

chlorite, 39835-22-8; *tert*-butyl hypochlorite, 507-40-4; methyl hypochlorite, 593-78-2; chlorine, 7782-50-5; *p*-xylene, 106-42-3; *o*-xylene, 95-47-6; naphthalene, 91-20-3.

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**Preparation and Characterization of
Dichlorocyclopentadienylborane and
Attempted Preparation of
1-Chloro-2,3,4,5,6-pentacarba-*nido*-hexaborane
Cation**

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The properties and structure of dialkylcyclopentadienylboranes have been reported by Grundke and Paetzold.¹ We wish to report a dichloro analog which appears to differ significantly in stability and acidity from the alkyl systems, but whose boron-11 and proton nmr spectra are sufficiently comparable to allow similar structural conclusions to be made. Because the formal loss of Cl⁻ from this compound would result in the possible formation of a *B*-chloro derivative of the hypothetical *nido*-C₅BH₆⁺ ion, attempts were made to effect this conversion.

Experimental Section

Materials.—Sodium cyclopentadienide was obtained from the Eastman Chemical Co. as an 18% solution in tetrahydrofuran. The solvent was removed under reduced pressure. Boron trichloride, Matheson Co., was fractionated through -130° traps to remove HCl, and butyllithium in hexane was obtained from the Foote Mineral Co. Aluminum chloride was freshly sublimed. Most experimental procedures were carried out using conventional vacuum techniques.

Dichlorocyclopentadienylborane.—Since the reaction of boron trichloride and its vapor with cyclopentadienide was found to be highly exothermic, NaC₅H₅ was added as a powder to liquid BCl₃ previously cooled to -78°. This was accomplished by pulverizing the salt, freed from its solvent, tetrahydrofuran, under an inert atmosphere, and transferral of the powder to a rotatable side arm attached to the reactor vessel. Then sodium cyclopentadienide (75.9 mmol) was slowly added with stirring to 40 ml of boron trichloride maintained at -78°. The temperature was raised over a period of a few hours to 0° after which the reaction was allowed to continue for 3 hr more. The volatile components were removed at reduced temperature and pressure and fractionated through traps at -78° and -190°. When all the liquid BCl₃ had been removed from the reaction vessel, the insoluble brown solid residue remaining was gradually warmed to room temperature, and then, over a period of several hours, heated to ~300° while the volatiles were continued to be pumped through the cold traps. Approximately 0.3–0.4 ml of the product C₅H₅BCl₂ was retained in the -78° trap as a solid. Dichlorocyclopentadienylborane was a colorless liquid which darkened noticeably within an hour at room temperature. It had a vapor

pressure of ~3 mm at 25°. The ¹¹B nmr spectrum was a singlet at about δ -47 ppm (neat) (BF₃·OEt₂, δ 0) which tended to broaden considerably at temperatures below -30°. In methylene chloride the chemical shift was -51 ppm. The proton spectrum exhibited four peaks with no observable fine structure in an apparent 1:1:1:2 ratio at τ 2.36, 3.14, 3.36, and 6.68, respectively, for the neat material. In chloroform the values were τ 2.16, 2.94, 3.17, and 6.66. The ¹¹B signals were observed to decrease in intensity after 5 min at room temperature with no new resonances appearing. The proton spectrum revealed a total decomposition of C₅H₅BCl₂ after 1 hr at 25° as evidenced by the loss of all olefinic signals and a growth in peaks at higher field attributed to hydrogen on saturated carbons.

The mass spectrum of the pure C₅H₅BCl₂ exhibited major peak envelopes at *m/e* 143–150 and 108–113 as well as a number of other peaks at lower masses. The parent region intensities were *m/e* 150 (rel intensity 9.4), 149 (3.3), 148 (62.0), 147 (20.7), 146 (100.0), 145 (31.5), 144 (17.7), and 143 (4.0). This corresponds to the monoisotopic species: at *m/e* 146, ¹²C₅¹H₅¹⁰B³⁵Cl₂ (relative intensity 100.0); *m/e* 145, ¹²C₅¹H₄¹⁰B³⁵Cl₂ (8.3); *m/e* 144, ¹²C₅¹H₃¹⁰B³⁵Cl₂ (18.5).

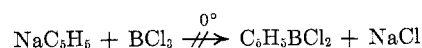
Reaction of C₅H₅BCl₂ with Butyllithium.—About 0.11 mol of butyllithium in hexane was syringed into a dry 5-mm nmr tube, cooled to -196° and the system evacuated. Approximately 0.1 mmol of C₅H₅BCl₂ was then condensed into the tube. The ¹¹B nmr spectrum was obtained of the mixture at increasing temperature starting at -40°. Little change was observed in the chemical shift or appearance of the single peak even after standing at room temperature several days, the resonances appearing at about -49 ± 1.5 ppm depending on the temperature. The ¹H nmr spectrum at 25° showed only two doublets of approximately the same intensity appearing at τ 2.82 and 3.29 (*J* = 2.2 Hz and 1.9 Hz, respectively) which suggest the presence of olefinic hydrogens. The nmr sample was opened and the contents were fractionated to remove hexane. The only volatile product was butane.

Reaction of C₅H₅BCl₂ with Al₂Cl₆.—When dichlorocyclopentadienylborane was treated with aluminum chloride in either methylene chloride or chloroform, rapid and total decomposition of the borane to a dark brown sludge was the only reaction observed. This process, which was followed by ¹H nmr and ¹¹B nmr, was essentially complete in less than 1 hr at 25° as revealed by the loss of olefinic signals in the proton spectrum and the boron singlet in the boron spectrum. The decomposition of C₅H₅BCl₂ under these conditions appeared to be more rapid than in CH₂Cl₂ or neat in the absence of Al₂Cl₆.

Discussion

The reported preparative method of the reaction of a Lewis base adduct of a halodialkylborane with cyclopentadienide ion and subsequent treatment with a Lewis acid¹ was unsuccessful when boron trichloride was used in place of the halodialkylborane. However, low yields of dichlorocyclopentadienylborane are obtainable from the reaction of sodium cyclopentadienide directly with boron trichloride, the latter reactant also serving as solvent. This reaction is not without complications and these are commented upon.

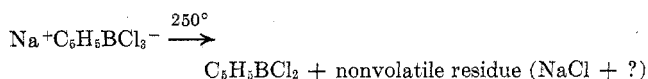
The reaction between NaC₅H₅ and BCl₃ may be reasonably expected to produce C₅H₅BCl₂ and NaCl. However, when the reactants are carefully mixed, the only product isolated is a brown boron trichloride insoluble solid that shows no evidence of C₅H₅BCl₂.



The presence of this insoluble solid in the boron trichloride solution, coupled with the absence of a volatile product even near ambient temperature suggests that the initial substance may be Na⁺C₅H₅BCl₃⁻. This adduct appears quite stable at temperatures to 100°, but begins to decompose when heated at 150 to 250°.

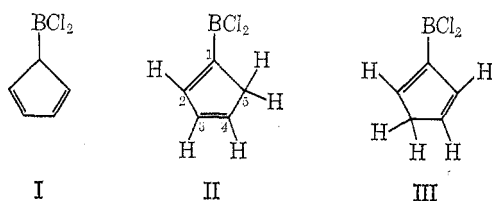
(1) H. Grundke and P. I. Paetzold, *Chem. Ber.*, **104**, 1136 (1971).

In this temperature range $C_5H_5BCl_2$ is produced suggesting that the following reaction occurs.



As described in the Experimental Section, dichlorocyclopentadienylborane is a compound of limited stability, and when treated with Al_2Cl_6 its rate of decomposition is noticeably enhanced. Since it has been reported that there is a parallel relationship between the rate of dimerization of diethylcyclopentadienylborane in the presence of Al_2Cl_6 and the rate of its dimerization in the absence of Al_2Cl_6 ,¹ it is possible that a similar phenomenon is operative in the dichloro compound. In this case, however, a pathway for decomposition may be available through formation of a dimer of low stability. No evidence was found to indicate the removal by Al_2Cl_6 of Cl^- from $C_5H_5BCl_2$ to form the cation $C_5H_5BCl^+$ which is potentially a *B*-chloro derivative of $C_5BH_6^+$ and isoelectronic with the boron hydride B_6H_{10} and the nido carborane series $C_nB_{6-n}H_{10-n}$.²

The singlet observed in the ^{11}B nmr spectrum at -47 ppm places the boron of $C_5H_5BCl_2$ in the general region of trigonal dichlorinated alkylboranes.³ Such a molecule is therefore consistent with a cyclopentadienyl group σ bonded to boron. The remaining structural question centers about the location of the double bonds in the ring. The following possibilities may be considered.

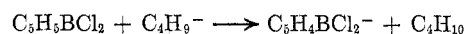


Since the proton nmr spectrum reveals three hydrogens of an apparent olefinic nature at τ 2.36, 3.14, and 3.36, and what appears to be two methylene hydrogens at τ 6.86, structure I can be eliminated. Distinguishing between II and III presents a problem since each could conceivably have three nonequivalent olefinic hydrogens which correspond to the three resonances in the vinyl region of the spectrum. To determine the correct structure solely on the basis of proton types in the pmr, therefore, becomes speculative at this time. However, if one postulates a not insignificant amount of electron delocalization from the cyclopentadienyl ring into the p_z orbital on the boron, perhaps the more highly conjugated structure II is energetically favored, should both isomers be kinetically accessible to a comparable extent during the reaction.

On the assumption that the compound has the double bonds placed as in structure II, the pmr spectrum may be assigned by a combination of resonance and inductive

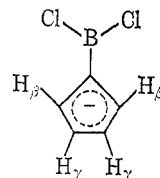
effects. This, and also by drawing analogies to pmr spectra of alkyl and alkenyl derivatives of trigonal boranes,^{1,4,5} the vinyl resonances at τ 2.36, 3.14, and 3.36 are assigned to H-2, H-3, and H-4, respectively.

Grundke and Paetzold¹ attempted the reaction of diethylcyclopentadienylborane with various strong bases in an examination of its Brønsted acidity. Breaking of the B-C (cyclopentadienyl) bond was reported to be the essential feature of the reactions and no deprotonation was observed. However, in the case of dichlorocyclopentadienylborane strong evidence is obtained for the presence of $C_5H_4BCl_2^-$ as a butyllithium reaction product. Thus, butane is recovered, having been produced by the apparent removal of a methylene proton by $C_4H_9^-$ according to the reaction



This behavior, which differs from that of the ethyl derivative, may be rationalized on the basis of the greater electronegativity of the chlorine atoms as compared to the ethyl groups. This would presumably lead to an increase in the positive character of the cyclopentadienyl ring, therefore allowing a proton to be more easily removed.

The two olefinic multiplets of similar intensity in $C_5H_4BCl_2^-$ appear at higher fields than the signals attributed to the olefin hydrogens of $C_5H_5BCl_2$, which is a factor consistent with the negative charge on the ion and the predictable increase in shielding of the ring protons. Since the C_5H_4 ring in $C_5H_4BCl_2^-$ probably has some aromatic character, the proton environment would tend to be more uniform than in the neutral species. However, inductive action by the boron attached chlorine atoms may affect the β protons more than the γ protons, lowering the field of the former relative to the latter. Based on this premise the nmr signal at τ 2.82 may be assigned to the β hydrogens and the peak at τ 3.29 attributed to the γ hydrogens.



Deprotonation of dichlorocyclopentadienylborane does not appear to significantly affect the chemical shift of the boron atom. However, the increase in stability of the anion over the neutral molecule may reflect the reluctance of two negatively charged ions to approach each other and initiate decomposition through a dimerization mechanism.

Registry No.—Sodium cyclopentadienide, 4984-82-1; dichlorocyclopentadienylborane, 39839-30-0; butyllithium, 109-72-8; $AlCl_3$, 7446-70-0; $C_5H_4BCl_2^-$, 39839-31-1; BCl_3 , 10294-34-5.

Acknowledgment.—This project was supported, in part, by the Office of Naval Research.

(2) R. N. Grimes, "Carboranes," Academic Press, New York, N. Y., 1970.

(3) G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969.

(4) C. D. Good and D. M. Ritter, *J. Amer. Chem. Soc.*, **84**, 1162 (1962).

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