the input parameters were estimated by comparing the theoretical results obtained by a rough grid search[16] to experimental data. The results of our model calculations, included in Figure 1, suggest that large variations in interglycosidic torsional angles are responsible for the observed variation of $r^{\parallel}_{\mathrm{app}}$ for both the H1g-H4f and H1g-H1f interactions. It is important to note that the NOE-derived distances measured in this study do not correspond to statistical averages, as it often assumed[1,17] but to the motionally averaged values.[18a-e]

In summary, we have conclusively demonstrated the internal flexibility of sucrose in solution from interresidual, laboratory-frame cross-relaxation rates ($\sigma^{\parallel}$), a parameter that gives unique information about intramolecular dynamics.[18a,19a-d,20] In contrast, rotating-frame cross-relaxation rates as well as intraresidual, laboratory-frame cross-relaxation rates, like ^{13}C relaxation times,[3a-d] appeared virtually insensitive to this type of internal motion for a fast-tumbling molecule in solution. Paradoxically, it appeared that, for $\omega\tau_c \sim 1$, interresidue cross-relaxation rates measured from the *laboratory* frame of reference reflected *internal* molecular motions, i.e., they gave insight into a frame of reference corresponding to the viewpoint of an individual molecule.

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Registry No. Sucrose, 57-50-1.

Supplementary Material Available: ^1H NMR spectra (including 1D ROESY and 1D double-selective TOCSY-ROESY) of sucrose in H_2O (3 pages). Ordering information is given on any current masthead page.

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(15) For the calculations of spectral densities we assumed that sucrose tumbles isotropically, each unit is rigid, and the molecule changes its conformations by jumps around the glycosidic bond that are decoupled from the overall motion and can be described by a single correlation time, τ_i. In this case spectral density functions have a simple form (Lipari, G.; Szabo, A. *J. Am. Chem. Soc.* **1982**, *104*, 4546-4559):

$$J_n = \tilde{S}^2 \frac{\tau_0}{1 + (n\omega\tau_0)^2} + (\langle r^{-6} \rangle - \tilde{S}^2) \frac{\tau}{1 + (n\omega\tau)^2}$$

$$\text{where } \tilde{S}^2 = \sum_{m=-2}^{m=2} \left| \left\langle \frac{Y_{2m}(\Omega)}{r^3} \right\rangle \right|^2$$

$Y_{2m}(\Omega)$ are spherical harmonics functions with r and Ω corresponding to the distance and polar angle of a given proton pair in the molecular frame, $\langle \cdots \rangle$ denotes ensemble average, and $\tau^{-1} = \tau_0^{-1} + \tau_i^{-1}$. More elaborate models can be found: Tropp, J. *J. Chem. Phys.* **1980**, *72*, 6035-6043. Baldo, M.; Grassi, A.; Perly, B. *Mol. Phys.* **1988**, *64*, 51-63.

(16) Based on previous results[4a,b] we assumed that sucrose flips among three minimum energy conformations in (Φ, Ψ) space: $A = (-5°, -50°)$, $B = (-20°, -170°)$, and $C = (17°, 50°)$ obtained after a few steps of MM2 energy minimization. Φ = H1g-C1g-O1-C2f and Ψ = C1g-O1-C2f-O5f. We assumed that overall and internal motions are thermally activated processes[3d] having the form

$$\tau_{0,i} = A_{0,i} \exp\left(\frac{E_{0,i}}{RT} \right)$$

R is the gas constant, T is temperature, and $A_{0,i}$ and $E_{0,i}$ are adjustable parameters. For the H1g-H4f interaction measured in the temperature range from 263 to 330 K at 500 MHz, and at two temperatures (272 and 285 K) at four different magnetic fields (250, 400, 500, and 600 MHz), we obtained the following set of parameters: populations $(p_A, p_B, p_C) = (0.38, 0.38, 0.24)$, distances $(r_A, r_B, r_C) = (4.0, 4.0, 2.1\ \text{Å})$, $\tilde{S}^2 = 0.000425$, $E_0 = 28$ kJ/mol, $A_0 = 2$ fs, $E_i = 16$ kJ/mol, $A_i = 11$ fs. Almost the same parameters E_0 and A_0 were obtained from the temperature dependence of τ_0 calculated from cross-relaxation rates for the H1g-H2g proton pair.

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3-Carboranylcarbene: A Boron-Substituted Carbene[1]

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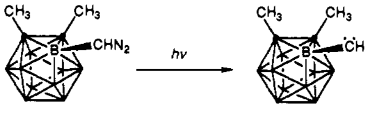
The chemistry of carbenes substituted with electron-donating groups is an old and rich one, with all manner of substituents well explored.[2] The chemistry of carbenes substituted with electropositive elements is so far restricted to theoretical studies. In particular, there is no example of a boron-substituted carbene outside of a computer. Only a few potential precursors are known,[3] although some beautiful new diazo compounds have recently been made by the group of Bertrand.[4] Here we describe the synthesis of 1,2-dimethyl-3-(diazomethyl)-*o*-carborane (**1**) and the first reactions of the carbene derived from it, **2**.



1 **2**

In these figures the dots represent carbons and all other vertices are borons. There is a hydrogen at each unoccupied vertex. The boron shown as a "B" is at the 3 position.

Boron-substituted carbenes have received substantial theoretical attention and are species of considerable interest. As with many carbenes, an issue of importance is the presence of two low-lying spin states, the singlet and triplet. In simple species such as H_2B-CH, the boron acts to stabilize the singlet state through overlap of its empty 2p orbital with the filled orbital of the carbene containing the two nonbonding electrons. At the same time, the relatively electropositive boron atom acts through the σ system to stabilize the triplet. Calculations agree that this balancing act yields a pair of spin states quite close in energy.[5] In the case of **2**, in which there is not expected to be good connection between extracage and cage orbitals,[6] it is as if the singlet stabilization had been turned off. Accordingly, one might expect enhanced triplet activity.

Tosylhydrazone **3** was made by insertion of a vinyl-substituted boron into $Li_2B_9C_2H_{11}$,[7] methylation of the two cage carbons, ozonolysis, and reaction with tosylhydrazine. Heating the sodium salt under vacuum (120 °C/0.02 Torr) led to the diazo compound

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(1) Support from the National Science Foundation through Grant CHE-90-24996 is gratefully acknowledged.

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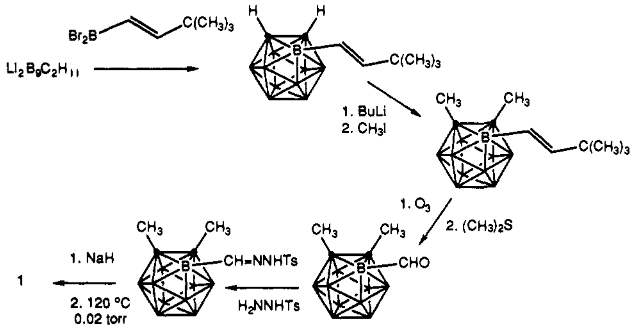
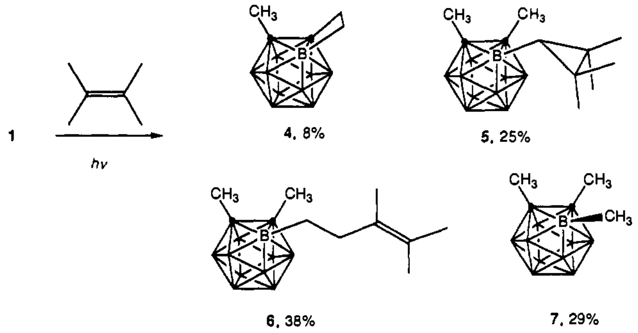
1 in 82% yield. Compound **1** appears stable, but should be treated with caution in view of the possible explosion hazard.

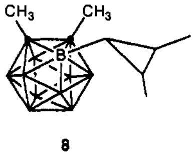


Irradiation of **1** in 2,3-dimethyl-2-butene through Pyrex with a 450-W Hanovia medium-pressure mercury arc led to four products in 60% yield. Intramolecular insertion gave **4**, which is the first compound reported that contains a two-carbon carbon-to-boron bridge.[8] Addition to the double bond gives **5**, and formal insertion into an allylic carbon-hydrogen bond produces **6**. Most unusual is the formation of 1,2,3-trimethyl-*o*-carborane (**7**), a major product and the apparent result of a double abstraction by carbene **2**.[9]



The substantial formation of **7** is unusual, and a likely origin is double abstraction of hydrogen by triplet **2**. Compound **4** does not give **7** either photochemically or on heating at the temperature of the photolysis of **1** (ca. 35 °C). As **7** is formed in solution, there is no reason to suspect rearrangements of "hot" molecules.

However, analysis of the products of reaction with *cis*- and *trans*-2-butene shows that the cycloaddition reaction is largely stereospecific. This indicates substantial singlet reactivity. In these reactions, **4** and products of carbon-hydrogen insertion are still formed, and compound **7** remains a major product.[10] The most economical explanation is that both spin states of carbene are present, with the singlet leading to most of the cyclopropanes and the triplet to most of the products of hydrogen abstraction as well as, presumably, the small amounts of cyclopropanes formed with loss of the stereochemistry present in the original olefins.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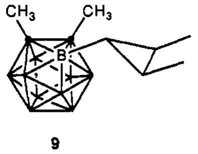
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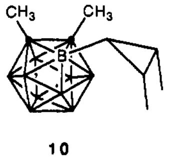
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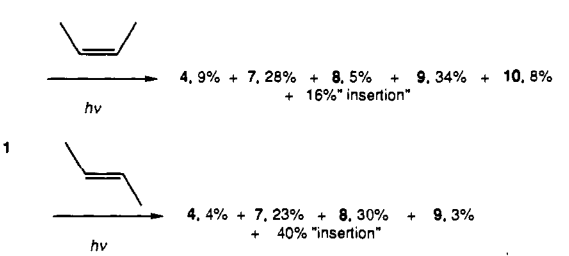

This behavior contrasts both with reactions of 1-*o*-carboranylcarbene[11] and with those of the two-dimensionally aromatic phenylcarbene.[12] For neither of these carbenes are reactions of the triplet detectable, even though the triplet is the ground state in each case.[6,13] Thus, preliminary results bear out the expectation that carbene **2** should show enhanced triplet activity.

Supplementary Material Available: NMR, IR, and mass spectral data of compounds **1**, **4**, **5**, and **7-10** and experimental details for the synthesis and photolysis of **1** (3 pages). Ordering information is given on any current masthead page.

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(9) All new compounds have been characterized by NMR and IR spectroscopy and analyzed by either combustion analysis or precise mass spectrometry.

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A Single-Source Precursor to Titanium Nitride Thin Films. Evidence for the Intermediacy of Imido Complexes in the Chemical Vapor Deposition Process

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Monomeric titanium and zirconium complexes with multiple bonds to oxygen,[2] sulfur,[3] and nitrogen[4] have attracted considerable attention due to their novel structural features and interesting reactivity.[2-5] Recently, we have initiated a research program that is designed to prepare models for complexes involved in chemical

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