



9-Carboranylcarbene by indirection

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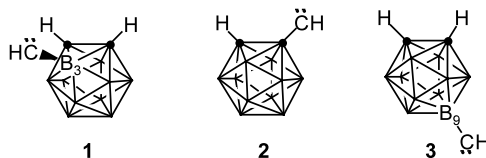
Abstract—9-Carboranylcarbene is formed by reaction of carbon atoms with *o*-carborane. The triplet state reacts with alkenes by hydrogen abstraction, not the more usual addition reaction. © 2002 Elsevier Science Ltd. All rights reserved.

3-*o*-Carboranylcarbene (**1**) was the first boron-substituted carbene to be described experimentally in detail.¹ In that paper the properties of **1** were contrasted to those of 1-*o*-carboranylcarbene (**2**), the carbon-substituted *o*-carboranylcarbene, and some properties of 9-*o*-carboranylcarbene (**3**) were anticipated.¹

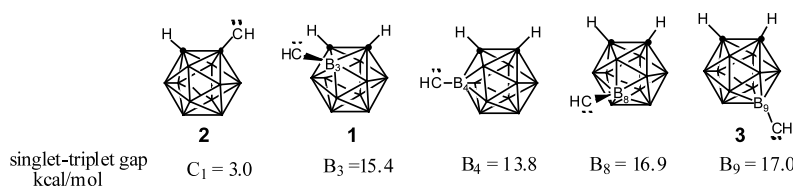
In contrast to ‘normal’ boron-substituted carbenes, in B-carboranylcarbenes it can be expected that the normal π effect in which the singlet state is stabilized through filled–empty orbital overlap will be largely shut off. The $2p$ orbital of boron will be used in constructing the web of three-center, two-electron bonding that stabilizes these cage compounds. On the other hand, the σ effect in which the triplet is stabilized through withdrawal of electrons is fully operative.² Thus, we might expect B-substituted carboranylcarbenes to be ground state triplets, and perhaps to react as triplets as well. New density functional calculations at the B3LYP/6-31G(d)+ZPC level³ with the GAUSSIAN98 program⁴ confirm these expectations and are in agreement with

previous results.⁵ The singlet triplet splittings in all the carboranylcarbenes are shown below. Density functional calculations may tend to overestimate slightly the stability of the triplet with respect to the singlet.⁶ By way of calibration, Geise and Hadad find triplet phenylcarbene to be 5.4 kcal/mol more stable than the singlet and estimate that this calculated value is about 1.5 kcal/mol too high. In solution (in which the singlet may be preferentially stabilized) the triplet is thought to be only 1–2 kcal/mol more stable than the singlet.⁶ Thus, we are confident that the numbers shown below are quite accurate. Certainly the trend from **2** to **3** is correct.

Experiments have already revealed that 3-*o*-carboranylcarbene **1** shows unusual amounts of triplet reactivity.¹ Carbene **2** showed roughly 8% triplet reactions with *cis*-2-butene, whereas **1** reacted about 22% through the triplet state. Sterically encumbered *C*-methyl derivatives of **1** showed up to 33% triplet reactivity. What was most striking was the observation that double hydrogen



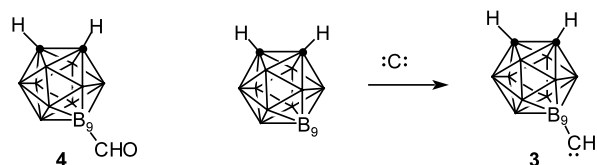
In this and succeeding figures, the dots represent carbons. All other vertices are borons, and there is an unshown hydrogen at every unoccupied vertex.



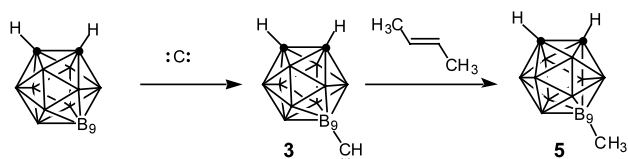
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abstraction to give 3-methyl-*o*-carboranes was the major reaction of the triplet B₃-substituted carbenes. Hydrogen abstraction is not generally competitive with the addition reaction for most triplets.⁷ Li, et al., anticipated that **3**, in which the carbene is attached to the relatively electron-rich boron most remote from the cage carbons, would be even farther to the triplet side of the singlet–triplet equilibrium, and would also show hydrogen abstraction as its major reaction pathway.¹ Many, many attempts to make **3** through standard routes have failed. The main reason appears to be the instability of the 9-aldehyde **4**, which is a most sensitive compound.⁸

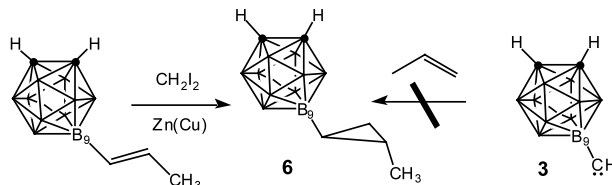
Having failed so miserably to use ‘standard’ chemistry, we stayed alert for more exotic opportunities. We were rewarded when Zheng, et al. reported that naphthylcarbenes, formed from the gas-phase reaction of carbon atoms with naphthalene, could be trapped by alkenes frozen on the surface of the reactor.⁹ We already knew that carbenes reacted preferentially at the 9-position of *o*-carborane,¹⁰ and as the reaction profiles of carbenes and carbon atoms are roughly comparable, we were confident that the initial reaction between C and *o*-carborane would be to generate exactly the carbene we wanted, **3**. Zheng’s earlier work⁹ also gave us confidence that we would be able to trap **3**.



Formation of carbon atoms in the presence of *o*-carborane in the reactor described previously¹¹ led to no products of the molecular weight of methylcarboranes. Instead, low molecular weight carboranes were formed. When a potential hydrogen source (2-butene, toluene, or propene) was first coated on the cold wall of the reactor (−196°C), 9-methyl-*o*-carborane (**5**) was formed. Identification rests on comparison with an authentic sample made by the method of Li.¹² The characteristic high-field signal at δ 0.3 ppm appeared in the ¹H NMR spectrum of the crude product and GC/MS revealed a single peak of the correct mass peak at exactly (spiking experiment) the correct retention time. Other B-methyl-*o*-carboranes have different retention times, and different ¹H NMR spectra.¹³ There is no evidence for other methyl compounds; we see only the 9-isomer. At longer retention times other peaks appear with molecular weights and retention times appropriate for *o*-carborane dimers. Treatment of *o*-carborane in benzene with benzoyl peroxide leads to similar compounds.



No evidence for cyclopropane formation can be found. There are no peaks of the proper molecular weight in the appropriate region of the chromatogram. But, might not three-membered rings at the 9-position be unstable? Cyclopropanes formed from **1** and **2** are stable, but so are the related aldehydes, and the 9-aldehyde is not very stable. We generated a 9-substituted cyclopropane through Simmons–Smith addition of methylene to 9-propenyl-*o*-carborane, itself made through isomerization of 9-allyl-*o*-carborane.¹² The cyclopropane **6** is completely stable, and is not detectable by GC or ¹H NMR spectroscopy (characteristic peak at −1.0 ppm) when propene is used as hydrogen source in the carbon-atom reactor.



Although we cannot make **3** in the normal ways, we have been able to generate it through indirection. Reactivity best characterized as coming from the triplet appears. Why these carbenes ‘prefer’ hydrogen abstraction to addition remains to be determined.

Acknowledgements

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