Carboranylnitrenes[1]

Rodney J. Blanch,[*,†] **Linda C. Bush,**[‡] **and Maitland Jones, Jr.**[†]

Departments of Chemistry, Princeton University, Princeton, New Jersey 08544,
and Yale University, New Haven, Connecticut 06511

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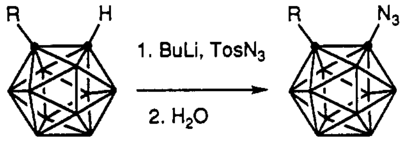
The EPR spectra of carbon- and boron-attached carboranylnitrenes are described. The zero-field splitting parameter $|D/hc|$ shows that there is little delocalization of the nonbonding electrons into the cage.

Carbon-substituted azides have been known since 1864 and are so common as to be fitting subjects of extensive reviews.[2,3] Boron-substituted azides have also been known for many years in a variety of structural types.[4] Borazides with simple alkyl[5] and aryl[6] substituents can be found, as well as those attached to borazines[7] and relatively exotic boron clusters.[8] Alkyl and other azides are common sources of monovalent nitrogen-containing intermediates, the nitrenes.[9] Although concerted rearrangements are prominent in the chemistry of the boron-substituted azides, nitrenes attached to boron have been implicated in some reactions and are especially important in photochemical processes.[4,10] There are, however, no reports of the EPR spectra of nitrenes attached to boron. Boron-substituted *o*- and *m*-carboranyl azides have been known for over a decade thanks to the group of Grushin,[11] but, oddly enough, carbon-substituted azides have not been described. Here we report the syntheses of some 1-*o*-carboranyl azides and the EPR spectra of both carbon-substituted and boron-substituted carboranylnitrenes.

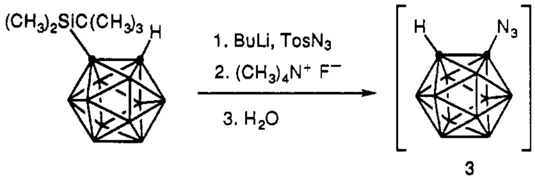
Substituted 1-azido-2-R-*o*-carboranes [R = CH_3, $(CH_3)_3CSi(CH_3)_2$] were simply prepared through treatment of the starting carborane with butyllithium and tosyl azide in THF, followed by aqueous workup. Recrystallization from methanol/water gave pure compounds.



1, R = CH_3

2, R = $(CH_3)_2SiC(CH_3)_3$

Azides **1** and **2** showed appropriate bands in the infrared (**1**, 2126 cm^{-1}; **2**, 2123 cm^{-1}) and were characterized further by routine analysis of spectra. Both compounds **1** and **2** were stable indefinitely at 4 °C. [*Caution*! Although we have experienced no explosions, azides must always be treated with great care.] In contrast to **1** and **2**, the parent azide, **3**, is not so stable. In this case we attempted to desilate the azide **2** with the method of Gomez and Hawthorne.[12] The unsubstituted azide can be isolated by simple evaporation of the solvent THF after filtration through silica gel but decomposes overnight at −10 °C and has not been characterized beyond its infrared band at 2106 cm^{-1}.



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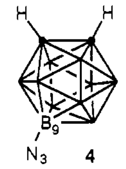
The instability of **3** also contrasts with the stability of 9-*o*-carboranyl azide (**4**),[11a] a molecule that survives gas chromatography at a column temperature of 200 °C and an injector temperature of 250 °C.



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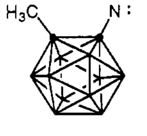
Solutions of the azides **1**–**4** (~10 mM in methylcyclohexane) were degassed and frozen at 5–10 K. The organic glasses were then photolyzed through quartz in the EPR cavity with a 250-W high-pressure Hg/Xe lamp. The resulting spectra were stable at 10 K but could not be observed when the azides were photolyzed at 77 K. A sample spectrum of **5**, the product of photolysis of **1**, is included as Figure 1.

The zero-field splitting parameters $|D/hc|$ and $|E/hc|$ for the nitrenes **5**–**8** are collected in Table 1. The value $|D/hc|$ is related to $1/r^3$, where r is the average distance between the two nonbonding electrons. In propylnitrene, where delocalization is impossible, $|D/hc| = 1.607$ cm^{-1} whereas in a series of phenylnitrenes it is ~1



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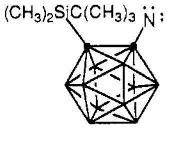

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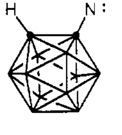

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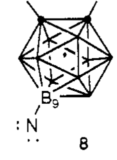

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[†] Princeton University.

[‡] Yale University.

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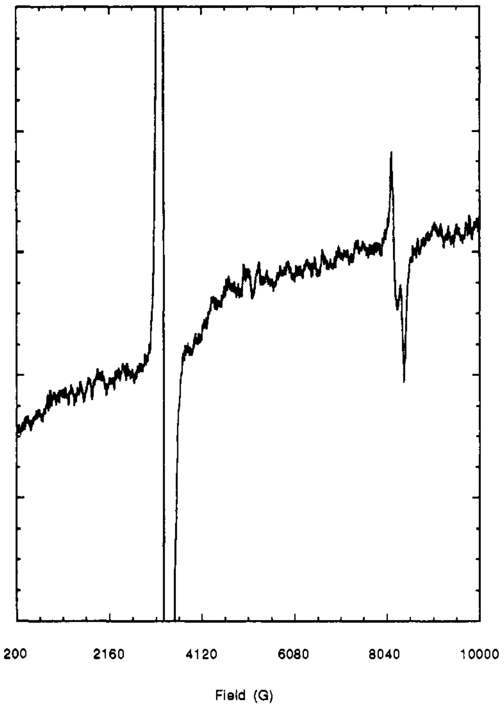

Figure 1. EPR spectrum of **5**.

Table 1. Zero-Field Splitting Parameters for Nitrenes

compd	$\lvert D/hc \rvert$	$\lvert E/hc \rvert$
propylnitrene[13]	1.607	0.0034
phenylnitrene[13]	0.9978	<0.002
5	1.643	0.0037
6	1.597	0.0027
7	1.603	0.0029
8	1.536	<0.002

cm^{-1}.[13] The values of $\lvert D/hc \rvert$ for **5**–**8** show that the two unpaired nonbonding electrons are largely localized on nitrogen. There is little delocalization of the nonbonding electrons into the cage. In this respect nitrenes **5**–**8** resemble the carboranylcarbenes.[14] The other zero-field splitting parameter, $\lvert E/hc \rvert$, is a measure of the difference in magnetic properties along the x and y axes and thus can be used to approximate the deviation from cylindrical symmetry. The value of $\lvert E/hc \rvert$ for the carbon-attached nitrenes is close to that for a simple alkylnitrene such as propylnitrene,[13] but that for the boron-attached species is smaller. This diminution indicates a closer approach to equivalence of the triplet nitrene's SOMO's. This is probably the result of the difference in local symmetry between nitrenes attached at the 1-position and the 9-position. The local environment around the 9-nitrene has 5-fold symmetry whereas that surrounding the 1-nitrene does not.

The increased stability of **4** over **1**–**3** is accompanied by changes in reactivity. For example, **1** is a highly reactive 1,3-dipolar reagent toward alkenes, but **4** is not. Photolysis of **4** in alkenes leads to chemistry apparently derived from nitrene **8**, whereas photolysis of **1** in both alkenes and alkanes gives only minor products of nitrene chemistry. We hope to report in detail on the properties of **4** later.

We regret to report the gas-phase decomposition of **1** at 500 °C/<10^{-4} mm does not lead to the so-far unknown icosahedral azacarborane. We tentatively attribute this to the triplet nature of the nitrene **5**.

Experimental Section

General Methods. EPR spectra were recorded at 4–10 K on either a Bruker ESP 300 or Varian E-12 instrument fitted with Oxford Instruments ESR 910 continuous-flow liquid-helium cryostats. Samples for EPR spectra were prepared by dissolving the azides in methylcyclohexane at ~10 mmol concentrations. The samples were degassed by bubbling argon through the sample for 15 min, placed in the cryostat, and cooled. The frozen matrices were then photolyzed for 1 h at 4–10 K in the cavity with the broad band output of a 250-W high-pressure Hg/Xe lamp. Spectra were recorded both during photolysis and for several hours after photolysis had ceased. NMR spectra were recorded on a JEOL GSX 270-MHz instrument in either $CDCl_3$ or C_6D_6.

1-Azido-2-methyl-*o*-carborane. 1-Methyl-*o*-carborane (5 g, 0.03 mol) was dissolved in dry ether (50 mL), and BuLi (15 mL, 2.35 M in hexanes) was added. The reaction mixture was then stirred for 30 min at room temperature. *p*-Toluenesulfonyl azide (6.9 g, 1.1 equiv) in dry ether (50 mL) was added slowly (~30 min) and the solution stirred for a further 60 min. The resulting yellow/orange solution was then poured onto 100 mL of iced water. The organic layer was collected, and the aqueous layer was washed with ether (3 × 50 mL). The combined organic layers were then dried over sodium sulfate and evaporated to dryness to yield a yellow waxy mass, which was then recrystallized from methanol/water. Yield: 3.42 g (54.3%) of 1-azido-2-methyl-*o*-carborane.[15]

IR: 2591 (s, B–H stretch), 2126 (vs, N_3 stretch), 1266 (s), 1009 (m), 755 (m) cm^{-1}. ^1H NMR (δ, $CDCl_3$): 3.6–1.1 (br m, B–*H*), 2.09 (s, CH_3) ppm. ^{13}C NMR (δ, C_6D_6): 87.04, 77.15, 21.63 ppm.

1-Azido-2-(dimethyl-*tert*-butylsilyl)-*o*-carborane. 1-(Dimethyl-*tert*-butylsilyl)-*o*-carborane[12] (5.16 g, 0.02 mol) was dissolved in dry THF (100 mL), and the solution was cooled to –78 °C under argon. Butyllithium (8 mL, 2.5 M) was then added slowly (over 5 min) and the reaction mixture stirred for a further 15 min. Tosyl azide (4.33 g, 1.1 equiv) in dry THF (20 mL) was then added and the mixture stirred for a further 30 min at –78 °C. This mixture was then warmed to room temperature, which resulted in the formation of a heavy precipitate. The reaction mixture was stirred for 30 min at room temperature and filtered, and the filtrate was evaporated to dryness. Ethanol (50 mL) was added to the oily mass and the mixture refrigerated over night at 4 °C. Crystals were then collected.[15] Yield: 3.54 g (59%).

IR: 2123 cm^{-1} (N_3, stretch). ^1H NMR (δ, C_6D_6): 3.5–1.0 (br m, B-*H*), 1.03 (s, Si–C–$(CH_3)_3$), 0.30 ppm (s, Si–$(CH_3)_2$). ^{13}C NMR (δ, C_6D_6): 88.88, 76.53, 27.13, 19.96, -3.58 ppm.

Desilylation of 1-Azido-2-(dimethyl-*tert*-butylsilyl)-*o*-carborane to 1-Azido-*o*-carborane. 1-Azido-2-(dimethyl-*tert*-butylsilyl)-*o*-carborane (1.5 g, 5 mmol) was dissolved in dry THF (20 mL), and the solution was cooled to –78 °C. Tetrabutylammonium fluoride (5.5 mL, 1 M in THF) was then added slowly (over 5 min), and the reaction mixture was allowed to warm to room temperature. Water (20 mL) was added and the solution extracted with ether (3 × 50 mL). The organic layer was collected, dried over sodium sulfate, and evaporated to dryness to give a pale yellow waxy solid. This crude material was filtered through a short silica gel column with methylene chloride immediately prior to use. The IR spectrum had an absorbance at 2106 cm^{-1}, which was attributed to the N_3 stretch of 1-azido-*o*-carborane.

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(15) Satisfactory melting points were not obtained as attempts led to a sandy refractory material without evident melting.