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REACTIONS OF Me_3P, Me_3N AND R_2NH WITH THE SMALL *closo*-CARBORANES $C_2B_xH_{x+2}$ ($x = 3, 4, 5$)

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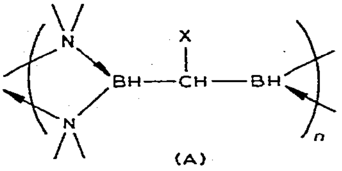
Summary

The reactivity of the small carboranes with Me_3L ($L = P$ or N) follows the order $1,5\text{-}C_2B_3H_5 > 1,6\text{-}C_2B_4H_6 > 2,4\text{-}C_2B_5H_7$. The smallest cage forms unstable adducts whereas $1,6\text{-}C_2B_4H_6$ gives the dipolar $Me_3\overset{+}{L}\text{—}C_2B_4H_6^-$. The largest cage does not react with Me_3L, but Me_2NH readily cleaves $C_2B_5H_7$ to give $Me_2NH \cdot BH_3$, a nonvolatile polymer which probably has the basic structure A, Me_2NBHMe,



(A)

$(X = H \text{ and/or } Me_2NBH-)$

and other volatile products that can formally be accounted for in terms of a disproportionation of the latter compound.

Introduction

Until recently [1] it was generally believed that all of the smaller *closo*-carboranes $C_2B_3H_5$, $C_2B_4H_6$ and $C_2B_5H_7$ were stable toward a number of rather common Lewis-base type reagents, including trimethylamine [2]. It is known, of course, that most polyboron hydrides and many monoboron compounds (without bulky attachments) react with a variety of moderate-to-strong nucleophiles to give adducts *. It was with this in mind that the present study was undertaken to determine the reactivity of the small *closo*-carboranes with sim-

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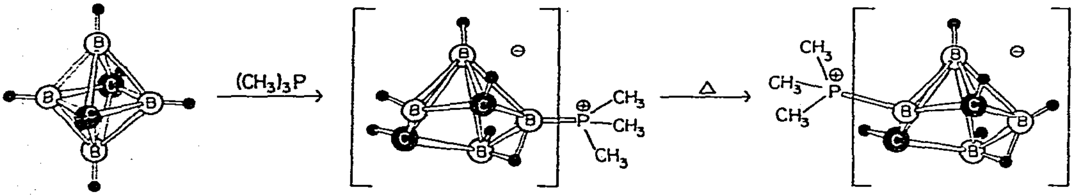
* For sample reviews see [3].

ple organic amines and phosphines, and to identify the major products obtained from such reactions.

Results and discussion

The reactivity of the small carboranes with either Me_3P or Me_3N follows the order $1,5\text{-}C_2B_3H_5 > 1,6\text{-}C_2B_4H_6 > 2,4\text{-}C_2B_5H_7$ with the smallest cage system reacting below ambient temperatures and the largest of the three demonstrating stability toward the reagents up to the decomposition temperatures of the nucleophile. Trimethylphosphine reacts very slowly with $1,6\text{-}C_2B_4H_6$ at ambient temperatures to form a dipolar adduct having a *nido* arrangement of cage carbon and boron atoms, Scheme 1. This product is an analogue of that formed from a slightly more facile reaction between trimethylamine and the same octahedral carborane [1]. The 5-trimethylphosphine adduct can be rearranged to the isomeric $3\text{-}Me_3\overset{+}{P}\text{-}2,4\text{-}C_2B_4H_6^-$ but the rearrangement is accompanied by extensive decomposition. Unlike $5\text{-}Me_3N^+\text{-}2,4\text{-}C_2B_4H_6^-$, the trimethylphosphine derivative does not react with NaH to form the parent $2,4\text{-}C_2B_4H_7^-$ ion.

SCHEME 1. REACTION OF $1,6\text{-}C_2B_4H_6$ WITH Me_3P



While $2,4\text{-}C_2B_5H_7$ is quite stable toward Me_3N, it reacts readily with the secondary amine Me_2NH. It does not form a stable 1 : 1 zwitterionic adduct, $Me_2NH^+\text{—}C_2B_5H_7^-$, analogous to that product found [1] from the reaction between $1,6\text{-}C_2B_4H_6$ and Me_3N. Instead, the reaction proceeds in an approximate 5 : 1 $Me_2NH/2,4\text{-}C_2B_5H_7$ ratio to give an assortment of cleavage products. This same ratio is observed even when the reaction is carried out with excess carborane and at reduced temperatures. The volatile products are given in Scheme 2, and in all, over 40% of the boron content is accountable in terms of these simple nitrogen—boron compounds. Furthermore, nearly 90% of one of the carborane carbon atoms is manifested as a boron-attached methyl group in four

SCHEME 2

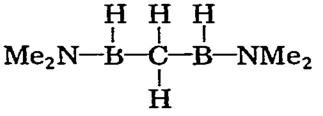
$$2,4\text{-}C_2B_5H_7 \xrightarrow{5\,Me_2NH} (Me_2NBHMe)_n + (Me_2NBH_2)_2 + Me_2\overline{NBHMe(NMe_2)B}H_2 +$$

1.00 mmol	$n = 2$ 0.362 $n = 1$ 0.065	0.094	trace

$$Me_2NH \cdot BH_3 + Me_2NBMe_2 + (Me_2N)_2BH + (Me_2N)_2BMe$$

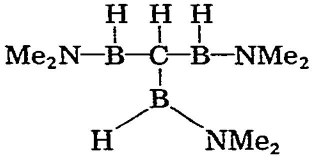
0.090	0.028	0.21	0.027

of the seven products in Scheme 2. Only a trace of hydrogen gas is liberated suggesting that nearly all of the N—H bonds that disappear in the reaction are utilized in cleaving C—B and/or B—B, but not B—H, bonds. A clear nonvolatile residue accounts for about 50% by weight of the products and this slightly viscous residue exhibits a broad ^{11}B NMR pattern which sharpens somewhat upon the addition of ether solvents. Broad resonances are exhibited in both the low field monomer and middle field dimer regions of $>$B—NMe$_2$ as well as weak peaks in the —N : BH$_3$ adduct high field region. The proton NMR exhibits an intense but broad NMe$_2$ resonance and several weak peaks in the BCH region of τ 9.5—11. Attempts to obtain a pure compound from this polymeric residue were unsuccessful; however, diborane reacts to a minor extent with the residue to give H$_2$BNMe$_2$(dimer) suggesting that exchangeable $>$B—NMe$_2$ groups are present. The above evidence suggests that a nonvolatile oligomer based on monomeric units of I and/or II joined together by means of four (or six) membered ($>$B—N$<$)$_n$ rings, e.g. III, with an occasional terminating $-\overset{|}{\underset{|}{\mathrm{N}}}\rightarrow \mathrm{BH_3}$ group, make up the bulk of the residue. A material balance suggests a C/B/NMe$_2$/H ratio * somewhere between 1 : 2 : 2 : 4 and 1 : 3 : 3 : 4 for the monomeric residue which satisfies the two ratio extremes of I and II, and it is readily imagined that both may be present **.

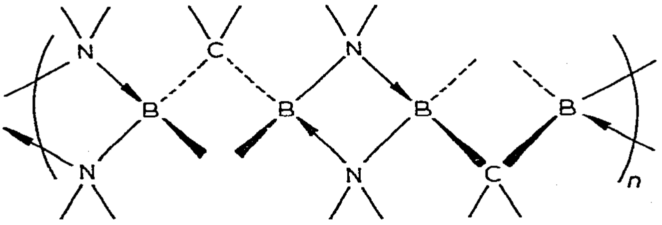


$\mathrm{Me_2N{-}\overset{H}{B}{-}\underset{H}{\overset{H}{C}}{-}\overset{H}{B}{-}NMe_2}$

(I)



(II)



(III)

One hypothetical mode of cage cleavage is suggested below which takes into account the production of the two most prevalent volatile amineborane products and one of the proposed polyborane polymer precursors. It was hoped that a study using Me$_2$ND might lend further insight into the reaction mechanism; and although the reaction of C$_2$B$_5$H$_7$ with this deuteroamine leads to extensive C—D

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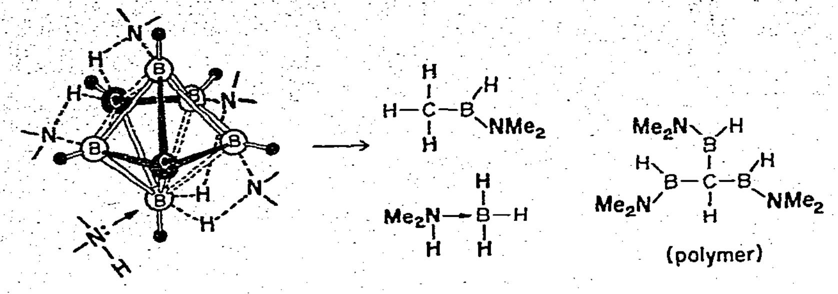
* Values for C and H are those other than contributing to the NMe$_2$ groups.

** Allowance for B—H and B—NMe$_2$ exchange must be made which could lead to some BH$_2$ and B(NMe)$_2$ groups but polymers of these can be visualized through single bridging B$\leftarrow$N(Me)$_2$—B groups.

SCHEME 3. A SUGGESTED OVERALL MODE OF CLEAVAGE OF $2,4\text{-}C_2B_5H_7$ WITH Me_2NH



formation in the MeB$<$ products, B—D appears to be distributed indiscriminantly in all boron—hydrogen sites. This may be a combination of fast B—H, B—D exchange after the initial cleavage reaction, and tautomeric hydrogen migrations during the cage opening of the carborane by the secondary amine.

In the secondary amine series Me_2NH, Et_2NH, i-Pr_2NH, PhNHMe, it is observed that each reacts with $2,4\text{-}C_2B_5H_7$ in ca. a 5 : 1 ratio to give $>$B—N$<$ cleavage products in each case. The bulkier amines react less readily and, as expected, produce less dimeric and more monomeric $>$B—N$<$ compounds. Similar observations and products are observed for the reaction of $C_2B_4H_6$ with secondary amines.

The smallest *closo*-carborane, $C_2B_3H_5$, forms strong adducts with both $(CH_3)_3N$ [4] and $(CH_3)_3P$. The product adducts are moisture sensitive and further, do not appear homogeneous; attempts at thermally induced vacuum sublimation give only small amounts of $(CH_3)_3L : BH_3$ (L = N, P), obviously a result of extensive cage degradation, and also intractable polymeric residues.

Experimental

Physical measurements. Both the ^1H ($\tau(TMS) = 10.00$) and ^{11}B ($\delta(BF_3 \cdot Et_2O) = 0$) nuclear magnetic resonance spectra were obtained from a Varian HA-100 spectrometer operating at 100 MHz and 32.1 MHz, respectively. Heteronuclear decoupling was carried out in a manner described earlier [1,5]. Mass spectroscopic data were recorded using a Varian Massspektrometer CH5 equipped with a Data-machine 6201 printout. Infrared spectra were obtained from a Beckman Acculab-3 instrument.

Materials. The carboranes, $1,5\text{-}C_2B_3H_5$, $1,6\text{-}C_2B_4H_6$, and $2,4\text{-}C_2B_5H_7$ were obtained from Williams and Ditter, Chemical Systems, Santa Anna, California. The $1,5\text{-}C_2B_3H_5$ was purified by a single pass through a —80°C trap, and $1,6\text{-}C_2B_4H_6$ was purified both by GLC and by cold column fractionation. Pentaborane impurities in $2,4\text{-}C_2B_5H_7$ were removed by treatment with tetramethylethylenediamine and subsequently passing the carborane through a —45°C trap. The amines were dried over sodium hydroxide and distilled prior to use. Tetrahydrofuran was dried over sodium and redistilled. Trimethylphosphine was obtained from H. Goldwhite, this department. All materials were handled in conventional high-vacuum equipment, or in a dry-box under an atmosphere of dry nitrogen.

Preparation of 5-Me_3P^+-2,4-$C_2B_4H_6^-$

A sealed tube containing 3.70 mmol 1,6-$C_2B_4H_6$ and 4.15 mmol Me_3P was allowed to stand at room temperature for 2 months after which ca. 1 mmol of white crystalline 5-Me_3P^+-2,4-$C_2B_4H_6^-$ was formed. Heating the reactants at 35°C does facilitate the reaction somewhat but a reaction carried out at 80°C gave, over a 12 day period, a viscous black-brown sludge above which appeared a small amount of some clear colorless needles which proved to be $Me_3P \cdot BH_3$ by ^{11}B NMR spectroscopy [6]. The black-brown sludge showed some unidentifiable signals in the ^{11}B NMR but no evidence for $Me_3P^+—C_2B_4H_6^-$.

The boron-decoupled proton NMR of 5-Me_3P^+-2,4-$C_2B_4H_6^-$ exhibits resonances at τ 13.91 ($H\mu$), 11.19 (H_1), 8.38 (Me), 5.53 (H_3); and buried under the solvent (monoglyme) peaks τ 6.45—6.85 are assumed to be both the H_6 and H—C resonances. The resonance at τ 8.38 in the undecoupled spectrum is a doublet (J 13 Hz) which collapses to a sharp singlet upon ^{31}P decoupling and is therefore assigned to P—CH_3 spin coupling. The proton-decoupled ^{31}P NMR exhibits a 1 : 1 : 1 : 1 quartet, $J(^{31}P—^{11}B)$ 158 Hz, 16.7 ppm upfield from H_3PO_4. The ^{11}B NMR data are given in Table 1. The apparent ambiguity of the assignment of ^{11}B signals at $\delta - 20.7$ and $\delta - 4.4$ was resolved by selective decoupling of ^{11}B resonances while observing the proton spectrum. The decoupling frequency required to spin-decouple the $\delta - 4.4$ ^{11}B resonance also decoupled the bridge hydrogen to give a sharp singlet whereas the ^{11}B frequency at $\delta - 20.7$ did not appreciably sharpen the bridge hydrogen signal but decoupled H_3 only.

Isomerization of 5-Me_3P^+-2,4-$C_2B_4H_6^-$ to the 3-Me_3P^+-isomer

A saturated monoglyme solution of 5-Me_3P^+-2,4-$C_2B_4H_6^-$ was heated for 8 days at 80°C after which the ^{11}B NMR exhibited weak signals assigned to 3-Me_3P^+-2,3-$C_2B_4H_6^-$ (Table 1) as well as a doublet of quartets at $\delta + 37.8$ (J(B—H) 96 Hz; J(B—P) 64 Hz) attributed to $Me_3P \cdot BH_3$ [6]. The mole ratio of these three compounds is 7 : 2 : 1, respectively, from area measurements which change to 3 : 2 : 2 after 15 days of heating at 80°C, and then to 1 : 1 : 2 after 23 days. The color of the solution slowly became dirty brown and after 29 days at 80°C only signals due to $Me_3P \cdot BH_3$ and the 3-Me_3P^+-isomer were

TABLE 1

^{11}B NMR DATA

Compound	δ(ppm, BF_3/Et_2O = 0)	J (Hz)	Relative area
3-Me_3P^+-2,4-$C_2B_4H_6^-$			
B(1)	+56.2	157 (B—H; 1 : 1 d) [a]	1
B(3)	—10.3	126 (B—P; 1 : 1 d)	1
B(5,6)	—2.9	158 (B—H; 1 : 1 d)	2
5-Me_3P^+-2,4-$C_2B_4H_6^-$			
B(1)	+53.2	157 (B—H; 1 : 1 d)	1
B(3)	—20.7	126 (B—H; 1 : 1 d)	1
B(5)	+7.3	166 (B—P; 1 : 1 d) 58 (B—Hμ; 1 : 1 d)	1
B(6)	—4.4	141 (B—H; 1 : 1 d)	1

[a] d, doublet.

observable in the ^{11}B NMR, the latter almost undetectable due to decomposition. A black-brown sludge was deposited, by this time, from the solution. Although chloroform was successful in the rearrangement [1] of the 5-Me_3N^+-derivative of 2,4-$C_2B_4H_7^-$, a reaction of undetermined nature occurs between this solvent and the 5-Me_3P^+-derivative causing extensive decomposition.

Reaction of 5-$(CH_3)_3P^+$-2,4-$C_2B_4H_6^-$ with NaH

5-$(CH_3)_3P^+$-2,4-$C_2B_4H_6^-$ (1.10 mmol), NaH (1.17 mmol) and monoglyme (5 ml) were sealed off in a 50 ml round bottom flask fitted with a magnetic stirrer, a break-seal, and an NMR tube. The ^{11}B NMR spectrum of the reaction mixture was recorded periodically over a 7 day interval and showed that, apart from the production of a compound (borates from ether cleavage?) with a resonance at δ —18, the 5-$(CH_3)_3P^+$-2,4-$C_2B_4H_6^-$ was essentially unchanged.

One-step preparation of 3-Me_3N^+-2,4-$C_2B_4H_6^-$ from 1,6-$C_2B_4H_6$

A 1 : 1 mmol ratio of 1,6-$C_2B_4H_6$ and Me_3N in monoglyme solution was heated for 16 h at 80°C after which the ^{11}B NMR exhibited the pattern previously assigned [1] to 3-Me_3N^+-2,4-$C_2B_4H_6^-$. Shorter times of reaction produced less of the 3-Me_3N^+-isomer and more of the 5-Me_3N^+-isomer.

Dimethylamine and 2,4-$C_2B_5H_7$

A mixture of dimethylamine (5.0 mmol) and 2,4-$C_2B_5H_7$ (1.0 mmol) was slowly warmed to room temperature from —190°C. After a period of 5 days at ambient temperature the products were fractionated through 0°C and —190°C traps. Only 0.01 mmol of non-condensable gas was formed, and a non-volatile clear, colorless, viscous residue (approximately 50% by weight of original mixture) remained in the reaction flask. The 0°C trap contained 0.90 mmol $Me_2NH \cdot BH_3$, identified by both ^{11}B NMR {δ + 14.45, 1 : 3 : 3 : 1 quartet, $J(^{11}B—H)$ 94 Hz [7]} and mass spectroscopic comparison (*m/e* 59, 7.5% of base peak at *m/e* 58, $Me_2NHBH_3^+$; *m/e* 58, 100%, $Me_2NBH_3^+$) with an authentic sample prepared from Me_2NH and diborane. A cold column fractionation of the contents in the —190°C trap gave both the monomer (0.065 mmol) and dimer [8—10] (0.362 mmol) of Me_2NBHMe, in addition to $(Me_2NBH_2)_2$ * [9,11—14] (0.094 mmol), $(Me_2N)_2BH$ * [11,15—17] (0.207 mmol), $(Me_2N)_2BMe$ [10,16,18] (0.027 mmol), and Me_2NBMe_2 * [15,18] (0.028 mmol). There were small quantities of a few other materials which were not positively identified but one was thought to be $Me_2NBHMe(NMe_2)BH_2$ [10] from an overlapping ^{11}B NMR triplet and doublet pattern each with J ca. 100 Hz in the region of δ — 4 to —7 and a mass spectrum with an envelope of peaks *m/e* 121—128.

Confirmatory identification using mass spectroscopy was made for Me_2NBHMe [monomer, dimer both present; *m/e* 142 (very weak) $(Me_2NBHMe)_2^+$; *m/e* 71 (40.3% of base peak) Me_2NBHMe^+, *m/e* 70 (100%, base peak) Me_2NBMe^+], and for $(Me_2N)_2BH$ [*m/e* 100 (14.7% of base peak) $(Me_2N)_2BH^+$; *m/e* 44 (100%, base peak), Me_2N^+]. Both compounds have a number of additional peaks at lower masses.

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* Infrared spectrum of an authentic sample was provided by J. Spielman for comparison.

TABLE 2

SECONDARY AMINES AND 2,4-$C_2B_5H_7$

Amine	Reaction conditions	Area ratio of product ^{11}B NMR resonances		
		δ −44 to −37	δ −9 to −4	δ + 10 to +15
Me_2NH	Reaction very fast and complete within 2 min at room temperature	1.0	2.7	1.8
Et_2NH	Reaction moderately rapid at room temperature	3.4	2.3	1.0
i-Pr_2NH	Requires 100°C for completion	2.0 (1.0, at δ — 31)		
PhNHMe	Requires 100°C for partial reaction	3.0 (2.0 at δ — 28.4)		

Reaction of secondary amines with 2,4-$C_2B_4H_7$ in tetrahydrofuran solvent

A 5 : 1 mole ratio of amine/$C_2B_5H_7$ in an approximately equal amount of tetrahydrofuran was sealed in an NMR tube. The disappearance of both amine and carborane and the appearance of boron-containing products were monitored both in the proton and ^{11}B NMR. Most of the boron resonances that developed subsequent to the onset of reaction appeared in one or more of three distinct regions, regardless of the amine used (Table 2). From the type of products found in the workup of the $Me_2NH/C_2B_5H_7$ reaction, and from chemical shift values compiled for numerous boron compounds in a review of the literature [19] it can be readily concluded that these regions are assignable to R_2NBHR' (or R_2NBR_2') monomer, R_2NBHR' (or R_2NBH_2 or $R_2NBR'_2$) dimer, and R_2NHBH (or $R_2NH \cdot BH_2R'$) respectively. In the case where *N*-methylaniline was used a substantial amount of a doublet resonance at δ — 28.4 appeared and is attributed to $(PhMeN)_2BH$ [19].

When a smaller amine/carborane ratio is used, e.g., 3 : 1 or 1 : 1, the disappearance of reactants indicate that the amine still reacts with the carborane in a ratio of ca. 5 : 1.

Reaction of Me_3P with 1,5-$C_2B_3H_5$

Trimethylphosphine (0.425 mmol) and 1,5-$C_2B_3H_5$ (0.425 mmol) reacted in a sealed glass tube below 0°C to give a white solid with no measurable dissociation pressure at room temperature after a small amount of unreacted $C_2B_3H_5$ (0.07 mmol) had been pumped off. The solid was soluble in tetrahydrofuran and gave a colorless solution which slowly became yellow at room temperature. The solution gave a very broad ^{11}B NMR signal (220—380 K) centered at $\delta + 18$ with a half-width ca. 40 ppm, a complex PMR pattern at around τ 9.0 and at least four ^{31}P resonance peaks all broad and featureless in the range 6—36 ppm relative to external H_3PO_4. Heating the solid to 150°C gave a small quantity of Me_3P and a less volatile crystalline solid identified as Me_3PBH_3, ^{11}B NMR, $\delta + 35$. relative to BF_3/Et_2O, $J(B—H) \simeq 96$ Hz, $J(B—P) \simeq 60$ Hz; ^1H NMR, $\delta(CH_3)$ 8.70, $J(H—C—P)$ 10.5 Hz.

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