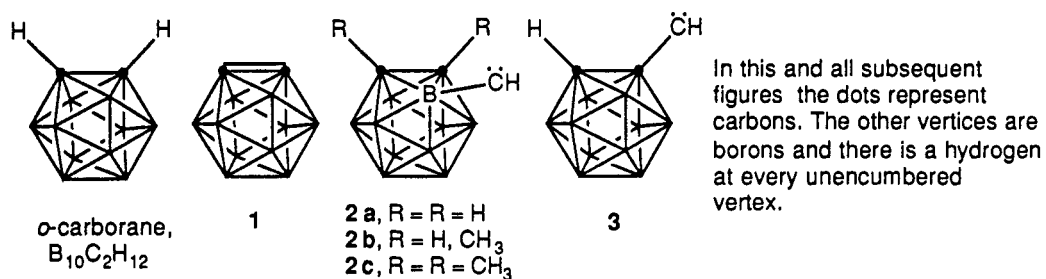


## Carboranylcarbenes and dehydrocarboranes

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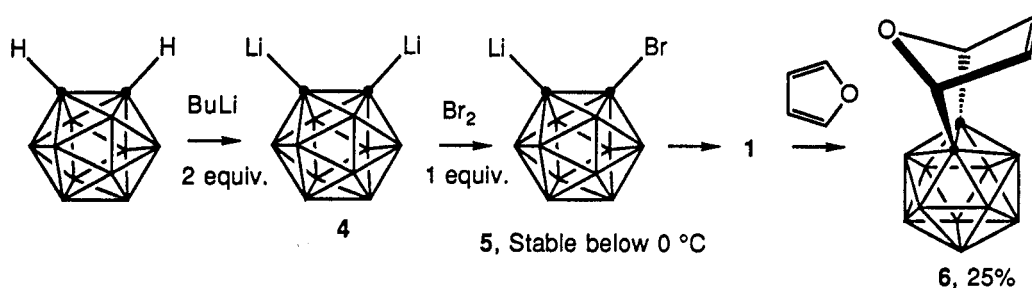
**Abstract:** Reactions of 1,2-dehydro-*o*-carborane, a benzyne analogue, and three boron-substituted *o*-carboranylcarbenes are described. Dehydro-*o*-carborane contains a reactive, but normal “dehydro” bond. The carbenes show exceptional triplet reactivity.

Every fledgling organic chemist quickly learns of the benzenoid compounds, but there is another class of aromatic molecules not so widely known, the icosahedral carboranes,  $B_{10}C_2H_{12}$  (ref. 1). These compounds resemble benzenes in both thermodynamic stability and, often, in chemical reactions. For example, carboranes survive heating to several hundred degrees and undergo aromatic substitution reactions with electrophilic reagents. In this paper we will describe two kinds of carborane-based reactive intermediate, 1,2-dehydro-*o*-carborane (**1**), a relative of “benzyne,” and 3-*o*-carboranyl-carbenes (**2**), the first boron-substituted carbenes, remote cousins of the phenylcarbenes, and brothers and sisters of **3**, the known 1-*o*-carboranylcarbene (ref. 2).

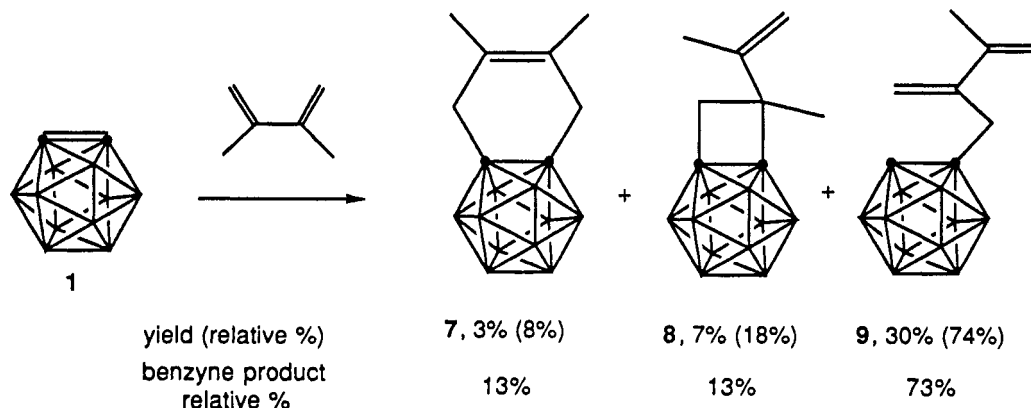


### FORMATION AND REACTIONS OF 1,2-DEHYDRO-*o*-CARBORANE

Dehydroaromatic molecules can be formed in a variety of ways. One of the earliest discovered uses the elimination of halide from an  $\alpha$ -halo anion (ref. 3). An effective procedure for **1** first forms the dianion **4** by deprotonation of *o*-carborane with two equivalents of butyllithium. Precipitated **4** is then treated with a single equivalent of bromine at 0 °C to form the soluble bromo anion **5**. Addition of 10 equivalents of furan to the solution of **5** followed by reflux in ether leads to adduct **6** in 25% isolated yield (ref. 4).



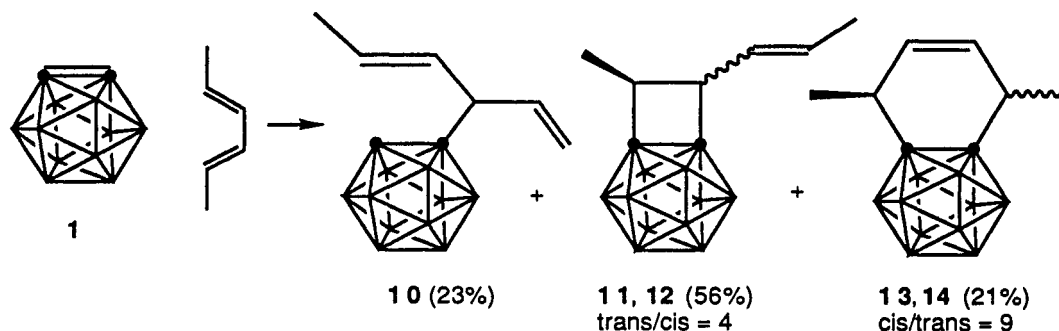
A more versatile trapping agent, 2,3-dimethyl-1,3-butadiene, provides avenues for three kinds of reaction, 2 + 4 cycloaddition (Diels-Alder reaction), 2 + 2 cycloaddition, and the ene reaction, a 2 + 4 cycloaddition in which a carbon-hydrogen bond plays the part of one of the diene double bonds. Benzyne is known to undergo all three kinds of reaction, with the ene process strongly preferred (ref. 5). 1,2-Dehydro-*o*-carborane is remarkably similar to dehydrobenzene in its reactions with this molecule. The three possible processes all occur, giving adducts **7**, **8**, and **9**. As for benzyne, it is the ene product that dominates.



#### THE NATURE OF THE INTERMEDIATE

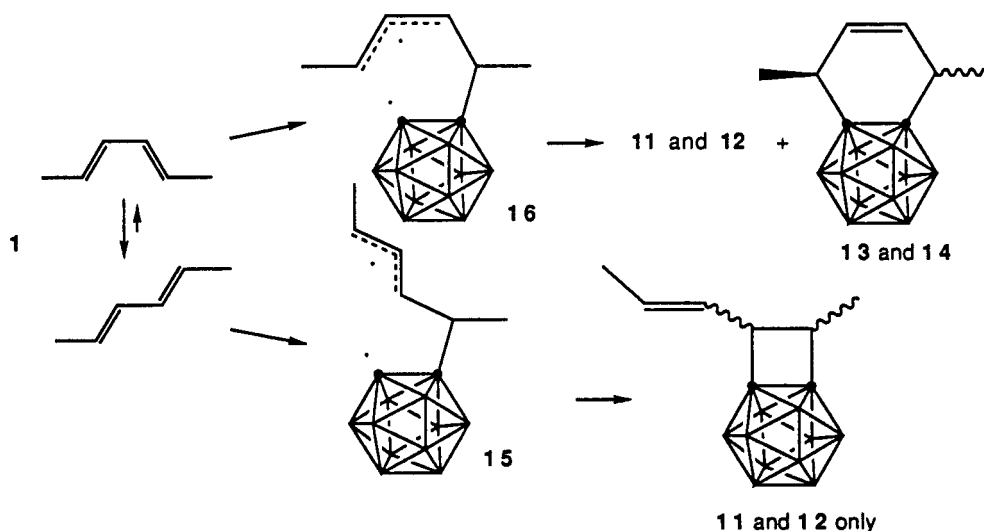
The *exo*-ring  $\pi$  bond of benzyne was characterized as "normal," if reactive, through an examination of the stereochemical outcome of the 2 + 4 and 2 + 2 cycloaddition reactions (ref. 6). The Diels-Alder reaction was found to be stereospecific and the 2 + 2 cycloaddition nonstereospecific, just as orbital symmetry requires of a bond in which the usual phase relationships in the HOMO (symmetrical) and LUMO (unsymmetrical) obtained. Our plan was to use the same technique for **1**.

Five compounds are formed in the reaction of **1** with *trans,trans*-2,4-hexadiene. There is a single product, **10**, derived from an ene reaction. Two other compounds, **11** and **12**, are the cyclobutanes formed through a 2 + 2 cycloaddition. There are two products of 2 + 4 cycloaddition (**13** and **14**), formed in the ratio 9:1. It appears that the products of 2 + 4 cycloaddition are formed largely, but not completely, in a stereospecific fashion (ref. 4).

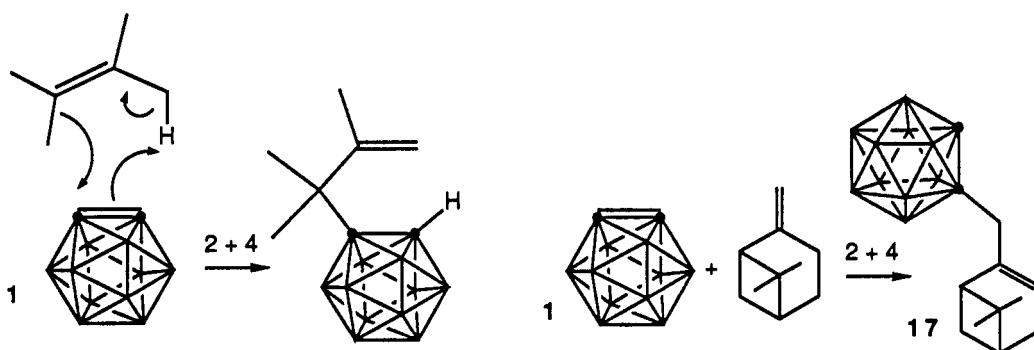


The most important difference between **1** and benzyne is the apparent lack of stereospecificity in the 2 + 4 reaction. We think this difference springs simply from the relative importance of the 2 + 2 reaction for 1,2-dehydro-*o*-carborane. The 2 + 2 reaction has been shown to be stepwise for dehydrobenzene and our data for **1** reveal a similar course of

reaction. There is about 90% retention of stereochemistry in the 2 + 4 cycloadditions of **1** with *trans,trans*-2,4-hexadiene (and *cis,trans*-2,4-hexadiene). Stepwise 2 + 2 additions of both **1** and dehydrobenzene thoroughly scramble stereochemical relationships, and do not induce the modest deviations from stereospecificity seen in these 2 + 4 reactions. Stepwise addition to a diene surely takes place mostly through the favored *s*-trans form, and thus produces an intermediate **15** destined for 2 + 2 formation and prevented from forming any 2 + 4 product. However, stepwise addition of **1** to the minor *s*-cis form of the diene gives an intermediate **16** that can eventually close to 2 + 2 and *both* 2 + 4 products.



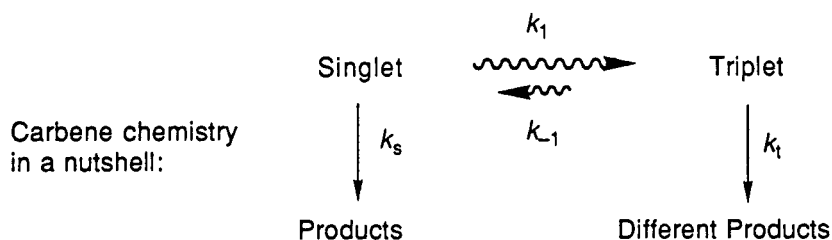
Although generally something of a poor relation in the house of thermal reactions, the ene reaction is nonetheless closely related to the more extensively documented "diene," or Diels-Alder reaction. Both the ene and Diels-Alder reactions are 2 + 4 cycloadditions, and therefore both are likely to be concerted. Investigations of the mechanism of the ene process have shown that this is generally the case (ref. 7). Three general mechanisms can be written, a concerted 2 + 4 cycloaddition, and two step-wise processes, abstraction-recombination and addition-hydrogen shift. The absence of allylic rearrangement in ene reactions of **1** rules out abstraction-recombination, and the sole formation of unrearranged "ene" products (**17**) from reaction of **1** with  $\beta$ -pinene makes addition-hydrogen shift most unlikely (ref. 8).



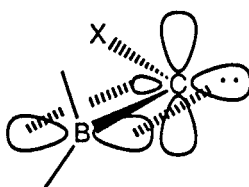
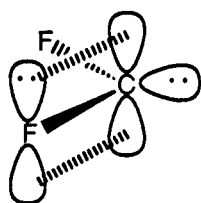
In sum, we see **1** as an intermediate best formulated as a "normal" dehydro compound, possessing a symmetrical HOMO and unsymmetrical LUMO. There are differences between dehydro-*o*-carborane and dehydrobenzene in the details of reaction preferences, conceivably largely dependent upon the increased steric demands of **1**, but an overall view of reactivity shows the two to be quite similar.

### *o*-CARBORANYLCARBENES

One theme in the exploration of carbene chemistry over the last three decades has been the differentiation of singlet and triplet reactions (ref. 9). Singlets add stereospecifically to alkenes in a concerted, if not symmetrical, process, insert into carbon-hydrogen bonds in a single step, and are little affected by added oxygen. Triplet chemistry is characterized by two-step reactions in which an intermediate separates starting material and products. Formation of the second bond follows creation of the first. In addition reactions this is revealed by loss of the stereochemical relationships present in the starting alkene. In insertion reactions the presence of radical intermediates can often be detected. Radical scavengers such as oxygen and, sometimes, dienes, are effective at removing triplets. Mechanistic analysis is often complicated by interconversion of singlets and triplets. In order to understand any carbene reaction, even qualitatively, it is necessary to take account of the potential interconversion of singlets and triplets ( $k_1$  and  $k_{-1}$ ) as well as the relative rate constants of singlet and triplet reactions ( $k_s$  and  $k_t$ ). Often, reactions of ground state triplets are not detectable because of the generally far greater rates of singlet reactions.



A second theme in carbene chemistry has been the effect of substituents on the mix of singlet and triplet reactions. Most attention has been paid to the rich chemistry of the narrowly separated singlet and triplet arylcarbenes and to the singlet-stabilizing effects of halogen substitution. Generally, halogen, oxygen, or nitrogen substitution preferentially stabilizes singlets, as electrons are shared between a filled p orbital on the heteroatom and the empty 2p orbital on carbon (ref. 10).



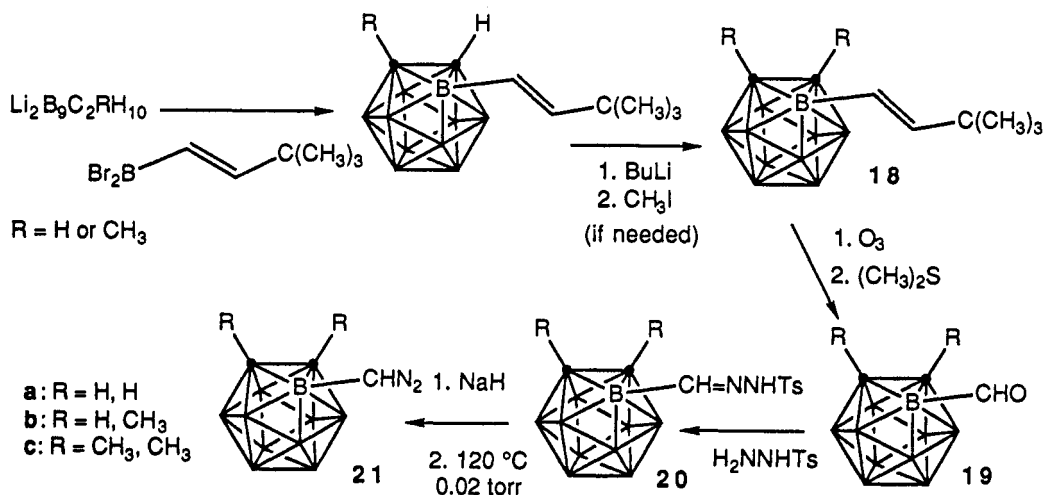
Stabilization of singlet carbenes through overlap of filled and empty orbitals.

Almost no experimental attention has been paid to the other side of the periodic table where relatively electropositive elements dwell, and where empty orbitals tend to be more prominent than filled. However, theoretical work gives us an idea of what to expect. For an atom such as boron, the presence of an empty p orbital should stabilize the singlet state through overlap with the filled orbital of the divalent carbon. In this case, however, there is a compensating effect stabilizing the triplet state. This operates through the  $\sigma$  system and depends upon the electronegativity difference between the two atoms. The effect is to donate electrons through the  $\sigma$  system, and for atoms less electronegative than carbon favors the triplet state. Thus, for a simple boron-substituted carbene such as  $\text{HC-BH}_2$ , there should be compensating effects stabilizing both the singlet and triplet states. Calculations bear this out, with the most recent efforts predicting the two spin states to be close in energy. In the most simple example, triplet  $\text{HC-BH}_2$  is the predicted ground state by 4-6 kcal/mol (ref. 11).

We have developed a route to boron-substituted carbenes through manipulations of substituted *o*-carboranes. Although this does yield a carbene adjacent to a boron atom, it must be emphasized that this is no ordinary boron. In particular, the empty 2p orbital, so influential in the chemistry of "normal" tri-substituted boranes, is largely absent, as it is occupied in the web of three-center, two-electron bonding making up the icosahedral cage. Although the singlet-stabilizing  $\pi$  effect seems likely to be largely absent in a carboranyl-carbene, the triplet-stabilizing  $\sigma$  effect remains. So, our preliminary expectation was that a boron-substituted carboranylcarbene might show enhanced triplet reactivity.

The new carbenes are generated by the traditional route, photolysis of a diazo compound. The diazo compounds are made from the tosylhydrazones salts, themselves available through the route shown. A set of 3-vinyl-*o*-carboranes **18a-c** was made by insertion of a vinyl-substituted boron into  $\text{Li}_2\text{B}_9\text{C}_2\text{H}_{11}$  or a methylated derivative. Further methylation (if needed) and ozonolysis led to **19a-c**, and reaction with tosylhydrazine to **20a-c**. Heating the sodium salts of the tosylhydrazones under vacuum (120 °C/0.02 torr) gave the diazo compounds **21a-c** in about 80% yield (ref. 12).

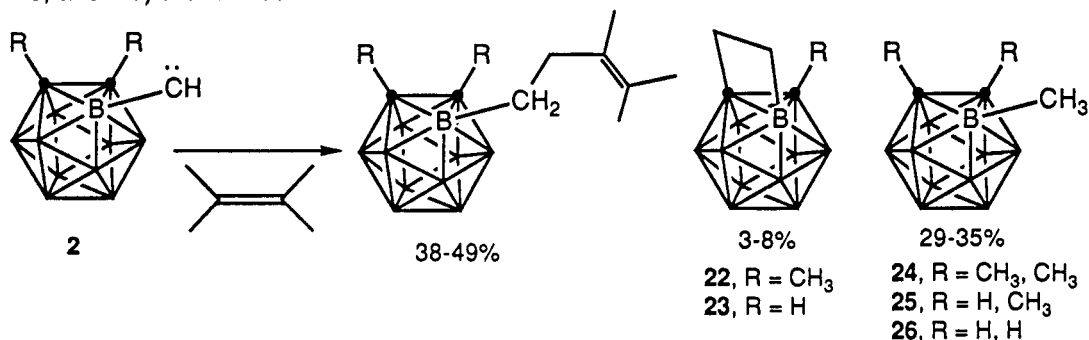
A traditional test of singlet vs. triplet reactivity has been the stereochemistry of additions to alkenes. Singlets add in a single step to preserve in the product cyclopropanes the stereochemical relationships present in the starting alkenes. Triplets also give cyclopropane products, but only after the formation of intermediate diradicals in which the stereochemical relationships present in the starting alkene are lost through rotations about carbon-



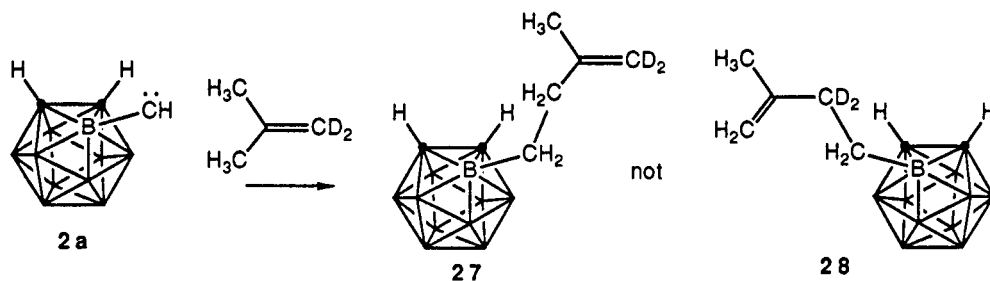
carbon single bonds. The figure compares the stereochemistry of addition of **2a**, and **2c** to *cis*- and *trans*-2-butene and gives an estimate of triplet reactivity in the addition reaction.

				% triplet reaction
<b>2a</b> + <i>trans</i> -2-butene	—	—	100	0
<b>2a</b> + <i>cis</i> -2-butene	74	24	2	3
<b>2c</b> + <i>trans</i> -2-butene	9	—	91	22
<b>2c</b> + <i>cis</i> -2-butene	63	25	12	18

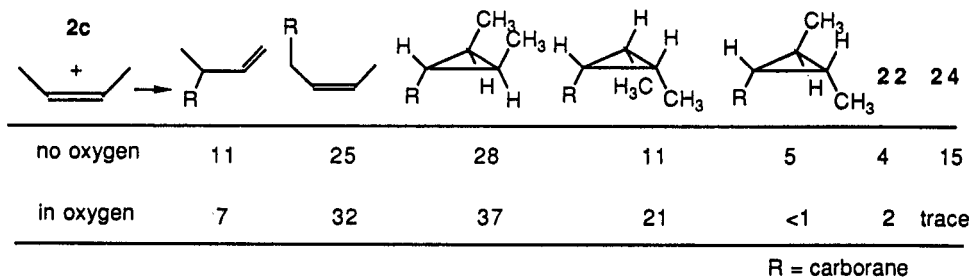
The reactions of carbenes **2** with alkenes lead to products other than cyclopropanes. Intermolecular carbon-hydrogen insertions give alkenes and intramolecular insertion produces the "cyclobutanes" **22** or **23**. Substantial amounts of 3-methyl-*o*-carboranes (**24**, **25**, and **26**) are formed as well.



In order to investigate the amount of triplet carbenes in the allylic insertion reaction, deuterium-labelled isobutylene was used as a substrate for **2a**. The triplet should reveal itself through the formation of rearranged compounds formed through an abstraction-recombination reaction. Analysis of the crude products by <sup>1</sup>H NMR spectroscopy showed only small amounts of protium in the position of absorption of the terminal methylenes of **27** (5-10%). Although it was not possible to make an accurate quantitative determination of the amount of triplet participation in allylic insertion, clearly the insertion product was overwhelmingly **27**, the isomer derived from the singlet, not **28**, the isomer diagnostic for the triplet.



It appears that the boron-substituted carbenes **2** give cyclopropanes and insertion products largely through their singlet states. What, then, of our expectation of increased triplet reaction? Where is the triplet? The answer seems to be, "In the methyl groups of **24**, **25**, and **26**." These compounds must arise by a double abstraction reaction and are most reasonably attributed to the triplet. In order to test this notion and to verify our mental separation of products into those formed from singlet (cyclopropanes of retained stereochemistry and most insertion products) and triplet products ("wrong" cyclopropanes plus an estimated portion of the other cyclopropanes, and methyl compounds) we repeated the reaction of **2c** with *cis*-2-butene in an atmosphere of oxygen. Oxygen is a known trap for triplets, and should reduce or eliminate compounds that owe their origin to a triplet reaction (ref.13). The figure shows the products of the reaction of **2c** with *cis*-2-butene in the absence and presence of oxygen.



As predicted, the products attributed to triplet carbene, the *trans* cyclopropane and methyl compound **24**, are greatly diminished. It is now reasonable to provide a new estimate of the amount of triplet reactivity present in the reactions of carbenes **2a-c** with *cis*- and *trans*-2-butenes (Table).

TABLE. Mix of reacting spin states for carboranylcarbenes.

Carbene	Alkene	% Triplet <sup>a</sup>	% Singlet <sup>b</sup>	
<b>2a</b>	<i>cis</i> -2-butene	22	78	a. ("wrong" cyclopropane plus some "right" cyclopropane, plus methyl compound)
	<i>trans</i> -2-butene	23	77	
	2,3-dimethyl-2-butene	>36	<64	
<b>2c</b>	<i>cis</i> -2-butene	46	54	b. ("right" cyclopropane plus allylic insertion, plus self-insertion)
	<i>trans</i> -2-butene	38	62	
	2,3-dimethyl-2-butene	>29	<71	
<b>2b</b>	2,3-dimethyl-2-butene	>31	< 69	

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#### REFERENCES

1. G. A. Olah, G. K. Surya Prakash, R. E. Williams, L. D. Field, and K. Wade, Hypercarbon Chemistry, Wiley, New York, (1987). E. L. Muetterties, Boron Hydride Chemistry, Academic, New York, (1975). R. N. Grimes, Carboranes, Academic, New York, (1970). T. Onak, Organoborane Chemistry, Academic, New York, (1975).
2. S. L. Chari, S.-H. Chiang, and M. Jones, Jr., J. Am. Chem. Soc. **104**, 3138 (1982). R. S. Hutton, H. D. Roth, and S. Chari, J. Phys. Chem. **85**, 753 (1981).
3. R. W. Hoffmann, Dehydrobenzene and Cycloalkynes, pp 43-44, Academic, New York, (1967),
4. T. Ghosh, H. L. Gingrich, C. K. Kam, E. C. Mobraaten, M. Jones, Jr., J. Am. Chem. Soc. **113**, 1313 (1991).
5. G. Wittig and H. Dürr, Liebigs Ann. Chem. **55**, 672 (1964).
6. M. Jones, Jr. and R. H. Levin, J. Am. Chem. Soc. **91**, 6411 (1969).
7. R. K. Hill, J. W. Morgan, R. V. Shetty, and M. E. Synerholm, J. Am. Chem. Soc. **96**, 4201 (1974). V. Garsky, D. F. Koster, and R. T. Arnold, J. Am. Chem. Soc. **96**, 4207 (1974). S.-H. Dai and W. R. Dolbier, J. Am. Chem. Soc. **94**, 3955 (1972).
8. Q. Huang, H. L. Gingrich, and M. Jones, Jr., Inorg. Chem. **30**, 3254 (1991).
9. W. Kirmse, Carbene Chemistry, 2nd Ed., Academic, New York, (1971). R. A. Moss, M. Jones, Jr., Carbenes, Vols. 1 and 2, Wiley, New York, (1973, 1975). M. Regitz, Ed., Carbene(oids), Georg Thieme, Stuttgart, (1989).
10. D. Feller, W. T. Borden, and E. R. Davidson, J. Chem. Phys. **71**, 4987 (1979).
11. B. T. Luke, J. A. Pople, M.-B. Krough-Jespersen, Y. Apeloig, M. Karni, J. Chandrasekhar, P. v. R. Schleyer, J. Am. Chem. Soc. **108**, 270 (1986). P. v. R. Schleyer, B. T. Luke, and J. A. Pople, Organometallics **6**, 1997 (1987).
12. J. Li and M. Jones, Jr., J. Am. Chem. Soc. **114**, 1094 (1992). J. Li, D. C. Caparrelli, and M. Jones, Jr., J. Am. Chem. Soc. submitted.
13. S. Morgan, M. S. Platz, M. Jones, Jr., and D. R. Myers, J. Org. Chem. **56**, 1351 (1991).