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B-Methyl Derivatives of the *closo*-Carborane 2,4-C₂B₅H₇

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B-Methyl derivatives of 2,4-C₂B₅H₇ have been prepared by the aluminum chloride catalyzed reaction of methyl chloride with the parent *closo*-carborane. Positional preference for substitution follows the order 5,6 > 1,7 > 3 which is in agreement with an electrophilic substitution mechanism. Boron-11 and proton nuclear magnetic resonance data are reported and an antipodal chemical shift effect is noted for the 1,7 position.

Introduction

Alkylation of a few cage boron compounds using Friedel-Crafts type catalysts¹⁻³ has usually occurred most readily at those cage boron atoms having greatest electron availability.⁴ A polyalkylation study of a *closo*-carborane has not yet been carried out; therefore, it was of some interest to see how the presence of cage-carbon atoms in a polyhedral boron compound such as 2,4-C₂B₅H₇ (see Figure 1) would affect the sequence of methylation under electrophilic substitution conditions.

Results and Discussion

Synthesis. Several polymethyl derivatives of C₂B₅H₇ have previously been prepared by the coprolysis of boron trimethyl and the *nido*-carborane, 4,5-C₂B₄H₈, at 300 °C.⁵ Various B-methylated derivatives also have been observed in trace amounts in the synthesis of *closo*-carboranes by reaction of pentaborane(9) with acetylene in a flow system at 500 °C⁶ and in the electric discharge reactions of diborane-acetylene mixtures.⁷

For the present study five B-methyl derivatives of 2,4-C₂B₅H₇ were synthesized by Friedel-Crafts reaction of 2,4-C₂B₅H₇ with methyl chloride in the presence of aluminum chloride at 50 °C. The aluminum chloride is required in large concentrations, not catalytic amounts. Methane is a major by-product, suggesting that some of the (unrecovered) products are chlorinated C₂B₅H₇. For small-scale separations the various methyl derivatives of 2,4-C₂B₅H₇ were isolated by gas chromatography with an Apiezon N stationary phase supported on Chromosorb P. For larger scale syntheses, the components were separated by fractional distillation on a Todd column at atmospheric pressure. In the monomethyl derivative the methyl group is located on the 5-boron (chemically equivalent to the mirror-image 6 position) of the carborane cage. The second methyl group attaches to the 6 position in the dimethyl derivative. Positional assignments in the trimethyl and tetramethyl derivatives indicate that methylation next takes place at the two apical (1,7) positions. Finally, the 3 position is methylated giving an overall preference of methylation: 5,6 > 1,7 > 3 > 2,4.

Friedel-Crafts reactions usually involve attack of a carbonium ion at a site of high electron availability in which an unstable positively charged complex is formed as an intermediate. This complex increases the coordination number of the skeletal atom undergoing substitution, and after subsequent loss of H⁺ to form the alkyl derivative, the substituted atom reverts back to the original coordination number. The "belt" atoms (positions 2-6) of the pentagonal bipyramid of C₂B₅H₇ would not increase to as high a coordination number upon formation of the complex as would the two apical atoms (positions 1 and 7) and would thus be favored if coordination numbers were the only important factor involved.

In terms of total electron density at each of the carborane skeletal atoms, it is clear that the 2,4 positions (location of

the two carbon atoms) should have a higher electron density than any of the boron atoms; however, this slightly higher negative electron density will be more than offset by the additional positive nuclear charge of the carbon atoms. Thus, the electron availability for further bonding does not coincide with the greatest electron density. The carbon atoms are not attacked either in the methyl chloride-aluminum chloride reaction described herein or in reactions of this carborane with the "electrophilic" trimethylborane.⁵ This is consistent with the assignment of electropositive character to the carbon atoms and is supported by the prior observation that only the carbon-attached hydrogens act in a protonic fashion in the reaction of this carborane with butyllithium to form butane and the Li₂C₂B₅H₅.⁸ Accepting electropositive character for the carbon leads to the conclusion that boron atoms with the greater number of nearest neighbor carbons will be more electropositive than borons with fewer adjacent carbon atoms. If Friedel-Crafts methylation depended only on the electron availability of the boron atoms, it would be predicted that substitution would follow the order 5,6 > 1,3,7. Moreover, because the carbon-apical boron bonds are longer, and therefore weaker, than the carbon-belt boron bonds,⁹ the apical borons (B(1) and B(7)) should be less susceptible to the electron-withdrawing nature of the two neighboring electropositive carbons than would be the belt boron B(3). This is entirely consistent with the experimental result that the Friedel-Crafts methylation prefers 5,6 > 1,7 > 3 boron positions and apparently shows that in this case the greater electron availability of the apex borons (B(1) and B(7)) is of greater importance than is the more desirable coordination number of B(3).

Nuclear Magnetic Resonance. ¹¹B. As expected,¹⁰⁻¹⁴ the boron contiguous to the methyl group shifts 5-10 ppm downfield from the chemical shift position of the compound with hydrogen attached [Table I]. Also, an antipodal effect¹⁴⁻¹⁶ is observed for the B(1,7) positions whereby methyl substitution at the B(1) vertex atom shifts the B(7) chemical shift upfield 5.1 ppm and B(1) shifts about the same amount, 5.5 ppm, upon B(7) methyl substitution. By taking an average contiguous effect of -8 ppm and an antipodal shift of +5.3 ppm it is possible to predict the approximate positions of every boron in the methyl derivatives of C₂B₅H₇. More exactly, however, it would be appropriate to assign substituent effects for all possible interactions.^{14,16} For the three boron types this can be expressed by

$$\delta_{B(1)} = +21.2 + \sigma_{11} + \sigma_{13} + \sigma_{15} + \sigma_{16} + \sigma_{17} \quad (1)$$

$$\delta_{B(3)} = -7.2 + \sigma_{31} + \sigma_{33} + \sigma_{35} + \sigma_{36} + \sigma_{37} \quad (2)$$

$$\delta_{B(5)} = -4.0 + \sigma_{51} + \sigma_{53} + \sigma_{55} + \sigma_{56} + \sigma_{57} \quad (3)$$

where σ_{11} is the effect on B(1) of methyl substitution on the same boron; σ_{13} is the effect of B(3) methyl substitution on B(1); σ_{15} is the effect of B(5) methyl substitution on B(1); σ_{17} is the effect of B(7) methyl substitution on the B(1) chemical shift; σ_{31} is the effect of B(1) methyl substitution

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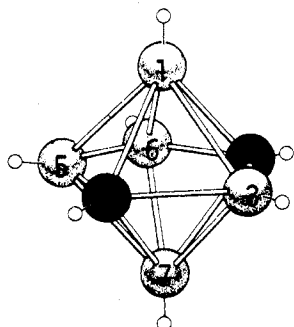
Table I. NMR Data for $C_2B_5H_7$ Derivatives

Nucleus ^a	$C_2B_5H_7$	5-Me $C_2B_5H_6$ ^b	5,6-Me $_2C_2B_5H_5$	1,5,6-Me $_3C_2B_5H_4$	1,5,6,7-Me $_4C_2B_5H_3$	1,3,5,6,7-Me $_5C_2B_5H_2$
B(1)	+21.2 (180)	+20.6 (175) [+20.6]	+20.1 (175) [+20.0]	+10.5 [+10.6]	+16.0 [+15.9]	+15.1 [+15.0]
B(7)	+21.2 (180)	+20.6 (177) [+20.6]	+20.1 (175) [+20.0]	+25.2 (175) [+25.3]	+16.0 [+15.9]	+15.1 [+15.0]
B(3)	-7.2 (182)	-6.8 (180) [-6.4]	-5.5 (177) [-5.6]	-6.9 (~173) [-6.7]	-7.7 (~180) [-7.8]	-14.4 [-14.5]
B(5)	-4.0 (167)	-11.3 [-11.2]	-9.7 [-9.8]	-9.6 [-9.8]	-9.8 [-9.8]	-9.7 [-9.7]
B(6)	-4.0 (167)	-2.7 (169) [-2.6]	-9.7 [-9.8]	-9.6 [-9.8]	-9.8 [-9.8]	-9.7 [-9.7]
H(1)	9.89 (180)	9.83 (179)	9.76 (176)	10.46 (CH ₃)	10.51 (CH ₃)	10.50 (CH ₃)
H(7)	9.89 (180)	9.83 (179)	9.76 (176)	9.91 (175)	10.51 (CH ₃)	10.50 (CH ₃)
H(2)	4.47	4.69	4.96	4.96	4.94	5.38
H(4)	4.47	4.89	4.96	4.96	4.94	5.38
H(3)	5.05 (183)	5.19 (184)	5.30 (181)	5.29 (180)	5.27 (178)	9.19 (CH ₃)
H(5)	5.87 (170)	9.28 (CH ₃)	9.38 (CH ₃)	9.42 (CH ₃)	9.44 (CH ₃)	9.48 (CH ₃)
H(6)	5.87 (170)	6.12 (169)	9.38 (CH ₃)	9.42 (CH ₃)	9.44 (CH ₃)	9.48 (CH ₃)

^a ¹¹B, $\delta_{BF_3 \cdot Et_2O}$; ¹H, τ_{TMS} 10.00; all BH borons observed as 1:1 doublets; all BH hydrogens observed as 1:1:1:1 quartets. ¹¹B NMR chemical shifts taken with external standard; ¹H NMR chemical shifts taken with internal standard; numbers in brackets are calculated from eq 1-3; numbers in parentheses are spin-coupling values. ^b The NMR data for this compound are in reasonable agreement with those reported in ref 7.

Table II. Methyl Substituent Contributions to the ¹¹B Chemical Shifts

Position of methyl substitution	σ					
	1	3	5	6	7	
1	-9.4	-1.1	0.0	0.0	+5.3	
3	-0.9	-6.7	+0.1	+0.1	-0.9	
5	-0.6	+0.8	-7.2	+1.4	-0.6	
6	-0.6	+0.8	+1.4	-7.2	-0.6	
7	+5.3	-1.1	0.0	0.0	-9.4	

Figure 1. Structure of the *closo*-carborane 2,4- $C_2B_5H_7$.

on B(3); etc. In Table II values for each of the contributions are given which are determined by averaging as many comparison chemical shifts as possible. The calculated δ values from eq 1-3 are given in parentheses in Table I and it can be seen that the predictive value is as good as previously observed in another cage system.^{14,16}

¹H. Significant effects observed in the ¹H NMR spectra are as follows: (a) an antipodal upfield shift of 0.15 ppm for H(7) is observed upon B(1) methyl substitution (compare 1,5,6-(CH₃)₃C₂B₅H₄ with 5,6-(CH₃)₂C₂B₅H₅); (b) apex Me-B chemical shift values are 1.0-1.3 ppm to higher field than equatorial Me-B shifts, which is in reasonable agreement with predicted chemical shift differences based on ring-current considerations¹⁷ in the C₂B₅H₇ cage; (c) upfield shifts are ca. 0.3-0.4 ppm for HC upon each neighboring B(3), B(5), or B(6) methyl substitution; (d) upfield shifts of HB or HC are ca. 0.1-0.2 ppm upon methyl substitution in a position 1,3 to that of the observed hydrogen along the equatorial belt; e.g., methyl substitution at the B(5) position causes an upfield shift of both H(3) and H(2); (e) coupling of ca. 7 Hz between H-B(3) and H-C is observed in all compounds except the

Table III. Results of Fractional Distillation of the Reaction Products of 2,4- $C_2B_5H_7$ with Methyl Chloride in the Presence of Aluminum Chloride

Component ^a	Bp, °C	Amt recovered, mol (g)	Yield, ^b %
CH ₃ C ₂ B ₅ H ₆	75-77	0.091 (9)	12.9
(CH ₃) ₂ C ₂ B ₅ H ₅	96-99	0.274 (31)	38.8
(CH ₃) ₃ C ₂ B ₅ H ₄	113-117	0.063 (8)	8.9
(CH ₃) ₄ C ₂ B ₅ H ₃	132-136	0.028 (4)	4.0
Total			64.6

^a Mass spectra of the methyl derivatives of C₂B₅H₇ are reported in the Ph.D. thesis of A. J. Gotcher, University of California, Irvine, Calif., 1975; University Microfilm 75-11,028, Ann Arbor, Mich. ^b Based on initial 2,4-C₂B₅H₇.

B-pentamethyl derivative. This is consistent with prior observations on the parent C₂B₅H₇.¹⁸

Experimental Section

Synthetic Procedure. Initial synthesis of the *B*-methyl derivatives was carried out in a small glass bulb which was charged with about 1 g of aluminum chloride and 10 ml of liquid C₂B₅H₇ at room temperature. Addition of the carborane to the aluminum chloride caused immediate change of color from colorless to yellow. With a Freon-12-cooled condenser to minimize escape of carborane from this reaction bulb, methyl chloride gas was bubbled through the solution for 2 h. A gradual color change from yellow to red-orange occurred. Only trace amounts of the monomethyl, dimethyl, and trimethyl derivatives of C₂B₅H₇ were detectable (by mass spectrometry). To permit heating of the reactants and operation at high pressures, subsequent reactions were run in stainless steel pressure vessels rated at 2000 psig.

In a typical reaction two 1600-ml stainless steel vessels were each charged with 30 g (0.35 mol) of 2,4-C₂B₅H₇, 43 g (0.85 mol) of methyl chloride, and 80 g (0.60 mol) of aluminum chloride. The vessels were then heated for 4 days at 50 °C, after which time only trace quantities of unreacted C₂B₅H₇ could be detected in the reaction products. The contents of the two vessels were then combined and fractionally distilled.

Fractional distillation yielded first a highly volatile *pyrophoric* compound or compounds which continued to evolve until the vapor temperature reached 70-75 °C. This fraction also contained small amounts of both the unreacted C₂B₅H₇ (bp 60 °C) and the monomethyl derivative (bp 75-77 °C). The identity of the *pyrophoric* material could not be determined from mass spectral analysis (major peaks at *m/e* 83, 109, 110, and 111). Other fractions obtained in this distillation are listed in Table III.

The pentamethyl derivative, in amounts sufficient for NMR analysis, was isolated from the products remaining in the distillation

pot by gas chromatographic fractionation. A trace quantity of a possible hexamethyl derivative, identified by GC/MS, also was observed.¹⁹

Nuclear Magnetic Resonance. Both ¹¹B (32.1 MHz) and ¹H (100.0 MHz) were recorded using a Varian HA-100 spectrometer operating at ambient conditions (Table I). Heteronuclear decoupled spectra were obtained with the auxiliary use of a Nuclear Magnetic Resonance Specialties Model HD-60 decoupler, modified for compatibility with the HA-100. The radiation frequency was controlled by a Hewlett-Packard 200CD wide-range oscillator. Another 200CD oscillator drives a pseudorandom binary noise generator the output of which phase-shifts the radiation frequency. Amplification of this signal by an Electronic Navigation Industries 3201 radiofrequency power amplifier is then applied to the HA-100 probe which has been double-tuned for decoupling.

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Registry No. C₂B₅H₇, 20693-69-0; 5-MeC₂B₅H₆, 23810-32-4; 5,6-Me₂C₂B₅H₅, 58548-76-8; 1,5,6-Me₃C₂B₅H₄, 58548-77-9; 1,5,6,7-Me₄C₂B₅H₃, 58540-73-1; 1,3,5,6,7-Me₅C₂B₅H₂, 18972-11-7.

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- (19) That the MS cutoff for this hexamethyl derivative increased by the mass of a CH₂ group over that of the pentamethyl derivative does not necessarily prove that an additional methyl group is attached to one of the carbons since alternatively it could simply result from an ethyl group attached to one of the boron atoms of the cage rather than a methyl group. Such alkyl growth reactions have been noted before: R. E. Williams, unpublished information. When Me₂BCl and lithium react, peralkyldiboranes are produced: (CH₃)₂BCl + Li → (CH₃)_{4-x}(C₂H₅)_xB₂H₂ + others. A possible mechanism could involve free radicals and methyl abstraction: [(CH₃)₂B] → CH₃BHCH₂; CH₃BHCH₂ + (CH₃)₂BCl → [CH₃BHCH₂CH₃]₂ + CH₃ClB. Similarly behaving species might be generated from mixtures involving CH₃Cl, C₂B₅H₇, and AlCl₃.

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Complexes of Titanium Tetrachloride with Terdentate Tripod Ligands. Competition among Oxygen, Sulfur, and Nitrogen for Coordination Sites on Titanium

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The precipitates obtained on mixing hexane solutions of equimolar quantities of titanium tetrachloride and the potentially terdentate tripod ligands CH₃C(X)(Y)(Z) (X = Y = Z = CH₂OMe; X = Y = CH₂OMe, Z = CH₂SMe and CH₂NMe₂; X = CH₂OMe, Y = CH₂SMe, Z = CH₂NMe₂) consist of mixtures of products which may include the corresponding 1:1 complex, products in which oxygen-methyl cleavage has occurred to give a titanium alkoxide, and a 3:2 complex. When the same components are mixed in chloroform, solutions of the 1:1 complexes are obtained. Reactions leading to the other products take place very much more slowly in this case. A variable-temperature NMR study of the chloroform solutions shows that all four ligands act only as bidentates toward titanium and that exchange can take place between free and coordinated ligand atoms. Nitrogen is found to bond more strongly to titanium than oxygen or sulfur, oxygen coordination being preferred to sulfur coordination when nitrogen is already bound, whereas sulfur coordination is preferred to oxygen coordination when oxygen already occupies a site on titanium.

Introduction

Although the complex chemistry of titanium tetrachloride has been the subject of extensive studies,^{1,2} there are few reports of investigations of the relative complexing abilities of ligands being of similar types but containing different donor atoms. In an early review³ of the complexing abilities of metals, Ti(IV) was considered to have class a character; i.e., the order of relative coordinating ability of donor atoms toward the metal is F >> Cl > Br > I, O >> S > Se > Te, and N >> P > As > Sb > Bi. This conclusion was apparently supported by the subsequent observation⁴ that whereas urea in the complex TiCl₄·2(urea) is oxygen bonded, thiourea in TiCl₄·2(thiourea) is nitrogen bonded. However, the prepa-

ration of stable complexes of TiCl₄ with phosphorus-, arsenic-, and sulfur-donor ligands made it appear likely that Ti(IV) has acceptor properties of borderline class a-class b character. Indeed, the ligand in TiCl₄·2(thioxane) is bonded to titanium via the sulfur atom rather than the oxygen.^{5,6} More recently,⁷ thermochemical measurements have shown that tetrahydrothiophene bonds to TiCl₄ less strongly than tetrahydrofuran but somewhat more strongly than tetrahydrofuran.

Reaction of TiCl₄ with the terdentate tripod ligands CH₃C(X)(Y)(Z) [X = Y = Z = CH₂OMe (1); X = Y = CH₂OMe, Z = CH₂SMe (2); X = Y = CH₂OMe, Z = CH₂NMe₂ (3); X = CH₂OMe, Y = CH₂SMe, Z = CH₂NMe₂ (4)] in a 1:1 mole ratio was expected to give the