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Alkylating Agents Stronger than Alkyl Triflates

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Abstract: A new class of potent electrophilic "R⁺" alkylating agents has been developed using weakly nucleophilic carborane anions as leaving groups. These reagents, R(CHB₁₁Me₅X₆) (R = Me, Et, and *i*-Pr; X = Cl, Br), are prepared via metathesis reactions with conventional alkylating agents such as alkyl triflates, using the high oxophilicity of silylium ion-like species, Et₃Si(carborane), as the driving force to obtain increased alkyl electrophilicity. The crystal structure of the isopropyl reagent, *i*-Pr(CHB₁₁Me₅Br₆), has been determined, revealing covalence in the alkyl-carborane bonding. This contrasts with the free *i*-Pr⁺ carbocation observed when the anion is less coordinating (e.g. Sb₂F₁₁⁻) or with tertiary alkyl centers, as in [*tert*-butyl][carborane] salts. In solution, the reagents exist as equilibrating isomers with the alkyl group at the 7–11 or 12 halide positions of the CB₁₁ icosahedral carborane anion. These alkylating agents are so electrophilic that they (a) react with alkanes at or below room temperature via hydride extraction to produce carbenium ions, (b) alkylate benzene without a Friedel–Crafts catalyst to give arenium ions, and (c) alkylate electron-deficient phosphorus compounds that are otherwise inert to conventional alkylating agents such as methyl triflate.

Introduction

Friedel–Crafts alkylation of arenes with alkyl halides is a classic example of electrophilic alkylation where the potency of the alkylating agent is enhanced by promoting the leaving group properties of the anion. Electrophilic R^{δ+} character in RX is enhanced by complexation of the halide X to a Lewis acid such as Al₂Cl₆, allowing it to leave as a less nucleophilic anion such as Al₂Cl₇⁻. Intrinsically less nucleophilic anions such as sulfate and triflate (CF₃SO₃⁻) give dimethyl sulfate and methyl triflate their efficacy as popular Lewis-acid-free alkylating agents. The most potent alkylating agents generated to date have weakly nucleophilic SbF₆⁻ or Sb₂F₁₁⁻ counterions,¹ but reagents based on these anions typically do not have the requisite thermal stability to be used as practical reagents.² In addition, the antimony pentafluoride latent in these anions or in situ from the media used to generate them can be a destructive and corrosive oxidant. Fluoroantimonate anions can also be the source of an unwanted F⁻ nucleophile.

Carborane anions (Figure 1) are among the most inert, least coordinating,³ least basic,^{4–6} and therefore among the least nucleophilic anions presently known.

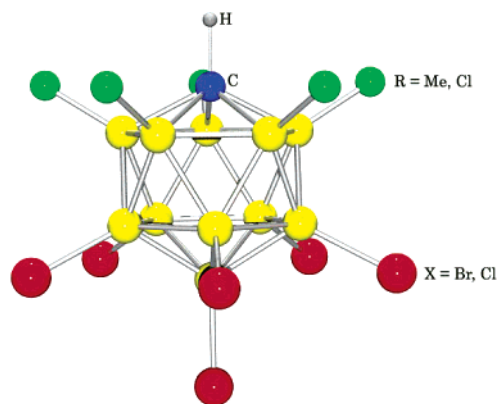


Figure 1. CHB₁₁R₅X₆⁻ carborane anions used in this work.

Unlike fluoroantimonates, they are non-oxidizing and are not a source of halide ions. In a preliminary communication,⁷ we reported that the pentamethylated hexabromocarborane anion, CHB₁₁Me₅Br₆⁻, allowed the isolation of a very strong "methyl⁺" alkylating reagent, CH₃(carborane). Its potency was indicated by the observation that methylation of benzene to give the toluenium ion occurred with stoichiometric amounts of the reagent under conditions where neat methyl triflate was unreactive. In the present paper, we expand on this work to include the corresponding ethyl and isopropyl reagents, improve the synthetic method, provide detailed structural characterization of the reagents, and further illustrate their enhanced reactivity

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toward weakly nucleophilic substrates such as alkanes and electron-deficient phosphorus.

Experimental Section

General. Air-sensitive solids were handled in a Vacuum Atmospheres Co. glovebox (O_2 , H_2O < 0.5 ppm). All reactions were done in Schlenk tubes with Teflon stopcocks. Solvents were dried over Na/K or P_2O_5 and distilled prior to use. NMR spectra were recorded on a Varian Inova 500 for 1H , ^{13}C , ^{31}P , and ^{11}B and on a Varian Inova 300 for ^{19}F . IR spectra were run as KBr disks on a Shimadzu-8300 FT spectrometer and were identical to those run as solids between thin films of Teflon, showing that KBr was unreactive on the time scale of the measurements.

Cesium salts of $CHB_{11}Me_5Br_6^-$, $CHB_{11}Me_5Cl_6^-$, and $CHB_{11}Cl_{11}^-$ were prepared by literature methods^{6,7} and recrystallized two or three times from acetone/toluene/hexanes to high purity (colorless). Silver and trityl salts were prepared by standard methods.²³ Triethylsilylcarboranes were prepared in ca. 85% isolated yield by a slight modification of published methods^{8,18} as follows. Toluene (ca. 5 mL) was added to cover crystalline trityl salt $[Ph_3C][carborane]$ (2 g), and triethylsilane (1–2 mL) was added. The mixture was stirred until the solids dissolved and the solution became a pale orange-yellow (ca. 2 h). The solution was filtered via syringe and concentrated to a smaller volume, and the product precipitated by the addition of dry hexanes with stirring overnight. The white or pale pink solid was washed with several aliquots of hexanes.

Preparation of $CH_3(CHB_{11}Me_5Br_6)$ (2a). Hexanes was added to $Et_3Si(CHB_{11}Me_5Br_6)$ (0.2 g) to just cover the solid, followed by methyl triflate (31 μ L, 1.1 equiv). The suspension was immediately cooled to 0 °C and sonicated for 2 h, maintaining the lowered temperature. The volatiles were then removed under vacuum to give an off-white solid in quantitative yield. 1H NMR (SO_2 , δ , 500 MHz, -60 °C): (**2a-I**) 0.55 (s, 15H, BCH_3), 2.98 (s, 1H, BCH), 4.43 (s, 3H, CH_3); (**2a-II**) 0.55 (s, 9H, BCH_3), 0.74 (s, 6H, BCH_3), 2.92 (s, 1H, BCH), 4.45 (s, 3H, CH_3). ^{13}C NMR (CD_2Cl_2 , δ , 125 MHz, -80 °C): (**2a-I**) -0.3 (br, BCH_3), 33.3 (q, $^1J_{CH} = 162.6$ Hz, CH_3), 57.4 (BCH); (**2a-II**) -0.3 (br, BCH_3), 34.3 (q, $^1J_{CH} = 162.8$ Hz, CH_3), 57.4 (BCH). [See Figure 3 at natural abundance and Figure 4 for 99% ^{13}C -enriched sample.] IR (KBr): 3078 (ν_{as}), 3063 (ν_s), 1400 (δ_{as}), 1292 (δ_s) cm^{-1} . [See Figure S1 for 1H and Figure S2 ^{11}B NMR spectra of the hydrolysis reaction.]

$CH_3(CHB_{11}Me_5Cl_6)$ (2b). This was prepared as a pale yellow powder in a manner similar to used for **2a** using trimethylsilyl in place of the triethylsilyl reagent. 1H NMR (SO_2 , δ , 500 MHz, -60 °C): (**2b-I**) 0.52 (s, 15H, BCH_3), 2.37 (s, 1H, BCH), 4.75 (s, 3H, CH_3); (**2b-II**)

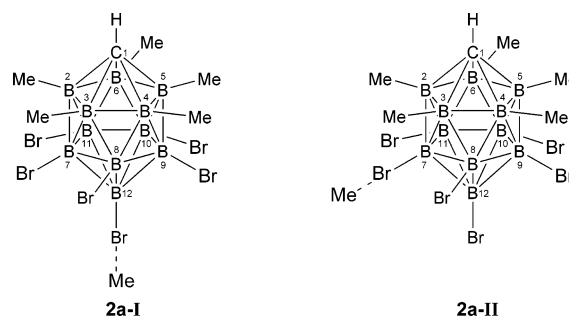


Figure 2. 12- and 7-isomers of $Me(CB_{11}Me_5Br_6)$, **2a-I** and **2a-II**.

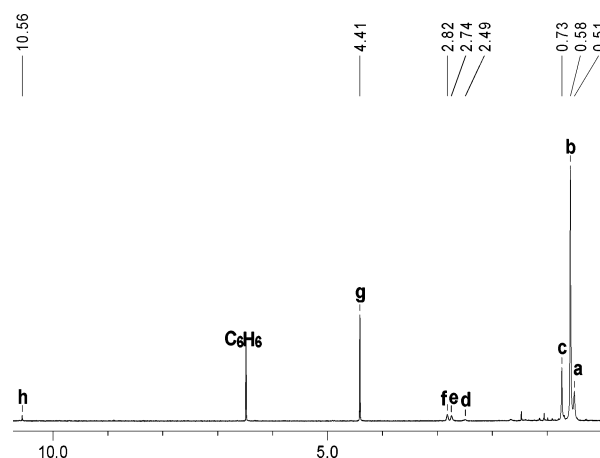


Figure 3. 1H NMR of $Me(CHB_{11}Me_5Br_6)$ (**2a**) in liquid SO_2 at room temperature.

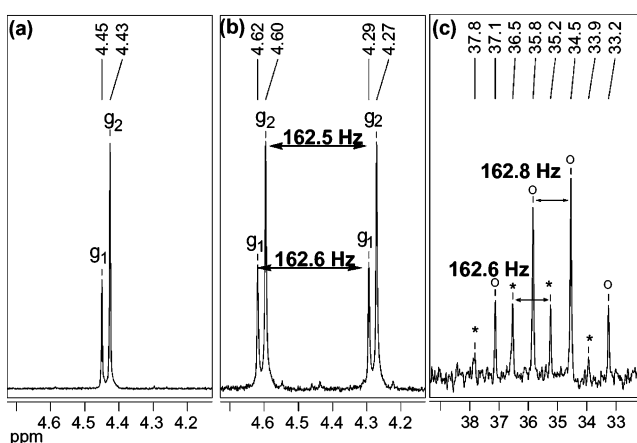


Figure 4. NMR spectra at -60 °C with $>95\%$ ^{13}C labeling of the active methyl group of $Me(CHB_{11}Me_5Br_6)$ (**2a**). (a) 1H NMR of unenriched **2a**, (b) 1H NMR of $^{13}C_3(CHB_{11}Me_5Br_6)$, and (c) ^{13}C NMR of $^{13}C_3(CHB_{11}Me_5Br_6)$. *, **2a-I** (12-isomer); \circ , **2a-II** (7-isomer).

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0.51 (s, 9H, BCH_3), 0.68 (s, 6H, BCH_3), 2.28 (s, 1H, BCH), 4.78 (s, 3H, CH_3). ^{13}C NMR (SO_2 , δ , 125 MHz, -80 °C): (**2b-I**) -3.9 (br, BCH_3), 46.8 (q, $^1J_{CH} = 162.6$ Hz, CH_3), 48.7 (BCH); (**2b-II**) -3.9 (br, BCH_3), 46.6 (q, $^1J_{CH} = 162.8$ Hz, CH_3), 48.9 (BCH).

$C_2H_5(CHB_{11}Me_5Br_6)$ (3a). This was prepared in the same manner as **2a** using ethyl triflate in place of methyl triflate. 1H NMR (SO_2 , δ , 500 MHz, 25 °C, Figure S3): (**3a-I**) 0.58 (s, 15H, BCH_3), 2.36 (t, $^3J_{HH} = 7.22$ Hz, CH_3), 2.82 (s, BCH), 5.66 (q, $^3J_{HH} = 7.22$ Hz, CH_2); (**3a-II**) 0.58 (s, 9H, BCH_3), 0.71 (s, 6H, BCH_3), 2.40 (t, $^3J_{HH} = 7.22$ Hz, CH_3), 2.74 (s, BCH), 5.66 (q, $^3J_{HH} = 7.22$ Hz, CH_2). [See Figures S4 and S5 for low-temperature spectra.] ^{13}C NMR (CD_2Cl_2 , δ , 125 MHz, -80 °C, Figure S6): (**3a-I**) -0.3 (BCH), 18.0 (q, $^1J_{CH} = 131.3$ Hz, CH_3), 57.3 (s, BCH), 62.8 (t, $^1J_{CH} = 166.6$ Hz, CH_2); (**3a-II**) -0.3

(BCH₃), 18.2 (q, ¹J_{CH} = 132.4 Hz, CH₃), 57.3 (s, BCH), 63.0 (t, ¹J_{CH} = 164.7 Hz, CH₂).

Preparation of C₃H₇(CHB₁₁Me₅Br₆) (4a). Compound **2a** (50 mg) was dissolved in cold (−30 °C) dichloromethane (1.0 mL), and a few drops of 2-chloropropane were added. The mixture was stored at −30 °C for 2 days, and colorless crystals formed. The solution part was removed using a syringe, and the crystalline part was washed with cold dichloromethane and dried under a vacuum. ¹H NMR (CD₂Cl₂/SO₂, δ, 500 MHz, −60 °C, Figure S7): −0.01 (s, BCH₃, 15H), 1.99 (d, ³J_{HH} = 5.75 Hz, CH₃, 6H), 2.24 (s, BCH, 1H), 6.85 (br, CH, 1H). ¹³C NMR (CD₂Cl₂, δ, 125 MHz, −80 °C, Figure S8): −2.25 (BCH₃), 28.49 (CH₃), 55.47 (BCH), 103.70 (CH).

Reaction of 2a with *i*-PrCl. *i*-PrCl (11 μL) was added to a cold solution of **2a** (50 mg) in SO₂ at −70 °C. The solution was analyzed by 500 MHz ¹H NMR at −60 °C: 0.40 (s, 15H, BCH₃), 2.31 (d, ³J_{HH} = 5.67 Hz, 6H, CH₃), 3.54 (s, 1H, BCH), 6.27 (br, 1H, CH).

Preparation of Ar^F–P=P–Ar^F (Ar^F = 2,4,6-Tris(trifluoromethyl)phenyl) (7). The diphosphene **7** was previously prepared either by reaction of Ar^F–PCl₂ with Ar^F–PH₂ and DBU as base²⁴ or by dehalogenation of Ar^F–PCl₂ with a bis(imidazolide).²⁵ We found that **7** can be conveniently prepared in an acceptable yield by simply reacting Ar^F–PCl₂ with lithium metal as a commercially available reducing agent. Ar^F–PCl₂ **7** (985 mg, 2.6 mmol) was sonicated with finely divided lithium metal (36 mg, 5.2 mmol) in tetrahydrofuran (20 mL) at room temperature until the metal was completely consumed (about 4–5 h). The solvent was removed in a vacuum, and the dark-colored residue was recrystallized from hot toluene, yielding pale yellow fine needles (487 mg, 60%). The analytical data were identical with those published.^{24,25}

Reaction of 2a with Ar^F–P=P–Ar^F (Ar^F = 2,4,6-Tris(trifluoromethyl)phenyl). SO₂ was condensed into a NMR tube in which **2a** and diphosphene were loaded at −80 °C. After warming of the solution to room temperature, the product **8** was analyzed by NMR without purification. ¹H NMR (SO₂, δ, 500 MHz, 25 °C): 0.48 (s, 15H, BCH₃), 2.48 (s, 1H, BCH), 3.36 (dd, 3H, ³J_{PH} = 4.4 Hz, ²J_{PH} = 23.7 Hz, PCH₃), 8.95 (s, 2H, Ar^F), 9.02 (s, 2H, Ar^F). ³¹P NMR (SO₂, δ, 202 MHz, 25 °C): 260.0 (m, ¹J_{PP} = 610 Hz, =PMeAr^F), 279.2 (m, ¹J_{PP} = 610 Hz, Ar^FP=). ¹⁹F NMR (SO₂, δ, 282 MHz, 25 °C): 29.1 (s, 3F, *p*-CF₃), 29.4 (s, 3F, *p*-CF₃), 35.0 (m, ⁴J_{PF} = ⁵J_{PF} = 37.5, 6F, *m*-CF₃), 37.5 (m, 6F, *m*-CF₃).

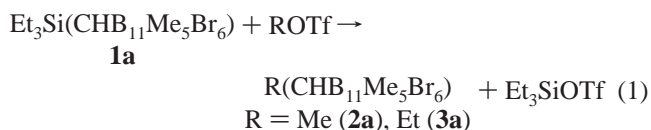
Crystal Structure Determination of 4a. A colorless fragment of a prism (0.42 × 0.35 × 0.31 mm³) was used for the single-crystal X-ray diffraction study of C₃H₇(CHB₁₁Me₅Br₆) (sample cr471s; *i*-PrCB). The crystal was coated with Paratone oil and mounted on a glass fiber. X-ray intensity data were collected at 223(2) K on a Bruker SMART 1000 platform-CCD X-ray diffractometer system (Mo radiation, λ = 0.71073 Å, 50 kV/30 mA power). The CCD detector was placed at a distance of 3.9540 cm from the crystal. The Bruker SHELXTL (Version 6.10) software package was used for phase determination and structure refinement. The distribution of intensities (*E*² − 1 = 0.940) and systematically absent reflections indicated one possible space group: *P*2(1)/*n*. This was later determined to be correct. Direct methods of phase determination followed by two Fourier cycles of refinement led to an electron density map from which most of the non-hydrogen atoms were identified in the asymmetry unit of the unit cell. With subsequent isotropic refinement, all of the non-hydrogen atoms were identified. There was one C₃H₇ moiety and one carborane anion present in the asymmetry unit of the unit cell. C₉H₂₃B₁₁Br₆, *M* = 729.64, monoclinic, *P*2(1)/*c*, *a* = 9.2876(9), *b* = 19.4342(19), and *c* = 13.2672(14) Å, α = 90°, β = 100.707(2)°, γ = 90°, *V* = 2353.0(4) Å³, *T* = 223(2) K, *Z* = 4, μ(Mo Kα) = 10.232 mm^{−1}, 27 167 reflections collected (7182 independent) [*R*(int) = 0.0360], *R*1 [*I* > 2σ(*I*)] = 0.0323, *wR*2 (all data) = 0.0775.

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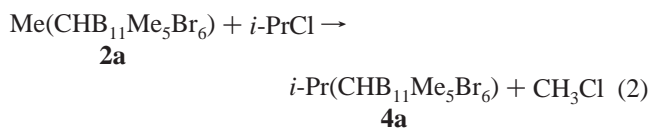
Synthesis

The methyl and ethyl reagents with the hexabromocarborane anion, CHB₁₁Me₅Br₆[−] (**2a** and **3a**), were prepared in high yield by metathesis of triethylsilylium carborane **1a** with methyl or ethyl triflate (eq 1). The success of this reaction is dependent



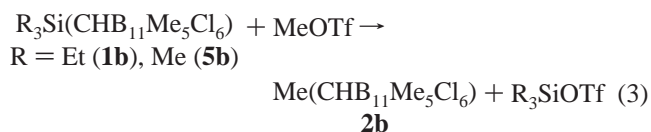
on precipitating the product rapidly and having a volatile byproduct. The reaction was therefore carried out in hexanes suspension at 0 °C with sonication to promote completion of the solid-to-solid reaction. A more crystalline product could be obtained by carrying out the reaction in liquid SO₂ at −50 °C, but the yield was lower and the procedure more difficult. Higher temperatures in either procedure gave impurities which appear to arise from subsequent reactions of the desired R(CHB₁₁Me₅Br₆) products with hexanes.

In an attempt to prepare the corresponding isopropyl reagent **4a**, isopropyl chloride was substituted for alkyl triflate in eq 1. However, NMR analysis of the resulting product revealed that a mixture of hexyl carbocations was produced (Figures S9 and S10, Supporting Information). Evidently the desired product **4a** was formed but, probably because of increased solubility in the solvent, reactivity with hexanes ensued. A successful method of producing **4a** was to treat the methylcarborane reagent with isopropyl chloride in dichloromethane at −30 °C (eq 2).



Chloro-substituted carborane anions are less coordinating than bromo-substituted analogues toward the silylium ion.⁸ The conjugate acids of carborane anions, H(CB₁₁H₆X₆), are stronger for X = Cl than for X = Br.^{5,6} Thus, we expected that alkyl reagents based on chloro-substituted carboranes would be more electrophilic than those based on bromo-substituted analogues. This is reflected in the greater difficulty of preparing R(CHB₁₁Me₅X₆) reagents for X = Cl.

The metathesis reaction of eq 1 gives an impure red-colored product when the hexachlorocarborane is used in place of the hexabromocarborane. However, if trimethylsilylium **5b** carborane is used instead of triethylsilylium **1b**, the desired Me-(CHB₁₁Me₅Cl₆) (**2b**) can be prepared in hexanes suspension at 0 °C (eq 3). The increased volatility of trimethylsilyl triflate

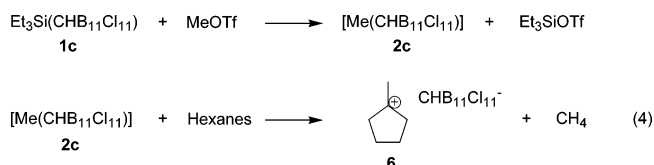


allows faster and cleaner isolation of the desired product.

The corresponding isopropyl reagent **4b** with the hexachlorocarborane is so reactive that it cannot be isolated. Nevertheless, NMR studies indicate that, in liquid SO₂ or at −90 °C in dichloromethane, reaction of **2b** with *i*-PrCl does produce the

desired *i*-Pr(CHB₁₁Me₅Cl₆) (**4b**) reagent. However, it decomposes in liquid SO₂ within 2 h at −60 °C.

The undecachloro-substituted carborane anion, CHB₁₁Cl₁₁^{−9}, is expected to be even less nucleophilic than the hexachloro pentamethyl anion, CHB₁₁Me₆Cl₆[−], because of the electronegativity of Cl relative to a CH₃ group. Thus, the Me(carborane) reagent derived from CHB₁₁Cl₁₁[−] is expected to be the most reactive methylating agent of all. This appears to be the case because the reaction of eq 1 in hexanes using Et₃Si(CHB₁₁Cl₁₁) (**1c**) produced the methylcyclopentyl carbenium ion salt **6**. Evidently, the desired Me(CHB₁₁Cl₁₁) (**2c**) reagent is produced transiently, but it reacts immediately with methylcyclopentane in the hexanes solvent mixture via hydride abstraction (eq 4) to give **6** and eliminate methane.¹⁰



Characterization

NMR. The ¹H NMR spectrum of Me(CHB₁₁Me₅Br₆) (**2a**) was initially quite puzzling. It showed three distinct sets of signals for the carborane anion but only one for the active methyl group (“Me⁺”). We have traced these observations to (a) the inevitable presence of traces of water, giving small amounts of free carborane anion in an [H₃O]⁺ or [Et₃Si(OH₂)]⁺ salt, and (b) the existence of two isomers of Me(CHB₁₁Me₅Br₆), depending upon whether methylation is at bromine in the 7- or 12-position of the carborane anion (Figure 2).

The ¹H NMR spectrum of Me(CHB₁₁Me₅Br₆), taken in liquid SO₂ at room temperature, is shown in Figure 3.

Peaks **a**, **b**, and **c** arise from the 2,3,4,5,6-pentamethyl substituents of the carborane anion, and peaks **d**, **e**, and **f** arise from C–H at the 1-position. Peaks **a** and **d**, which always accompany the signal **h**, are assigned to free carborane anion in an [H₃O]⁺ or [Et₃Si(OH₂)]⁺ salt, a probable remnant of hydrolysis of the silylium starting material. These peaks are coincident with resonances seen in other salts (e.g., trityl) and represent only a small part of the sample. They become the sole peaks in the anion spectrum after 1 h of exposure to moisture as Me(CHB₁₁Me₅Br₆) becomes completely hydrolyzed. A signal at 4.9 ppm grows in, assigned to the CH₃ group of the MeOH₂⁺ ion in the hydrolyzed product. Peak **h** at 10.5 ppm, arising from O–H in aquated ions, gradually shifts to 9.5 ppm as hydrolysis proceeds. The formation of the free carborane anion upon hydrolysis was confirmed in the ¹¹B NMR spectrum. The complex pattern ¹¹B of resonances from Me(CHB₁₁Me₅Br₆) was reduced to the simple 1:5:5 pattern of the C_{5v}-symmetric free ion.

Initially, it appeared that the complexity of the ¹¹B NMR spectrum of Me(CHB₁₁Me₅Br₆) and the presence of two ¹H peaks (**b** and **c**) from the 2–6 pentamethyl substituents could be explained by the symmetry-lowering effect of methylation at the 7-position (Figure 2, **2a-II**). Silylation of hexahalocarborane anions in R₃Si(CHB₁₁Me₅X₆) is known to occur exclusively at the 7-position rather than the 12-position.^{8,11} However, the single room-temperature ¹H peak **g** of the Me⁺ group at 4.41 ppm splits into two distinct resonances (**g**₁ and

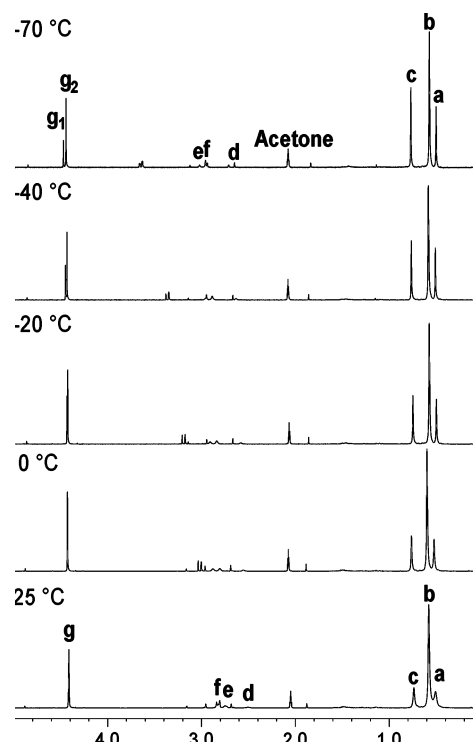


Figure 5. Variable-temperature ¹H NMR spectrum of **2a** in SO₂.

g₂) upon cooling. At −60 °C, two distinct peaks can be observed at 4.45 and 4.43 ppm in a ratio of 1:2.2 (Figure 4a). These can be assigned to 12- and 7-isomers (**2a-I** and **2a-II**), respectively (Figure 2) via a detailed analysis of behavior of the other methyl groups in the variable-temperature ¹H spectrum (see below). Proof that the two ¹H peaks in the −60 °C spectrum arise from distinct Me⁺ isomers was obtained by >95% ¹³C labeling of the active methyl group. As shown in Figure 4b, the two signals show complete ¹³C coupling with J_{CH} = 162.6 Hz. Moreover, the identical coupling is observed in the ¹³C spectrum, where signals appear as overlapping quartets at 35.8 and 35.2 ppm (Figure 4c). There is no ¹³C incorporation into the five methyl groups on the carborane anion, indicating that the bonding of the active methyl group is confined to the bromine substituents of the carborane anion. The complete ¹³C spectrum was obtained in dichloromethane at low temperatures, where Me(CHB₁₁Me₅Br₆) is more soluble than in liquid SO₂. However, decomposition occurs above −30 °C, and a ¹H resonance appearing at 3.09 ppm indicates the formation of CH₃Cl via chloride abstraction from CH₂Cl₂.

The variable-temperature behavior of the ¹H spectrum of **2a** between −70 and 25 °C (Figure 5) was used to confirm the presence of two isomers and assign their spectra. As expected, the ratio of the integrated intensities of the sum of peaks **b** and **c** (15 carborane Me) to peaks **e** and **f** (1 carborane C–H) to peaks **g** or **g**₁ and **g**₂ (3H from active methyl group) remains constant at 15:1:3. The ratio of **g**₁:**f** remains constant at 3:1 and **g**₂:**e**:**c** remains constant at 3:1:6, despite changing **g**₁:**g**₂ and **f**:**e** ratios at different temperatures. This indicates that **g**₁ and **f** belong to one isomer of Me(CHB₁₁Me₅Br₆) while **g**₂, **e**, and **c** belong to the other. The 3:1:6 integrated intensity ratio in the latter can only arise from broken C_{5v} symmetry, so **g**₁ and **f** are assigned to the 12-methylated isomer (Figure 2, **2a-I**) while **g**₂, **e**, and **c** are assigned to the 7-methylated isomer **2a-II**. Peak **b** contains accidentally overlapping resonances from the five

Table 1. Ratio of 12- and 7-Isomers of Me(CHB₁₁Me₅Br₆), **2a-I** and **2b-II**, Respectively

temp, °C	2a-I:2a-II
-60	30:70
-30	45:65
-10	57:53
10	50:50
25	55:45

equivalent methyl groups of the 12-isomer plus three methyl groups from the 7-isomer. Indeed, asymmetry in the peak shape of **b** can be seen when the ppm scale is expanded.

The integrated intensities give the abundance ratios of the 7- versus 12-isomers listed in Table 1. Evidently, isomerization is slow enough on the NMR time scale to observe separate species but fast enough on the synthetic time scale to achieve chemical equilibrium. The 7-isomer is favored by a 1:2.2 ratio at low temperature, suggesting that the 7-position bromine atom is slightly more coordinating toward carbocations than that at the 12-position. At room temperature, however, the two isomers are approximately equally abundant. The variation of the ratio with temperature is probably due to a subtle effect of entropy pertaining to symmetry and dipole moment interactions with the SO₂ solvent. In the lower dielectric solvent dichloromethane, at -80 °C, the 12-isomer is slightly favored over the 7-isomer, but a reliable variable-temperature analysis is thwarted by gradual decomposition at higher temperatures.

The ethylcarborane species, Et(CHB₁₁Me₅Br₆) (**3a**), behaves very similarly to the methyl species. Two distinct sets of resonances, assigned to the 12- and 7-ethylation site isomers (**3a-I** and **3a-II**), are observed in the ¹H and ¹³C NMR spectra at -78 °C in dichloromethane solution. On the other hand, the isopropyl species, *i*-Pr(CHB₁₁Me₅Br₆) (**4a**), does not show immediate evidence of isomers. The ¹H and ¹³C NMR spectra at -60 °C, taken in SO₂/dichloromethane mixture (because of poor solubility in pure SO₂), show only a single set of resonances. Moreover, there is only a single resonance arising from the 15 protons of the pentamethylated carborane (0.5 ppm). Either the isopropyl group is exclusively at the 12-position, preserving C_{5v} symmetry, or it is less strongly bound to the carborane anion and is rapidly fluxional between the five 7-positions and the 12-position on the NMR time scale. Since the X-ray structure shows bonding through the 7-position (see below), we favor the latter explanation. Weaker binding of an isopropyl group to the carborane can be rationalized in terms of greater ionic character in the R^{δ+}(carborane^{δ-}) bonding. Methyl and ethyl groups are primary with respect to carbocation formation, while isopropyl is secondary. Tertiary groups such as *tert*-butyl are fully ionic.¹⁰ Increasing stabilization of the cationic charge occurs via C-H bond hyperconjugation as the bonded C atom becomes more carbon substituted.

The ¹³C chemical shifts of the active C atom in the methyl, ethyl, and isopropyl R(carborane) species are all indicative of covalent rather than ionic species. The 35.8 and 35.2 ppm shifts of the methyl group in the two isomers of Me(CHB₁₁Me₅Br₆) are similar to that of the dimethylbromonium ion in [Me₂Br]-[SbF₆] (37 ppm)¹² and well shy of that expected for a free (and presently unobserved) methyl cation.¹³

The ethyl group in Et(CHB₁₁Me₅Br₆) has distinct C_α and C_β resonances at 63.6 (t, J_{CH} = 164 Hz) and 18.2 (q, ¹J_{CH} = 164 Hz), respectively, which is not consistent with the symmetrical

structure favored for the free C₂H₅⁺ cation.¹⁴ The C_α resonance at 63.6 ppm is not sufficiently deshielded for an ionic formulation, and we do not see any evidence for H exchange between C_α and C_β.¹

The isopropyl group in *i*-Pr(CHB₁₁Me₅Br₆) has a ¹³C resonance at 103 ppm (J_{CH} = 169 Hz) for the carbon atom at the 2-position. While far short of the 321 ppm value (J_{CH} = 169 Hz) in the free 2-propyl cation as a fluoroantimonate salt,¹⁵ the >100 ppm downfield shift is consistent with the idea of developing cationic character that increases Me < Et < *i*-Pr. For comparison, the ¹³C shift for the 2-position carbon atom isopropyl bromide is 45 ppm.

Concomitant with this downfield ¹³C shift, the associated ¹H resonance for the unique isopropyl H atom also occurs considerably downfield at 6.9 ppm. That for isopropyl bromide appears at 3.7 ppm, while that of the free isopropyl cation occurs at 14 ppm in SbF₅ media.¹⁵ These observations support the idea that the isopropyl group is less covalently bonded to the carborane halide substituents than methyl or ethyl groups and rationalizes the faster 7-to-12 isomerization. A closely related example of 7-to-12 isomerization has recently been reported in a zirconium metallocene complex with an undecamethylated carborane anion.²⁶

Infrared Spectroscopy. The synthesis of CH₃(CHB₁₁Me₅Br₆) and its deuterated analogue CD₃(CHB₁₁Me₅Br₆) allowed good-quality difference IR spectra to be obtained in the νC-H and δC-H region for the active methyl group, without ambiguity arising from the absorption bands of the carborane anion. Spectra were obtained anaerobically as KBr disks, and the compounds were shown to be unreactive toward KBr over the time frame of the measurement. Difference spectra were obtained by normalizing the spectral bands of the anion and subtracting the CH₃ spectrum from the CD₃ spectrum. These are shown in Figure 6 as bands with positive intensity for C-H and negative intensity for C-D.

The mirror-image shape of the major C-H bands relative to the C-D bands is especially good for the A₁ and E νC-H stretches, although imperfect subtraction of anion bands does leave shoulders on the bands. The H/D frequency ratios are in the range 1.33–1.36 for all bands, in agreement with standard reduced-mass calculations. These observations confirm the validity of the spectra. The number of bands, their frequencies, and their intensities are diagnostic of a methyl group with C_{3v} symmetry which is not significantly perturbed by the environment.¹⁶

As indicated in Table 2, the stretching frequencies are somewhat higher than those of methyl triflate and bending frequencies are somewhat lower. This means that the positive charge on the carbon atom of methyl group in CH₃(CHB₁₁Me₅Br₆) is higher than that in methyl triflate, suggesting that the C-Br bond in Me(CHB₁₁Me₅Br₆) is less covalent than the C-O bond in methyl triflate.

X-ray Crystallography. Single crystals of the isopropyl compound, *i*-Pr(CHB₁₁Me₅Br₆) (**4a**), suitable for X-ray crystallography were grown from CH₂Cl₂ at -30 °C. The structure is shown in Figure 7.

The anion is coordinated to the isopropyl group via a 7-position bromine atom. The absence of the 12-isomer, believed

(26) Ingleson, M. J.; Clarke, A.; Mahon, M. F.; Rourke, J. P.; Weller, A. S. *Chem. Commun.* **2003**, 1930–1931.

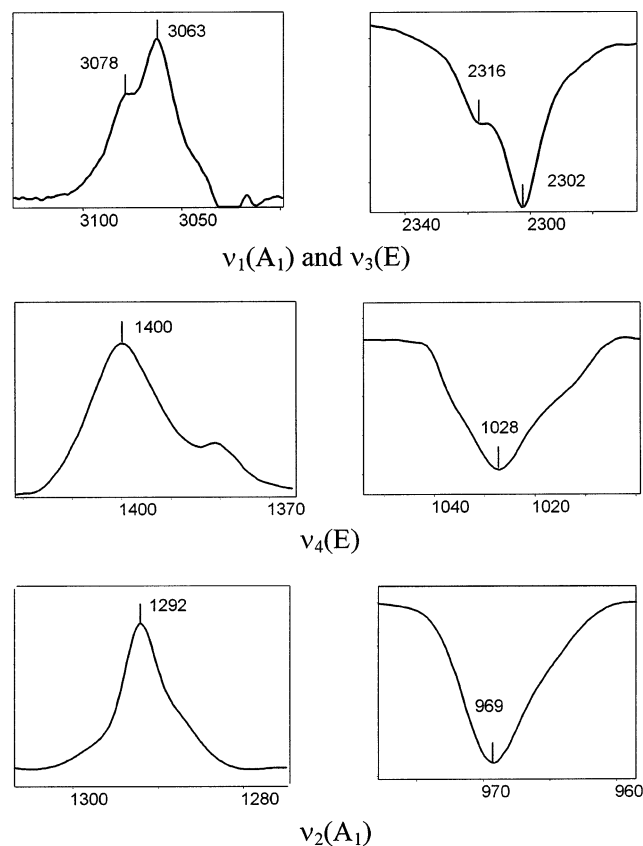
Absorbance / Wavenumber (cm⁻¹)

Figure 6. IR spectra of CH₃ (left, positive intensity) and CD₃ groups (right, negative intensity) in CH₃(CHB₁₁Me₅Br₆) and CD₃(CHB₁₁Me₅Br₆).

Table 2. Methyl Group Modes of Naturally Isotopic CH₃(CHB₁₁Me₅Br₆) and Deuterated CD₃(CHB₁₁Me₅Br₆) in Comparison with Those of Methyl Triflate (in Parentheses)¹⁷

	$\nu_3(\text{E})$	$\nu_1(\text{A}_1)$	$\nu_4(\text{E})$	$\nu_2(\text{A}_1)$
CH ₃ ⁺	3078 (3042)	3063 (2980)	1400 (1452)	1292
CD ₃ ⁺	2316 (2307)	2302 (2188)	1028 (1088)	969 (1065)
$\nu_{\text{H}}/\nu_{\text{D}}$	1.33	1.33	1.36	1.33

to be present in solution by NMR (see above), must be the result of preferential crystallization from the rapidly isomerizing mixture. The overall features of the structure are reminiscent of the many silylium carborane structures, R₃Si(carborane), that have been obtained in recent years.^{8,18} All are silylated at a 7-position halide. The B–Br–Si angles in these silylium species are flexible, averaging about ca. 115°, consistent with a predominantly electrostatic Si–Br interaction. The B–Br–C bond angle in the present structure is 111.8(1)°, consistent with somewhat more covalence and some halonium ion character. The coordinated B–Br bond is ca. 0.06 Å longer than the uncoordinated B–Br bonds, indicating minor perturbation of the anion by the carbocationic moiety.

The bond lengths and angles in the isopropyl moiety are consistent with a covalently bound group, but there are indications of developing cationic character. The C–C bond lengths are 1.480(5) and 1.494(5) Å, toward the short end of normal sp³–sp³ bonds, and similar to the sp³–sp³ bond in the fully ionic *tert*-pentyl cation (1.485(8) Å).¹⁰ The coordinated C–Br distance is 2.104(3) Å, but there are no suitable alkyl bromonium ion X-ray structures for useful comparison. The

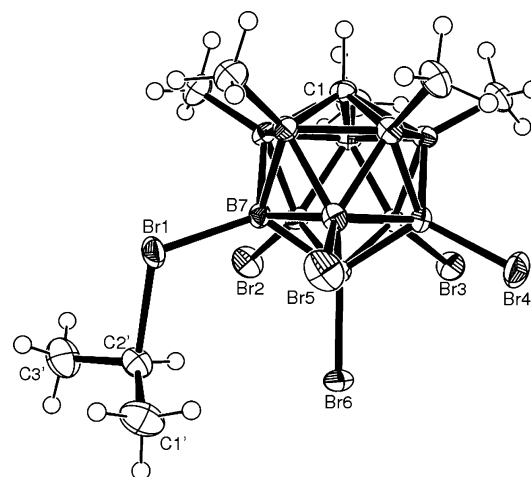


Figure 7. Molecular structure of **4a**. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles: C1'–C2' = 1.480(5), C2'–C3' = 1.494(5), C1'–C2'–C3' = 116.5(3)°, C2'–Br = 2.104(3), B7–Br1 = 2.004(3), B–Br(2–5)_{av} = 1.947(3).

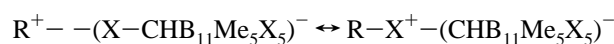
C–C–C angle is 116.5(3)°, somewhat larger than that observed in a typical isopropyl group (110 ± 3°).^{8,18} These indications of developing carbocationic character in the isopropyl group are consistent with the deduction that 7–12 isomerism is rapid on the NMR time scale.

Discussion

The major conclusion drawn from the characterization data is that R(CHB₁₁Me₅X₆) reagents for R = Me, Et, and *i*-Pr have covalent structures. Nevertheless, there are several indications of developing cationic R⁺ character that increases Me < Et < *i*-Pr. This is in keeping with increasing C–C bond hyperconjugative stabilization of carbocations: primary < secondary < tertiary. Indeed, for anions of the nucleophilicity of the present halocarboranes, the transition from covalent to ionic occurs between *i*-Pr and *t*-Bu. Thus, while *i*-Pr(carborane) is covalent, [*t*-Bu][carborane] is ionic.¹⁰ On the other hand, the covalent-to-ionic transition occurs between Et and *i*-Pr with less coordinating fluoroantimonate anions.¹⁹ With more coordinating anions such as triflate or perchlorate, all simple alkyl-based carbocationic moieties, whether primary, secondary, or tertiary, form covalent species. We note that there is a reversal of order of coordinating ability for cationic silicon relative to cationic carbon. Carboranes are *less* coordinating than fluoroantimonates toward silyl cations.¹¹

With respect to the nature of the halide substituents on the carborane anions, the order of increasing alkylating reactivity of the reagents is CHB₁₁Me₅Br₆[−] < CHB₁₁Me₅Cl₆[−] < CHB₁₁Cl₁₁[−]. This is evident from the conditions necessary for synthesis of Me(carborane) species, which cannot be isolated when the *undecachloro* anion is used. Reaction with the alkane solvent is too rapid, even at −40 °C. The same order of anion basicity is observed for silicon in R₃Si(carborane) species^{7,20} and for acidity in H(carborane).⁶

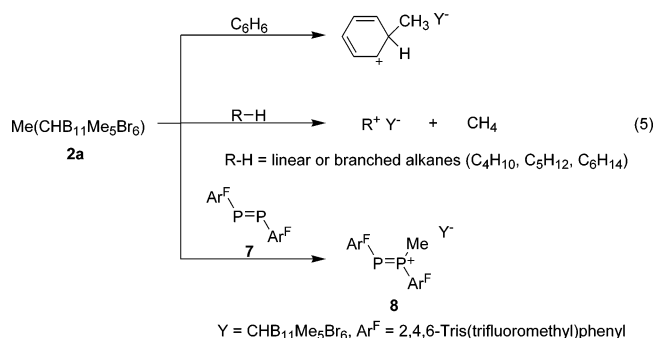
In principle, the Me, Et, and *i*-Pr reagents can be viewed as “alkyl⁺” reagents *or* as halonium ions. The appropriate resonance forms can be written



Given the reactivity described below, and the fact that the *t*-Bu analogue is fully ionic,¹⁰ the carbocationic character is clearly more dominant than the halonium ion character.

Reactivity

The high electrophilic reactivity of the present R(CHB₁₁-Me₅X₆) reagents is illustrated by three reactions (eq 5).



First, as previously communicated,⁷ benzene is methylated by Me(CHB₁₁Me₅Br₆) in stoichiometric amounts to give the toluenium ion, (CH₃)C₆H₆⁺. Under the same conditions, neat methyl triflate is unreactive. Second, all the present R(carborane) reagents react with alkanes at or below room temperature via hydride abstraction to form tertiary carbenium ions.¹⁰ This is a notably clean and efficient reaction, allowing tertiary carbocations to be isolated in high yield and crystallized for structural analysis by X-ray crystallography. Again, this reactivity is unknown for alkyl triflates. Third, phosphorus centers with

highly electron-withdrawing substituents can be so weakly nucleophilic that they are unreactive toward neat boiling methyl triflate. An example is the diphosphene Ar^FP=PAR^F, **7**, where Ar^F = 2,4,6-tris(trifluoromethyl)phenyl. While this substrate does not react with methyl triflate as solvent, Me(CHB₁₁Me₅Br₆) methylates it in stoichiometric amounts in liquid SO₂ at room temperature to give cation **8**. Alkylated phosphorus cations of this type²¹ are useful for reducing to novel diphosphanyl radicals.²²

Conclusion

The R(CHB₁₁Me₅X₆) (**2–4**) reagents reported in this work are very potent sources of Lewis-acid-free Me, Et, and *i*-Pr groups. Their electrophilicity easily eclipses that of alkyl triflates in both alkylation and hydride abstraction chemistry, and they are more practical than reagents based on fluoroantimonate anions. Although expensive, specialty applications can be expected in other areas of chemistry where weakly nucleophilic substrates fail to react with traditional electrophilic alkylating agents.

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Supporting Information Available: NMR spectra and complete X-ray structure determination data (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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