its greater electronegativity should cause an increased rate of isomerization if electronic effects were indeed responsible for the more facile rearrangement of the more highly phenylated silyl derivatives.

In order to examine more closely the effect of this postulated steric acceleration, kinetic data were obtained (Table II) for the polyhedral rearrangement of carborane itself and for a derivative bearing bulky substituents (**1**). The enthalpy of activation for the isomerization of **1** (45 kcal.) is considerably lower than that for the isomerization of unsubstituted carborane (62 kcal.). This result accords well with the above rationale involving relief of internal strain; *i.e.*, bond stretching, necessary for polyhedral rearrangement, is already present in the ground state of **1** and therefore results in a decreased ΔH^*.

Table II

Rate Data[a] for Thermal Rearrangements

1,2-Bis(methyldiphenylsilyl)carborane (**1**)

Temp., °C.	263	280	300
$k \times 10^4$, sec.$^{-1}$	0.03	0.22	1.28

$\Delta H^* = 45$ kcal., $\Delta S^* = -1$ e.u. at 280°

Carborane

Temp., °C.	425	455	475
$k \times 10^4$, sec.$^{-1}$	0.22	1.54	4.7

$\Delta H^* = 62$ kcal., $\Delta S^* = 7$ e.u. at 455°

[a] The rate of isomerization of **1** was measured by determining the relative integrals of the methyl proton n.m.r. signal for **1** and **2**. The isomerization of carborane was followed by g.l.p.c. First-order rate constants were determined from plots of log *C vs.* time. Activation parameters were calculated from an Arrhenius plot (A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 98–101). Because of difficulties in thermostating reactions at these temperatures, the activation parameters (particularly ΔS^*) can only be considered approximate.

The observed enhancement of the rearrangement rate by bulky C substituents suggests that carboranes bearing large groups other than the silyl groups studied in this investigation would also undergo polyhedral rearrangement at relatively low temperatures.

Contribution from Ethyl Corporation,
Baton Rouge, Louisiana

Reaction of Grignard Compounds with Diborane: Characterization of Chloromagnesium Borohydride

By Warren E. Becker and Eugene C. Ashby

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A study of the reaction of Grignard reagents with diborane was first reported by Wiberg and Strebel.[1,2] These workers reported this reaction to be useful for the synthesis of compounds having the composition HMgX. Using this system, they reported the preparation of HMgCl, HMgBr, and HMgI as the bis-diethyl etherates and HMgCl as the ditetrahydrofuranate, according to the equation

$$6\text{RMgX} + \text{B}_2\text{H}_6 \longrightarrow 6\text{HMgX} + 2\text{BR}_3 \qquad (1)$$

More recently Russian workers have also prepared these same compounds as the diethyl etherates by hydrogenolysis of the appropriate Grignard reagent.[3]

Before appearance of this latter publication, we attempted to prepare HMgX compounds according to the procedure of Wiberg and Strebel, using $\text{C}_2\text{H}_5\text{MgCl}$. A range of stoichiometries was investigated; in no case were we able to isolate HMgX, as reported by Wiberg and Strebel. Instead, we were able to isolate chloromagnesium borohydride, according to the equation

$$3\text{C}_2\text{H}_5\text{MgCl} + 2\text{B}_2\text{H}_6 \xrightarrow[25^\circ]{\text{THF}} 3\text{ClMgBH}_4 + \text{B}(\text{C}_2\text{H}_5)_3 \qquad (2)$$

Chloromagnesium borohydride was proposed by Strebel[2] as being the product from further reaction of HMgCl and diborane. However, the material was not isolated or characterized.

We have now prepared and isolated chloromagnesium borohydride in quantitative yield and in good purity as the ditetrahydrofuranate by the reaction shown in eq. 2. It has also been prepared according to the equations.

$$\text{MgCl}_2 + \text{Mg}(\text{BH}_4)_2 \xrightarrow[65^\circ]{\text{THF}} 2\text{ClMgBH}_4 \qquad (3)$$

$$\text{MgCl}_2 + \text{NaBH}_4 \xrightarrow[65^\circ]{\text{THF}} \text{ClMgBH}_4 + \text{NaCl} \qquad (4)$$

Reaction 3 produces quantitative yields of ClMgBH_4; reaction 4 does not give good yields and is not recommended as a preparative method. None of the above reactions proceeds simply and in good yield in diethyl ether; however, a small amount of $\text{ClMgBH}_4 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ was obtained from reaction 2 in diethyl ether solvent. Physical and chemical properties are reported for the ditetrahydrofuranate.

Chloromagnesium borohydride, as the ditetrahydrofuranate, is a white crystalline material which is isolated simply by removal of the tetrahydrofuran solvent under vacuum at room temperature. One mole of tetrahydrofuran per mole of magnesium can be removed under vacuum at 100°. The monotetrahydrofuranate is somewhat gummy in appearance. Its properties were not investigated.

The material $\text{ClMgBH}_4 \cdot 2\text{THF}$ is soluble in benzene but is insoluble in ether and in diglyme. It evolves hydrogen upon addition to water. The cryoscopic molecular weight in benzene is 440 (437 calculated for a dimer), but in boiling tetrahydrofuran it is monomeric.

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(1) E. Wiberg and P. Strebel, *Ann.*, **607**, 9 (1957).

(2) P. Strebel, Dissertation, University of Munich, Oct. 1958.

(3) T. N. Dymova and N. G. Eleseeva, *Russ. J. Inorg. Chem.*, **8**, 820 (1963).

The dipole moment is 6 D. as determined in benzene solution. The infrared spectrum in tetrahydrofuran shows B–H absorption at 2175 and at 2380 cm.$^{-1}$.

Fractional crystallization showed that $ClMgBH_4$ in tetrahydrofuran solution is stable toward disproportionation. Also, no $MgCl_2$ precipitates from a refluxing benzene solution of $ClMgBH_4 \cdot 2THF$, which is a further indication of its stability toward disproportionation.

A tetrahydrofuran solution of $ClMgBH_4$ reacts slowly with KBH_4 to form KCl and $Mg(BH_4)_2$. The solution still contained soluble Cl^- even after 2 weeks. Ethyllithium reacts rapidly with $ClMgBH_4 \cdot 2THF$ in benzene to form LiCl, which precipitates, and a soluble material which is presumably $C_2H_5MgBH_4$. This latter material was not isolated as a solid.

Experimental

Anhydrous $MgCl_2$, obtained from a private source, was analyzed and found to contain 25.65% Mg, 74.33% Cl, and 0.50% H_2O (by Karl Fischer). Complex metal hydrides were obtained from Metal Hydrides, Inc., except $NaAlH_4$ (Ethyl Corporation). All manipulations involving reactive materials were performed in a nitrogen box.

Solvents were dried by distillation over $NaAlH_4$ or $LiAlH_4$. Grignard reagents were prepared according to standard techniques. The solutions were standardized by analysis for halogen by the Volhard method and for magnesium by Versene titration. Ethyllithium was prepared in benzene by allowing lithium sand to react with ethyl chloride. The lithium chloride was removed by filtration and the solution was standardized by titrating with standard acid after hydrolysis.

Diborane was prepared by allowing $NaBH_4$ to react with $BF_3 \cdot (C_2H_5)_2$ in diglyme.[4] The diborane was passed through a Dry Ice trap and then bubbled directly into the reaction vessel.

Magnesium borohydride was prepared by a two-step synthesis according to the equations

$$C_2H_5MgCl + NaBH_4 \xrightarrow[(C_2H_5)_2O]{\text{THF or}} NaCl + C_2H_5MgBH_4 \qquad (5)$$

$$3C_2H_5MgBH_4 + 2B_2H_6 \xrightarrow[(C_2H_5)_2O]{\text{THF or}} 3Mg(BH_4)_2 + B(C_2H_5)_3 \qquad (6)$$

Reaction 5 requires about 1 week at room temperature with a well-stirred system using either tetrahydrofuran or ether as solvent. Substitution of $LiBH_4$ for $NaBH_4$ in the ether system is not satisfactory. Even after several weeks this system still contained appreciable soluble chloride.

We were not able to isolate $C_2H_5MgBH_4$ as a solid. Evaporation of the ether solution led to a viscous liquid which defied all attempts at crystallization.

It is not necessary to isolate $C_2H_5MgBH_4$ in order to prepare $Mg(BH_4)_2$. Diborane reacts readily at room temperature with $C_2H_5MgBH_4$ in either tetrahydrofuran or ether. Solid product can be obtained from either solution by removal of solvent under vacuum. Samples were analyzed by hydrolyzing a weighed amount. The evolved gas was analyzed by mass spectrometer. The residue was analyzed for magnesium by Versene titration and boron by the mannitol method.

Anal. Calcd. for $Mg(BH_4)_2 \cdot (C_2H_5)_2O$: Mg, 19.0; B, 16.9; H, 6.2; $(C_2H_5)_2O$, 57.8. Found: Mg, 18.9; B, 15.3; H, 6.0; $(C_2H_5)_2O$, 59.8.

Anal. Calcd. for $Mg(BH_4)_2 \cdot 3THF$: Mg, 9.00; B, 7.99; H, 2.9; THF, 80. Found: Mg, 8.60; B, 7.52; H, 2.9; THF, 81.

TABLE I

FRACTIONAL CRYSTALLIZATION OF THE PRODUCT FORMED BY REACTION OF C_2H_5MgCl WITH B_2H_6 IN THF

Fraction	Wt., g.	Anal., wt. % Mg	Anal., wt. % Cl	Ratio Cl:Mg
1	14.28	8.73	11.19	1.14:1.00
2	15.20	8.71	11.53	1.11:1.00
3	6.34	9.30	13.52	1.00:1.00
4	28.89	9.70	14.90	0.95:1.00

TABLE II

FRACTIONAL CRYSTALLIZATION OF $MgCl_2$–$Mg(BH_4)_2$ REACTION IN THF

Fraction	Wt., g.	Anal., wt. % Cl	Anal., wt. % Mg	Anal., wt. % B	Ratio Cl:Mg:B
1	21.3	11.01	8.29	4.00	1.00:1.10:1.19
2	11.6	11.16	8.35	3.97	1.00:1.10:1.17
3	16.5	10.41	8.47	3.83	1.00:1.19:1.21
4	32.8	10.91	8.56	3.65	1.00:1.14:1.09
5	15.6	11.86	8.60	3.49	1.00:1.06:0.97
6 (residue)	10.5	16.88	9.89	2.98	1.00:0.86:0.58

Preparation of $ClMgBH_4$. (1) **From Grignard and Diborane.**—In tetrahydrofuran the reaction proceeds according to eq. 2. In a typical experiment a slight excess of diborane was introduced into 0.5 mole of C_2H_5MgCl in tetrahydrofuran at 25°. The reaction is exothermic. After solvent was removed under vacuum from the resulting clear solution a white solid remained which was the ditetrahydrofuranate of $ClMgBH_4$. The yield was quantitative and the presence of $B(C_2H_5)_3$ in the distillate was verified by gas chromatography.

Anal. Calcd. for $ClMgBH_4 \cdot 2.3THF$: Cl, 14.8; Mg, 10.13; B, 4.51; H, 1.67; THF, 69.0. Found: Cl, 14.8; Mg, 9.72; B, 4.40; H, 1.55; THF, 69.5.

The cryoscopic molecular weight in benzene of this material was 440, while the ebullioscopic molecular weight in THF was 233. The dipole moment in benzene was 6.5 D.

In order to verify that the product was really $ClMgBH_4$ and not a mixture of $MgCl_2$ and $Mg(BH_4)_2$, one of the preparations was subjected to a fractional crystallization with the results shown in Table I.

Further evidence that the product cannot be a mixture of $MgCl_2$ and $Mg(BH_4)_2$ was obtained by determining the solubility of $MgCl_2 \cdot 2THF$ in benzene. This was determined to be 0.02 g./100 g. of benzene. The product $ClMgBH_4 \cdot 2THF$ is freely soluble in benzene.

The reaction is not clean in ether. Diborane (0.24 mole) and C_2H_5MgCl (0.36 mole) were allowed to react in 1 l. of ether. A precipitate formed during overnight stirring of the reaction mixture. This proved to be $MgCl_2$ (0.11 mole), which was removed by filtration. Upon evaporation the filtrate yielded an oil. This oil was shaken with a mixture of benzene and hexane resulting in a two-phase system which consisted of a light hexane–benzene layer and a heavier oil. The phases were separated and the oil crystallized overnight. It was subjected to vacuum for 2 days and analyzed.

Anal. Calcd. for $ClMgBH_4 \cdot (C_2H_5)_2O$: Cl, 23.9; Mg, 16.4; B, 7.3; H, 2.7; $(C_2H_5)_2O$, 49.8. Found: Cl, 19.0; Mg, 18.8; B, 9.70; H, 3.32; $(C_2H_5)_2O$, 49.9.

This material would appear to be $ClMgBH_4$ plus some $Mg(BH_4)_2$. Only an oil was recovered from the hexane solution.

(2) **From $MgCl_2$ and $Mg(BH_4)_2$.**—A mixture of 0.20 mole of $MgCl_2$ and 0.20 mole of $Mg(BH_4)_2$ in 500 ml. of tetrahydrofuran was refluxed several hours. A small amount of brown insoluble material was removed by filtration. The clear filtrate was then subjected to fractional crystallization by removing solvent under vacuum until a crop of crystals appeared. These were removed by filtration and analyzed for Cl, Mg, and B. The filtrate was subjected to further crystallization. The results are shown in Table II.

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[4] H. I. Schlesinger, H. C. Brown, H. R. Hoekstra, and L. R. Rapp, *J. Am. Chem. Soc.*, **75**, 199 (1953).

Fraction 5 was dried overnight under vacuum and reanalyzed.

Anal. Calcd. for $ClMgBH_4 \cdot 1.7THF$: Cl, 18.0 Mg, 12.3; B, 5.5; H, 2.0; THF, 62.2. Found: Cl, 18.5; Mg, 12.2; B, 5.2; H, 1.9; THF, 62.3.

The cryoscopic molecular weight of this sample in benzene was 445 and the dipole moment was 6.0 D. The product was identical with that prepared from Grignard and diborane.

(3) From $MgCl_2$ and Alkali Metal Borohydrides.—A mixture of 0.50 mole of $MgCl_2$ and 0.50 mole of $NaBH_4$ in about 700 ml. of tetrahydrofuran was refluxed for 1 week. Periodically the mixture was cooled and allowed to settle in order to allow sampling the supernatant liquid. This was analyzed so that the progress of the reaction could be followed. After 1 week the reaction had only gone to about 60% completion.

The reaction proceeds faster when KBH_4 is substituted for $NaBH_4$ but this is still not a satisfactory preparation for $ClMgBH_4$. This reaction reached 80% completion after 1 week compared to 60% for $NaBH_4$ and about 50% for the reaction of $LiBH_4$ with $MgCl_2$ in ether.

When $MgCl_2$ was allowed to react with 2 moles of KBH_4 in refluxing tetrahydrofuran, the product was a mixture of $ClMgBH_4$ and $Mg(BH_4)_2$, showing that $ClMgBH_4$ reacts further with KBH_4 to form $Mg(BH_4)_2$. Even after 10 days the amount of $Mg(BH_4)_2$ formed was only 25% of theory. It should be possible to "titrate" the product with $MgCl_2$ to form $ClMgBH_4$; however, the Grignard–diborane route to $ClMgBH_4$ is easier.

Desolvation of $ClMgBH_4 \cdot 2THF$ to $ClMgBH_4 \cdot THF$.—A 29-g. sample of $ClMgBH_4 \cdot 2THF$ was placed in a weighed round-bottom flask equipped with a stopcock. This was attached to a vacuum line and the flask was heated to 100° with an oil bath. Periodically the flask was removed from the vacuum line and weighed in order to follow the desolvation. After 5 hr. the weight loss reached 13.00 g. No more tetrahydrofuran could be removed even after an additional 15 hr.

The product was off-white in color and slightly wet or gummy in appearance.

Anal. Calcd. for $ClMgBH_4 \cdot THF$: Cl, 24.2; Mg, 16.6; B, 7.4; H, 2.7; THF, 49.2. Found: Cl, 24.0; Mg, 16.7; B, 7.1; H, 2.4; THF, 49.8.

Reaction of LiC_2H_5 with $ClMgBH_4$.—Ethyllithium (0.089 mole of 1.01 *N* benzene solution) was added to 0.089 mole of $ClMgBH_4 \cdot 2THF$ in 200 ml. of benzene. Lithium chloride precipitated immediately in quantitative yield.

The solution, then, must contain $C_2H_5MgBH_4$ or a mixture of $Mg(C_2H_5)_2$ and $Mg(BH_4)_2$. Ebullioscopic molecular weight determination showed that $C_2H_5MgBH_4$ is a monomer. This, of course, does not allow distinguishing monomeric $C_2H_5MgBH_4$ from a physical mixture of $Mg(C_2H_5)_2$ and $Mg(BH_4)_2$, both of which are monomeric also. Removal of solvent under vacuum from the solution resulted in a viscous oil which could not be crystallized.

Physical Measurements.—The cryoscopic molecular weights in benzene and the ebullioscopic molecular weights were done according to standard techniques. The solutions used contained approximately 2 wt. % of $ClMgBH_4 \cdot 2THF$. Dipole moments were determined by the dilute solution method in benzene. The dielectric constant measurements required were made with a Sargent Model V chemical oscillometer at 5 Mc.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Metal–Olefin Complexes. I. The Cyclodecadiene Complexes of Silver(I) and Copper(I)

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The reactions of olefinic and acetylenic hydrocarbons with silver(I) nitrate, copper(I) chloride, and copper(I) bromide have received a considerable amount of attention.[3] Recently the use of cyclic olefins as complexing agents has created much excitement. A variety of cyclic olefin complexes of the eight through twelve carbon atom series have been reported.[4–6] Cope, McLean, and Nelson[7] have prepared the silver(I) complexes of both *cis*- and *trans*-cyclodecene; however, no complexes with the unconjugated dienes of the cyclic C_{10} series have been reported. We have now synthesized some silver(I) and copper(I) diolefin compounds of *cis,trans*-cyclodeca-1,5-diene and *cis,cis*-cyclodeca-1,6-diene.[8,9]

Experimental

Reagents.—Cyclodeca-1,5-diene and cyclodeca-1,6-diene were obtained from the Columbian Carbon Co., Lake Charles Chemical Research Center, Lake Charles, La. The olefins were purified by vacuum distillation to yield (v.p.c.) 93% 1,5- and 96% 1,6-diene.

The salts used were Matheson Coleman and Bell reagent grade silver nitrate and anhydrous copper(II) bromide and Baker analyzed reagent grade copper(II) chloride dihydrate. Infrared spectra were taken on a Beckman Model IR-8 spectrophotometer.

Preparation of the Silver(I) Olefin Complexes.—To a solution of 1.7 g. (0.01 mole) of silver nitrate in 10 ml. of water was added a solution of 3 ml. of carbon tetrachloride or methanol and 3 ml. (0.04 mole) of cyclic olefin. The mixture was stirred for a few minutes. The white precipitate formed was filtered, washed with two 5-ml. portions of carbon tetrachloride, and dried under vacuum over calcium chloride (analysis in Table I).

Preparation of Copper(I) Olefin Complexes.—To a solution of 3.4 g. (0.02 mole) of copper(II) chloride dihydrate in 35 ml. of 95% ethanol was added 3 ml. (0.04 mole) of cyclic diolefin. Sulfur dioxide was bubbled into the solution while maintaining the temperature at 20–25°. Addition of sulfur dioxide was stopped after precipitation of product was noted. The mixture was kept at 20° for several hours and filtered, and the crystalline product was washed with 2 ml. of olefin followed by several 10-ml.

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[3] M. A. Bennett, *Chem. Rev.*, **62**, 611 (1962), and references cited therein.

[4] R. N. Keller, *ibid.*, **28**, 229 (1941).

[5] E. O. Fischer and H. Werner, "Metall-π-Komplexe mit di und oligo-olefinischen Liganden," Verlag Chemie, Weinheim, 1964.

[6] E. O. Fischer and H. Werner, *Angew. Chem. Intern. Ed. Engl.*, **2**, 80 (1963); *Angew. Chem.*, **75**, 57 (1963).

[7] A. C. Cope, D. C. McLean, and N. A. Nelson, *J. Am. Chem. Soc.*, **77**, 1628 (1955).

[8] C. A. Grob, H. Link, and P. W. Scheiss, *Helv. Chim. Acta*, **46**, 483 (1963).

[9] G. Wilke, *et al.*, *Angew. Chem. Intern. Ed. Engl.*, **2**, 105 (1963); *Angew. Chem.*, **75**, 10 (1963).