# Significance of the Trimethylsilyl Moiety in Synthetic Carborane Transformations: Conversion of *nido*-$[(CH_3)_3Si]_2C_2B_4H_6$ to *nido*-$[(CH_3)_3Si]_2C_4B_8H_{10}$ by Thermal Elimination of Trimethylsilane, an Important Advance in Carborane Chemistry

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Oxidative ligand fusion in which metallacarboranes such as $(R_2C_2B_4H_4)_2FeH_2$ and $(R_2C_2B_4H_4)_2CoH$ (R = $CH_3$, $C_2H_5$, or $C_3H_7$) undergo conversion to $R_4C_4B_8H_8$ was first reported by Grimes and co-workers.[1] Since this first report, a number of similar oxidative ligand fusions have been reported, all of which involved either a metal-complex intermediate or a metal catalyst.[2]

Recently, we have developed[3] several convenient high-yield methods for the synthesis of *nido*-2-$[(CH_3)_3Si]$-3-[R]-2,3-$C_2B_4H_6$ (R = $(CH_3)_3Si$, $CH_3$, or H). Although several *closo*-metallacarborane derivatives were synthesized,[4,5] the significance of the trimethylsilyl groups in the chemistry of these carboranes and metallacarboranes was not stressed. We report herein the direct, one-step, high-yield fusion of *nido*-2,3-$[(CH_3)_3Si]_2$-2,3-$C_2B_4H_6$ to give *nido*-$[(CH_3)_3Si]_2C_4B_8H_{10}$ without the need of a metal catalyst.

A 2.42-g (11.0 mmol) sample of 2,3-bis(trimethylsilyl)-2,3-dicarba-*nido*-hexaborane (**8**) was heated at 210 °C for 3 days in a sealed reactor tube equipped with a break-seal at one end. The break-seal was then opened in vacuo, and the volatile products were removed. Fractionation yielded 0.82 g of $(CH_3)_3SiH$ (11.08 mmol), collected at -196 °C, and 1.31 g of $[(CH_3)_3Si]_2C_4B_8H_{10}$ (4.49 mmol; 81.6% yield; bp 208 °C (10 torr of Ar)) collected at 0 °C. In addition, a very small quantity of noncondensable gas, presumably hydrogen, was also pumped out. A nonsublimable, brown polymeric material (0.19 g) remained in the reactor tube. Removal of all the exo-polyhedral *C*-trimethylsilyl groups could not be achieved even at 300 °C.

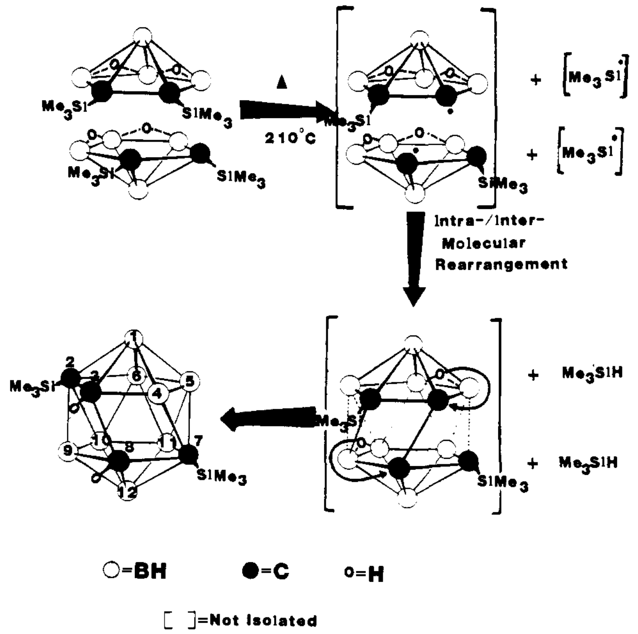
The electron-impact (EI) mass spectrum of $[(CH_3)_3Si]_2C_4B_8H_{10}$ exhibits an intense parent grouping $[(^{12}CH_3)_6{}^{28}Si_2{}^{12}C_4{}^{11}B_8H_{10}{}^+]$ with the major cutoff at *m/e* 292 and strong groups with local cutoffs at *m/e* 277, 263, 249, 219, 147, 73, and 45 that correspond to the fragments $(^{12}CH_3)_5{}^{28}Si_2{}^{12}C_4{}^{11}B_8H_{10}{}^+$, $(^{12}CH_3)_4{}^{28}Si_2{}^{12}C_4{}^{11}B_8H_{11}{}^+$, $(^{12}CH_3)_3{}^{28}Si_2{}^{12}C_4{}^{11}B_8H_{12}{}^+$, $(^{12}CH_3)_3{}^{28}Si^{12}C_4{}^{11}B_8H_{10}{}^+$, $^{12}C_4{}^{11}B_8H_{11}{}^+$, $(^{12}CH_3)_3{}^{28}Si^+$, and $^{12}CH_3{}^{28}SiH_2{}^+$, respectively. The pattern of intensities in each fragment is consistent with the natural isotopic distribution of boron and silicon.

Table I. FT NMR Data of $[(CH_3)_3Si]_2C_4B_8H_{10}$[a]

| nuclei | δ (*J*, Hz)[b] | relative area | assignment |
|---|---|---|---|
| $^1H$ | 7.02 br s | 1 | cage CH |
| | 5.66 (154) br | 1 | |
| | 5.12 (158) overlapping | 1 | $H_t$ (base, apex) |
| | 4.47 (179) quartets | 1 | |
| | 4.08 (181) | 1 | |
| | 0.19 s | 9 | $(CH_3)_3Si$ |
| $^{11}B$ | 9.98 (152) d | 1 | $B_{(4)}$–H |
| | 8.86 (156) d | 1 | $B_{(9)}$–H |
| | 6.15 (158) d | 2 | $B_{(6,11)}$–H |
| | −17.27 (178) d | 2 | $B_{(5,10)}$–H |
| | −20.85 (181) d | 2 | $B_{(1,12)}$–H |
| $^{13}C$ | 105.44 s | | cage carbon, CSiB |
| | 97.69 (195) d | | cage CH |
| | 0.05 (118) quartet | | $(CH_3)_3Si$ |
| $^{29}Si$ | 0.03 (6.1) m, 10 lines | | $(CH_3)_3Si$ |

[a] $^1H$, 200.132; $^{11}B$, 64.2; $^{13}C$, 50.32; $^{29}Si$, 39.76 MHz. [b] For all the spectra, a neat liquid sample was taken in an 8-mm tube, sealed off, and inserted in a 10-mm standard NMR tube containing $CDCl_3$ for deuterium lock. Chemical shifts (in ppm) are relative to $(CH_3)_4Si$ for the nuclei $^1H$, $^{13}C$, and $^{29}Si$ and $BF_3O(C_2H_5)_2$ for $^{11}B$, with a positive sign denoting a downfield shift.

Scheme I



The undecoupled and proton-decoupled $^{11}B$ and $^1H$ pulse Fourier-transform NMR data (Table I) confirm the presence of eight B–$H_{terminal}$ units with no bridging hydrogen atoms. The $^{11}B$ NMR spectrum of the tetracarbon carborane bears no similarity to that of the precursor, *nido*-$[(CH_3)_3Si]_2C_2B_4H_6$, which has a high-field doublet and a single low-field doublet with an integral ratio of 1:3 due to an apical B(1)–H and overlapping of basal B(4)–H, B(5)–H, and B(6)–H resonances, respectively.[3] Both the $^1H$ and $^{29}Si$ NMR spectra show only one type of trimethylsilyl group in the fused carborane. The $^{13}C$ pulse Fourier-transform NMR data (Table I) confirm the presence of one type of trimethylsilyl, one type of cage CH, and one type of cage SiCB carbon. Although the chemical shift of the trimethylsilyl carbon resonance is unchanged, the cage carbon resonances shifted significantly from those of the precursor, *nido*-$[(CH_3)_3Si]_2C_2B_4H_6$.[3]

The most significant feature in the infrared spectrum[6] is the absence of a stretching mode of vibration due to a B–H–B bridge bond.

The IR, NMR, and mass spectroscopic data for $[(CH_3)_3Si]_2C_4B_8H_{10}$ are all consistent with the structure proposed in Scheme I. The data are also analogous to those reported by Grimes et al.[7] for the $R_4C_4B_8H_8$ isomer having a distorted ico-

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(1) Maxwell, W. M.; Miller, V. R.; Grimes, R. N. *Inorg. Chem.* **1976**, *15*, 1343. Maxwell, W. M.; Miller, V. R.; Grimes, R. N. *J. Am. Chem. Soc.* **1976**, *98*, 4818. Maynard, R. B.; Grimes, R. N. *Inorg. Synth.* **1983**, *22*, 215. Maynard, R. B.; Grimes, R. N. *J. Am. Chem. Soc.* **1982**, *104*, 5983. Grimes, R. N.; Maynard, R. B.; Sinn, E.; Brewer, G.; Long, G. J. *J. Am. Chem. Soc.* **1982**, *104*, 5987. Grimes, R. N. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 55.

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(3) Hosmane, N. S.; Sirmokadam, N. N.; Buynak, J. D. *Abstr. IME-BORON-V*, **1983**, *CA22*, 39. Hosmane, N. S.; Sirmokadam, N. N.; Mollenhauer, M. N. *J. Organomet. Chem.* in press.

(4) Hosmane, N. S.; Sirmokadam, N. N. *Organometallics* **1984**, *3*, 1119.

(5) Hosmane, N. S.; Sirmokadam, N. N.; Mollenhauer, M. N. "Abstracts of Papers", 18th Organosilicon Symposium, Schenectady, NY, April 6, 1984. Hosmane, N. S.; Sirmokadam, N. N.; Herber, R. H. *Organometallics*, in press.

(6) IR ($CDCl_3$ vs. $CDCl_3$): 2959 (s), 2900 (m), 2590 (vs), 1410 (w), 1320 (w), 1252 (vs), 1170 (m br), 1020 (m br), 840 (vvs), 780 (sh), 670 (m), 620 (vw), and 380 cm$^{-1}$ (vw br).

(7) Freyberg, D. P.; Weiss, R.; Sinn, E.; Grimes, R. N. *Inorg. Chem.* **1977**, *16*, 1847.

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sahedral geometry similar to the one shown in Scheme I.

The *C*-trimethylsilyl-substituted tetracarbon carborane shows a remarkable resistance to fluxional behavior in its liquid state (neat sample) or in solution. This is in contrast with the observations made by Grimes et al.[1,2] where isomerization of $R_4C_4B_8H_8$ ($R = CH_3$ or $C_2H_5$) was found to occur in a matter of minutes in solution.

The nonsublimable material obtained among the products may be a carbon–carbon-linked free-radical polymer of the type $\{-[(CH_3)_3Si]_2C_4B_8H_8\}_n$–produced during the fusion process. The detailed characterization of this polymeric product is currently in progress but is far from complete owing to its insolubility in most organic solvents.

The exact mechanism of the fusion process is not known. The presence of trimethylsilane in the products requires the rupture of a Si–$C_{cage}$ bond and the abstraction of a hydrogen atom. Scheme I outlines a plausible sequence by which two *nido*-2,3-$[(CH_3)_3Si]_2$-2,3-$C_2B_4H_6$ molecules could fuse to give the *nido*-$[(CH_3)_3Si]_2C_4B_8H_{10}$. This scheme involves the high-temperature formation of a trimethylsilyl radical which then could extract one of the carborane bridge-hydrogen atoms forming trimethylsilane and a reactive carborane fragment that could easily condense with another such fragment to yield the fused carborane product. This scheme could also explain the relative ease of fusion of silyl-containing carboranes compared to the corresponding *C*-alkyl-substituted ones. The stronger C–C bonds would be less likely to rupture than the C–Si bonds, thus preventing the fusion process from taking place in the absence of a metal-complex intermediate or a metal catalyst.

This work demonstrates the significance of the *C*-trimethylsilyl groups of the small carboranes in synthetic transformations and opens up a new area of synthetic carborane chemistry. Studies on the fusion process involving other carboranes such as $[(CH_3)_3Si][CH_3]C_2B_4H_6$ and $[(CH_3)_3Si]C_2B_4H_7$ are now in progress.

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## Observation of Two-Bond $^{111}$Cd–$^{113}$Cd Nuclear Spin-Spin Coupling in $[Cd_4(SPh)_{10}]^{2-}$

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The $^{113}$Cd–$^{113}$Cd scalar couplings of 20–50 Hz observed in the $^{113}$Cd NMR spectra of $^{113}$Cd-enriched cadmium metallothionein ($^{113}$Cd-MT) have proved invaluable in elucidation of the spatial disposition of the several cadmium ions in the cysteinyl binding sites of the protein.[1,2] From such couplings, mammalian $^{113}$Cd-MT has been shown to contain two types of polynuclear cadmium clusters, one with three metal atoms, the other with four,[1] while $^{113}$Cd-MT from crab has been shown to contain two distinct three-atom clusters.[1,2] Apart from in $^{113}$Cd-MT, scalar coupling between $^{113}$Cd nuclei has only been observed in one case: very recently, Sadler and co-workers[3] reported the occurrence of 80 ± 4 Hz couplings in the $^{113}$Cd NMR spectrum of an as yet incompletely characterized probably polymeric cadmium complex of deprotonated dicysteinoethylenediaminetetraacetic acid. At present then, although various models have been proposed[4] for the metal *chemical shifts* of $^{113}$Cd-MT, it remains true of the $^{113}$Cd–$^{113}$Cd couplings that "it is not possible to extract additional structural details from the coupling constants since no other structurally defined polynuclear complexes have been reported which exhibit resolved $^{113}$Cd–$^{113}$Cd couplings with which the metallothionein coupling constants might be compared".[2] We report here the first example of $^{111}$Cd–$^{113}$Cd coupling, in the $^{111}$Cd and $^{113}$Cd NMR spectra of the structurally characterized[5] $[Cd_4(SPh)_{10}]^{2-}$ ion, and hence we are able to deduce the corresponding $^{113}$Cd–$^{113}$Cd coupling. From X-ray analysis of $(Et_4N)(Et_3NH)[Cd_4(SPh)_{10}]$ (**1**) the $[Cd_4(SPh)_{10}]^{2-}$ anion is known to possess a structure based on an adamantane-like $Cd_4(\mu\text{-}S)_6$ cage, each cadmium ion being associated with one terminal and three bridging benzenethiolate ligands.[5] The 291 K, 66.58-MHz $^{113}$Cd NMR spectrum of **1** in acetonitrile has been described as a single sharp resonance with $\delta_{Cd}$ 576 and $\Delta\nu_{1/2}$ = 25 Hz.[6,7]

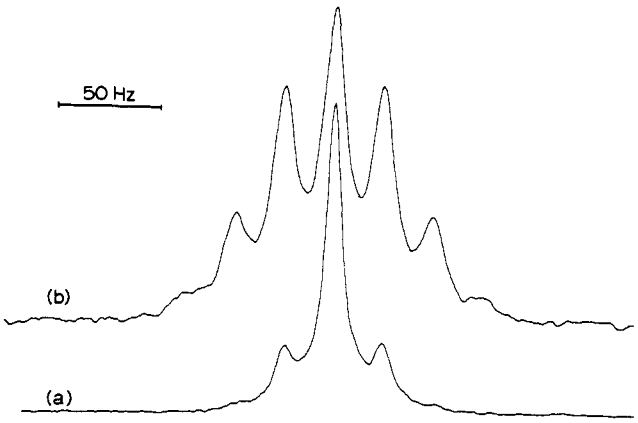

**Figure 1.** $^{111}$Cd NMR spectrum at 42.42 MHz and 295 K of (a) a 0.05 M solution of natural **2** in acetone. The spectrum results from accumulation of 11 315 45° (10 $\mu$s) pulses at 3-s intervals with an acquisition time of 1 s (a 2-Hz line broadening has been applied); (b) a 0.05 M solution of $^{113}$Cd-enriched **2** ($^{111}$Cd:$^{113}$Cd:zerospin Cd = 0.13:1:0.85) in acetone. The spectrum results from 28 060 transients obtained as in a; a 3-Hz line broadening has been applied. No proton decoupling was used in either a or b (see text).

At ambient probe temperature of 295 ± 1 K, without proton decoupling (see below), thermally equilibrated 0.05 M solutions of $(Me_4N)_2[Cd_4(SPh)_{10}]$ (**2**)[8] in acetonitrile or acetone show 42.42-MHz $^{111}$Cd and 44.37-MHz $^{113}$Cd NMR spectra consisting of a sharp center band with $\delta_{Cd}$ 578 (MeCN) and 575 ($Me_2CO$) and $\Delta\nu_{1/2} \approx 8$ Hz in both solvents, flanked symmetrically by one strong pair of satellites and a second much weaker more widely separated pair of satellites. A typical spectrum, the 295 K, 42.42-MHz $^{111}$Cd NMR spectrum of **2** in acetone, is shown in Figure 1a. The signal amplitudes[10] of the center band and stronger pair of satellites are approximately 0.22:1:0.22 in the $^{111}$Cd NMR spectrum and 0.24:1:0.24 in the corresponding $^{113}$Cd NMR spectrum. Intensities of 0.22:1:0.22 and 0.23:1:0.23 are expected

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[1] For a recent review of $^{113}$Cd NMR studies of metallothionein, see: Otvos, J. D.; Armitage, I. M. in "Biochemical Structure Determination by NMR"; Bothner-By, A. A., Glickson, J. D., Sykes, B. D., Eds.; Marcel Dekker: New York, 1982; Chapter 4.

[2] Otvos, J. D.; Olafson, R. W.; Armitage, I. M. *J. Biol. Chem.* **1982**, *257*, 2427–2431.

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[4] Lacelle, S.; Stevens, W. C.; Kurtz, D. M., Jr.; Richardson, J. W., Jr.; Jacobson, R. A. *Inorg. Chem.* **1984**, *23*, 930–935 and references therein.

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[6] Hagen, K. S.; Stephan, D. W.; Holm, R. H. *Inorg. Chem.* **1982**, *21*, 3928–3936.

[7] The $^{113}$Cd chemical shift was referenced to external 0.1 M $Cd(ClO_4)_2$(aq). The same technique and standard have been used in the present work.

[8] **2** was synthesized from $Cd(NO_3)_2 \cdot 4H_2O$, $Me_4NCl$, and a slight excess of NaSPh in MeOH. Anal. Calcd for ($C_{68}H_{74}Cd_4N_2S_{10}$): C, 48.34; H, 4.41. Found: C, 48.25; H, 4.44. $^{13}$C NMR $\delta_c$ ($(CD_3)_2CO$) 55.9 ($Me_4N$), 123.5 (Ar $C_4$), 128.4 (Ar $C_{3,5}$), 134.4 (Ar $C_{2,6}$), 140.5 (Ar $C_1$). The synthesis and characterization of this salt is also described in very recent work by Dance and co-workers.[9]

[9] Dance, I. G.; Choy, A.; Scudder, M. L. *J. Am. Chem. Soc.*, in press.

[10] Because of signal overlap, signal amplitudes are used as an approximation to signal intensities.