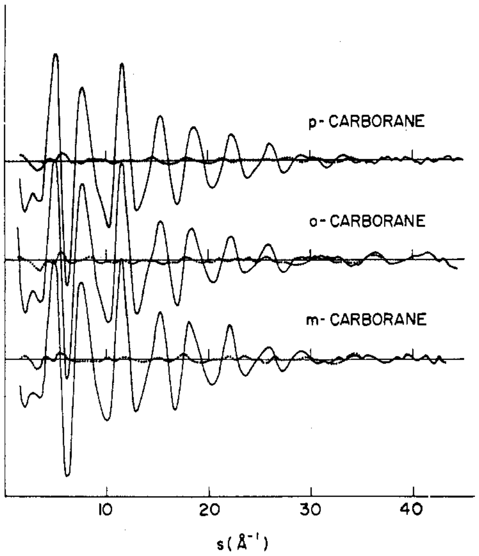

Figure 1.—$sM_{\mathrm{exp}}(s)$ (solid line) and the difference between it and the theoretical intensity calculated from the best model (dotted line) for *p*-, *o*-, and *m*-carborane, respectively.

TABLE II

STRUCTURAL PARAMETERS OF *p*-, *o*-, AND *m*-CARBORANE

	Para	Ortho	Meta
r(C-C),[a] Å		1.653 ± 0.049	
r(B-C), Å	1.710 ± 0.011	1.711 ± 0.014	1.720 ± 0.009
r(B-B), Å			1.831 ± 0.052[b]
	1.792 ± 0.007[c]	1.802 ± 0.013[d]	1.791 ± 0.015
	1.772 ± 0.013	1.789 ± 0.009	1.817 ± 0.013
r(C-H), Å	1.15 ± 0.09	1.15[e]	1.15[e]
r(B-H), Å	1.216 ± 0.021	1.216[e]	1.216[e]
LH-B2-B7, deg	130.0 ± 1.8		
l(X-X),[f] Å	0.063 ± 0.005	0.063 ± 0.006	0.057 ± 0.007
l(X-H), Å	0.093 ± 0.017	0.093[e]	0.093[e]
l(X-X-X), Å	0.075 ± 0.005	0.076 ± 0.009	0.077 ± 0.007
l(X-X-X-X), Å	0.071 ± 0.014	0.069 ± 0.032	0.070 ± 0.026
l(H-X-X), Å	0.127 ± 0.033	0.144 ± 0.029	0.130 ± 0.024
l(H-X-X-X), Å	0.129 ± 0.024	0.136 ± 0.034	0.133 ± 0.028
l(H-X-X-X-X), Å	0.098 ± 0.061	0.07 ± 0.12	0.10 ± 0.13
R_1[g]	7.7	13.6	9.9

[a] Each distance given is the center of gravity of the probability distribution, $r_g(0)$, and was obtained from $r_g(0) = r_g(1) + l^2/r_g(1)$ where $r_g(1)$ is the electron diffraction distance, *i.e.*, the center of gravity of r^{-1} times the probability distribution. [b] The B-B distances in *m*-carborane are, from top to bottom, B2-B3, B2-B6, B5-B6, and those more distant from the C atoms. [c] The B-B distances in *p*-carborane are, from top to bottom, B2-B3 and B2-B7. [d] The B-B distances in *o*-carborane are, from top to bottom, B6-B11 and B7-B11, *i.e.*, the B-B bond lengths girdling the C atoms and those more distant from the C atoms. [e] Assumed values. [f] X is either a B or C atom. [g] $R_1 = 100\Sigma|\Delta|/\Sigma|sM_{\mathrm{exp}}(s)|$: H. M. Seip, T. G. Strand, and R. Stølevik, *Chem. Phys. Lett.*, **3**, 617 (1969).

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(12) D. Nicolas, C. Tavard, and M. Rouault, *J. Chim. Phys.*, **64**, 540 (1967).

(13) A. Almenningen, O. Bastiansen, R. Seip, and H. M. Seip, *Acta Chem. Scand.*, **18**, 2115 (1964).

method and correlation among data points was thereby ignored, the standard deviations calculated from the variance–covariance matrix are too small. Therefore, the error limits reported for distances are the geometric mean of 3 times the standard deviation obtained from the least-squares analysis and 3 times an estimated $0.001r_{ij}$ standard deviation due to scaling errors. For angles and vibrational amplitudes the reported errors are 3 times the least-squares standard deviations.

The experimental radial distribution curve is shown at the top of Figure 2. Immediately beneath it is plotted the difference between the experimental and theoretical radial distribution functions. The small peak at 1.2 Å is due to the B–H and C–H distances, the large peak at 1.8 Å includes all the bonded distances within the icosahedral skeleton, the broad peak at 2.9 Å is mainly due to distances between boron and carbon atoms once removed from each other, the small peak at 3.4 Å is mainly caused by B···B diameters, the peak at 3.9 Å is due to distances between hydrogen atoms and the boron or carbon atoms three bonds removed, and the small peak about 4.6 Å is composed mainly of distances from a hydrogen atom to the boron diametrically opposite.

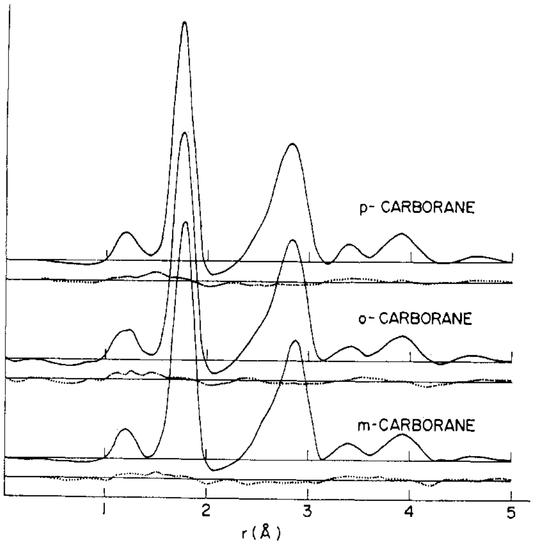

Figure 2.—The experimental radial distribution curve (solid line) with a damping constant of 0.0015 and the difference between it and the curve calculated from the best model (dotted line) for *p*-, *o*-, and *m*-carborane, respectively.

The values obtained for the bond lengths—1.710 ± 0.011 Å for C–B, 1.772 ± 0.013 and 1.792 ± 0.009 Å for B–B, and 1.22 ± 0.02 Å for B–H—are similar to bond lengths in related compounds. The 0.020-Å difference between the longitudinal and latitudinal B–B bonds is approximately 3 times the sum of the standard deviations of the two distances and is most likely real. The only unusual feature appearing in the structure is the external angle of 130.0 ± 1.8° between the B–H bond and the longitudinal B–B bond (Figure 3). All other external angles range between 114.5 and 117.6°. In a regular icosahedron the angle would be 121.7°. The molecule's structure is that of a regular icosahedron which has been shrunk about 10% along the C···C diameter and this distortion is probably related to the unusually large H–B–B bond angle. The H–C···C–H diameter is 5.35 (5) Å *vs.* 5.78 (3) Å for the H–B···B–H diameter. The agreement between the experimental data and the theoretical curves based on models of D_{5d} symmetry is excellent. Allowing a less symmetrical model with more parameters would not be expected to improve upon the agreement.

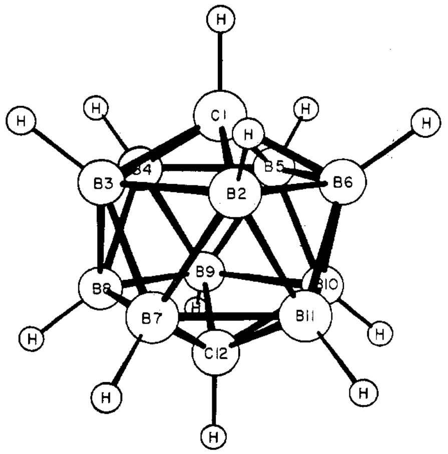

Figure 3.—A scaled, perspective view of *p*-carborane. The volumes of the spherical atoms are shown proportional to their scattering power, *i.e.*, atomic member: C. K. Johnson, "ORTEP, a Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," Report ORNL-3749, Oak Ridge National Laboratory, Oak, Ridge, Tenn., 1965.

o- **and** *m*-**Carborane.**—A glance at the molecular intensity curves in Figure 1 and the radial distribution curves in Figure 2 reveals that the structures of all three isomers are very similar and the distortions from icosahedral symmetry are not large. Determination of unique molecular structures of *o*- and *m*-carborane (Figures 4 and 5) is considerably more difficult than the determination of the structure of *p*-carborane due to the lower symmetry of *o*- and *m*-carborane. Even assuming C_{2v} symmetry there are ten different bond types within the icosahedral cage which all lie in the range 1.6–1.8 Å

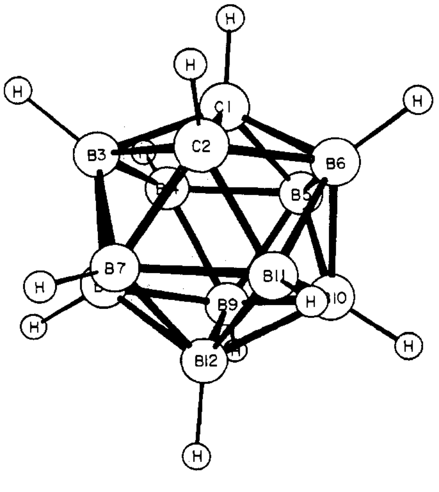

Figure 4.—A scaled, perspective view of *o*-carborane.

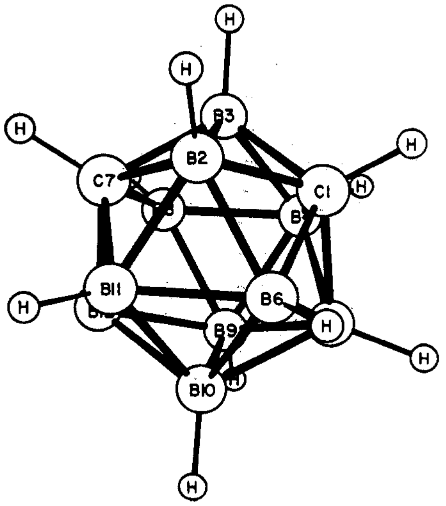

Figure 5.—A scaled, perspective view of *m*-carborane.

TABLE III

STRUCTURAL PARAMETERS OF SEVERAL MODELS OF *o*-CARBORANE

	No. of parameters		
	3	4	5
C–C, Å	1.635 (14)[a]	1.651 (16)	1.620 (17)
B–C, Å	1.707 (4)	1.707 (5)	1.710 (4)
B–B, Å	1.791 (1)	1.800 (4)[b]	1.800 (5)[b]
		1.787 (3)[c,d]	1.810 (8)[c]
			1.745 (11)[d]
l(C–C, B–C, B–B), Å	0.063 (2)	0.063 (2)	0.057 (4)
R_1[e]	1.36	1.36	13.5

[a] The distances are $r_g(1)$ (see footnote *a*, Table II) and the least-squares standard deviations in units of thousandths of 1 Å are enclosed in parentheses. [b] B3–B7, B7–B11. [c] B6–B10, B10–B11, B11–B12. [d] B9–B10, B9–B12. [e] See footnote *g*, Table II.

and which are not resolvable by electron diffraction techniques. Therefore, it was necessary to apply further constraints. In one set of calculations, one to six bond lengths selected in a variety of permutations were refined with the remaining cage bond lengths held constant. No conclusions could be drawn from these results, however, since the values obtained varied so much from one model to the next. Another set of constraints was based on the results of semiempirical molecular orbital calculations of Hoffmann and Lipscomb,[14] who assumed regular icosahedral symmetry. Constraints were applied to the model structures in which a linear relationship between overlap population as calculated by Hoffmann and Lipscomb and bond length was assumed. A variety of constants in the linear relationship were tried but no conclusive results were obtained.

The following approach did yield useful conclusions, however. A three-parameter model of *o*-carborane was refined. The three parameters were the C–C, B–C(av), and B–B(av) distances. The output of this refinement was used as the input for a four-parameter model. In this model the B–B distances were split into two groups: one group consisted of the six B–B distances which form a "girdle" about the carbon atoms and the other group consisted of the B–B distances more remote from the C atoms. The results of this refinement were used as input for a five-parameter model in which the remote B–B bond distances were separated into two categories, those most distant from the carbons and those intermediate in distance. Similarly, a six-parameter model was attempted but it would not refine. The parameter values obtained for each model are listed in Table III. A similar series of refinements was carried out on *m*-carborane. The simplest model had two independent parameters: the B–C(av) and B–B(av) bond lengths. The parameter values from the best two-parameter model were used as starting values for a three-parameter model in which the B–B bond lengths were divided into two groups: those girdling the carbon atoms and the rest. The four-parameter model allowed the B2–B3 distance to vary independently of the other girdling bonds, and in the five-parameter model, the latter distances were separated into two groups: those of the type B3–B4 and those of the type B4–B5. The parameter values obtained for each model are listed in Table IV. The constraints described above are not unique. For example, in *o*-carborane there are many ways in which the ten independent cage distances allowed by C_{2v} symmetry can be classified into four groups. For each of the models above, except for the three-parameter *o*-carborane and two-parameter *m*-carborane, several classifications were tested. Those discussed above were selected because they present a reasonably self-consistent picture of structural trends in the carboranes.

In each of the least-squares refinements of *o*- and *m*-carborane, in addition to the geometric parameters discussed above and a scale factor, six amplitudes of vibration were simultaneously refined. The vibrational amplitudes for the C–C, B–C, and B–B bonded pairs could not be distinguished but were set equal and refined as one vibrational amplitude. The other five families of vibrational amplitudes were the B · · · B or B · · · C once removed, the B · · · B and C · · · C diameters, the H · · · B or H · · · C once removed, the H · · · B or H · · · C twice removed, and the H · · · B or H · · · C three bonds removed, *i.e.*, H to B or C diametrically opposite. The values of the vibrational amplitudes varied negligibly as the number of independent distances was changed. The values obtained from the four-parameter models of *o*- and *m*-carborane are listed in Table II.

Contributions to the scattered intensity by H · · · H distances were ignored, shrinkage effects were neglected, and the B–H and C–H bond distances and average vibrational amplitude were held fixed at the values found in *p*-carborane. No attempt was made to determine the directions of the C–H and B–H bonds in *o*- and *m*-carborane. Each was assumed to form equal angles with the other bonds extending from the boron or carbon atom.

Discussion

The C–C, B–C, and B–B bond lengths obtained in this study are consistent with values determined from

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[14] R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 3489 (1962). Using a method based on model SCF–MO calculations for small molecules, F. P. Boer, Ph.D. Thesis, Harvard University, 1965, has calculated another set of electronic properties of the carboranes. The values obtained from the two methods are qualitatively similar.

TABLE IV

STRUCTURAL PARAMETERS OF SEVERAL MODELS OF *m*-CARBORANE

	No. of parameters				
	2	3	4	5	6
B–C, Å	1.724 (2)[a]	1.720 (3)	1.719 (2)	1.720 (2)	1.719 (5)
B–B, Å	1.803 (1)	1.798 (3)[b–d]	1.830 (17)[b]	1.835 (16)[b]	1.834 (17)[b]
		1.812 (4)	1.790 (4)[c,d]	1.771 (8)[c]	1.777 (13)[c]
			1.816 (4)	1.803 (8)[d]	1.798 (10)[d]
				1.818 (3)	1.812 (14)[e]
					1.826 (12)
l(B–C, B–B), Å	0.063 (1)	0.059 (2)	0.057 (2)	0.056 (2)	0.056 (2)
R_1[f]	10.1	9.9	9.9	9.8	9.8

[a] The distances are $r_g(1)$ (see footnote *a*, Table II) and the least-squares standard deviations are enclosed in parentheses. [b] B2–B3. [c] B3–B4. [d] B4–B5. [e] B2–B9, B2–B8. [f] See footnote *g*, Table II.

X-ray studies of *o*- and *m*-carborane derivatives. (See Tables V and VI.) The average bond lengths in the icosahedral cages of *o*- and *m*-carborane, 1.763 (2) and 1.776 (2) Å, respectively, are in excellent agreement with the results of the Russian electron diffraction workers, 1.76[7] and 1.775 (10) Å,[8] respectively. The more extensive data presented in this study have allowed a more precise characterization of the distortions in the icosahedral molecules. The only surprising feature is the rather large H-B2-B7 angle in *p*-carborane, 130.0 ± 1.8°. It is about 13° larger than any other similar angle in the molecule and is about 8° larger than the angle expected for a regular icosahedron.

TABLE V

BOND LENGTHS (Å) IN *o*-CARBORANE

	$o\text{-}B_{10}Cl_8\text{-}H_2C_2H_2$[a]		$o\text{-}B_{10}H_{10}\text{-}(CCH_2Br)_2$[b]		$o\text{-}B_{10}Br_2\text{-}H_8C_2H_2$[c]		$o\text{-}B_{10}Br_4H_6\text{-}(CCH_3)_2$[d]		$o\text{-}B_{10}\text{-}C_2H_{12}$[e]
C–C (1–2)	1.67		1.64		1.63		1.65		1.65
B–C (2–3)	1.73	1.71_5	1.71	1.72	1.71	1.72	1.73	1.72	1.70_8
(2–7)	1.70		1.73		1.73		1.71		
B–B (3–7)	1.81	1.80_3	1.78	1.78_3	1.76	1.77_3	1.78	1.78	1.80_0
(7–11)	1.79		1.79		1.80		1.78		
(6–10)	1.75	1.78_1	1.76	1.76_1	1.73	1.75_4	1.77	1.77_9	1.78_7
(10–11)	1.78		1.75		1.74		1.79		
(11–12)	1.76		1.75		1.76		1.76		
(10–12)	1.81		1.77		1.78		1.79		
(9–12)	1.81		1.81		1.73		1.78		

[a] J. A. Potenza and W. N. Lipscomb, *Inorg. Chem.*, **3**, 1673 (1964). [b] D. Voet and W. N. Lipscomb, *ibid.*, **3**, 1679 (1964). [c] J. A. Potenza and W. N. Lipscomb, *ibid.*, **5**, 1471 (1966). [d] J. A. Potenza and W. N. Lipscomb, *ibid.*, **5**, 1483 (1966). [e] This work.

TABLE VI

BOND LENGTHS (Å) IN *m*-CARBORANE

	$m\text{-}B_{10}Br_2H_8C_2H_2$[a]		$m\text{-}B_{10}C_2H_{12}$[b]
B–C (1–2)	1.64	1.67_6	1.71_9
(1–4)	1.68		
(1–5)	1.74		
B–B (2–3)	1.89		1.82_8
(2–6)	1.72	1.77_5	1.79_0
(4–5)	1.83		
(6–11)	1.81	1.76_3	1.81_6
(6–10)	1.80		
(5–9)	1.70		
(9–10)	1.77		

[a] H. Beall and W. N. Lipscomb, *Inorg. Chem.*, **6**, 874 (1967). [b] This work.

There appears to be a characteristic pattern in the variations of the various B–B bond lengths in the carboranes. B–B bond lengths nearer carbon atoms are longer than B–B bond lengths more remote. This result contradicts a previously reported conclusion.[15] In *p*-carborane the B–B bond length girdling the carbon atoms is 1.792 ± 0.007 Å and the bond length bridging the two pentagonal pyramid caps is 1.772 ± 0.013 Å. In *o*-carborane a similar pattern can be seen in the results of the four- and five-parameter models in Table III. X-Ray structural studies of *o*-carborane derivatives, whose crystals displayed no disorder effects thereby allowing determination of the separate bond lengths, also demonstrate the trend of longer B–B bond lengths in the vicinity of carbon atoms. These results are summarized in Table V. The bond lengths listed have been averaged to a C_{2v} structure which allows ten independent cage bond lengths. These have been averaged again according to the constraints used in our four-parameter model. The bonds are listed in order from those nearest the carbon atoms to those most remote. The general trend of longer bond lengths nearer carbon atoms is clear. This trend does not appear in the *m*-carborane results (Table IV), except for the unique B2–B3 bond. One *m*-carborane crystal structure has been reported which is not complicated by disorder.[16] Its structure is compared to our four-parameter model in Table VI. As in Table V the bond lengths have been averaged to C_{2v} symmetry and reaveraged according to the constraints of our four-parameter model. The bonds are listed in order from those nearest the carbon atoms to those most distant. The trend of longer B–B bond lengths nearer carbon atoms appears in the X-ray results. The long B2–B3 bond length observed in $m\text{-}B_{10}Br_2H_8C_2H_2$ by Beall and Lipscomb represents one extreme of the trend since each of the boron atoms is bonded to two carbon atoms. The structural trends among the B–B bond lengths are consistent with the concept of the more electronegative carbon atoms draining electron density away from their immediate surroundings thereby weakening and lengthening neighboring bonds. Calculations of charge densities and overlap populations in the carboranes[14] agree qualitatively with this picture.

Acknowledgments.—The authors are grateful to Dr. H. A. Schroeder for providing the samples of the carboranes. Cand. Real. Arne Almenningen took the

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

(16) H. Beall and W. N. Lipscomb, *ibid.*, **6**, 874 (1967).

diffraction photographs on the Oslo apparatus. NATO provided generous support through a fellowhsip (to R. K. B.), and the Norwegian Research Council supported M. D. B. and sponsored the calculations carried out at the Norwegian Computing Center. The authors wish to thank Professor Otto Bastiansen and Dr. Hans Seip for many stimulating discussions. Miss Bergliot Nyhus and Miss Snefrid Gullikstad assisted in the data analysis. The authors are grateful to Siv. Ing. Marit Traetteberg for calculating power spectra and sharpened radial distribution functions. The bulk of the computational work was carried out at the University of Connecticut Computing Center which enjoys support from National Science Foundation Grant GP-1819.

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Concerning the Reactions of Lithium, Sodium, and Potassium Hydrides with Magnesium Halides in Ether Solvents. A Convenient and Economic Route to Reactive Magnesium Hydride

BY E. C. ASHBY* AND R. D. SCHWARTZ

Received June 15, 1970

The reactions of lithium, sodium, and potassium hydrides with magnesium chloride, bromide, and iodide in diethyl ether and tetrahydrofuran, as a route to reactive magnesium hydride, have been studied. Magnesium hydride was formed in quantitative yield by the reaction of sodium hydride with magnesium bromide in tetrahydrofuran and by the reaction of sodium hydride or potassium hydride with magnesium iodide in diethyl ether. In the latter reactions the sodium iodide by-product was separated from magnesium hydride by extraction with tetrahydrofuran, and potassium iodide was separated by extraction with diglyme. Commercially available lithium hydride was found not to react with magnesium halides in tetrahydrofuran at room temperature although some reaction was detected at reflux temperatures. Lithium hydride prepared by hydrogenolysis of *tert*-butyllithium was found to react slowly with magnesium bromide in tetrahydrofuran and not at all with magnesium chloride in the same solvent. No complexes of the type M_nMgH_{2+n} were detected when excess alkali metal hydrides were used in these experiments.

Introduction

There are three general methods for preparing magnesium hydride.[1] The equations used to represent these methods are

$$(C_2H_5)_2Mg \xrightarrow{175^\circ} MgH_2 + 2C_2H_4 \tag{1}$$

$$LiAlH_4 + 2Mg(C_2H_5)_2 \longrightarrow 2MgH_2 + LiAl(C_2H_5)_4 \tag{2}$$

$$Mg + H_2 \xrightarrow[200\ \text{atm}]{570^\circ} MgH_2 \tag{3}$$

The pyrolysis of diethylmagnesium[2] (eq 1) produces an active form of magnesium hydride which is pyrophoric in air and reacts violently with water and other protic compounds. The reaction of lithium aluminum hydride with diethylmagnesium[3] (eq 2) also produces active magnesium hydride. The formation of magnesium hydride from the elements (eq 3) occurs at 570° and 200 atm using magnesium iodide as a catalyst.[4] This method is obviously an economic one and the magnesium hydride prepared by this method is commercially available. Unfortunately MgH_2 prepared by this method is quite unreactive even to air and water.

In 1951 Wiberg,[5] in a short note concerning the preparation of BeH_2, made a one-sentence statement that excess lithium hydride and magnesium chloride in diethyl ether react to form either magnesium hydride or Li_nMgH_{2+n}. Since a mixture of excess LiH and MgH_2 could not be distinguished from Li_nMgH_{2+n} except by powder diffraction analysis, one cannot be sure what was formed in this reaction and to what extent. No subsequent report has appeared.

The reaction of alkali metal hydrides with magnesium halides in ether solvents represents a substantially more convenient and economic route to reactive magnesium hydride than the methods now available. Ideally it was hoped that in a particular solvent an insoluble metal hydride would react with a soluble magnesium halide to form insoluble MgH_2 and soluble magnesium halide. Thus active MgH_2 could be easily isolated in a pure form by filtration. We therefore decided to explore the general scope and utility of the reaction $MH + MgX_2$ (where M = Li, Na, K and X = Cl, Br, I) in an attempt to produce active magnesium hydride free from the alkali metal halide by-product. We also wished to determine whether Li_nMgH_{2+n} is formed in the reaction of LiH and $MgCl_2$ and, if so, isolate the compound.

Experimental Section

All operations were carried out either in a nitrogen-filled glove

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(1) K. M. Mackay, "Hydrogen Compounds of the Metallic Elements," Wilmer Brothers Ltd., Birkenhead, Cheshire, England, 1966, p 39.

(2) E. Wiberg and R. Bauer, *Z. Naturforsch. B*, **5**, 396 (1950).

(3) G. D. Barbaras, C. Dillard, A. E. Finholt, T. Wartik, K. E. Wilzbach, and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **73**, 4585 (1951).

(4) E. Wiberg, H. Goeltzer, and R. Bauer, *Z. Naturforsch. B*, **6**, 394 (1951).

(5) E. Wiberg and R. Bauer, *ibid.*, *B*, **6**, 171 (1951).