state and in very fresh solution. On standing the *trans* form isomerizes to the *cis* form until equilibrium is established between the two, the ratio of *cis* to *trans* being of the order 1.6:1. It is proposed that this isomerization reflects the expected higher dipole moment of the *cis* form. The fairly polar solvents used would tend to shift the *cis–trans* equilibrium toward the *cis* isomer.

An alternative explanation of the nmr spectra would involve the partial dissociation of the bidentate acetylacetone groups to yield the diacetoxysilyl ester of the normal enolate of acetylacetone. This possibility was rejected on the basis of the infrared spectra of the solid material and its solution. The infrared spectra are reproduced in part in Figure 2. The spectra were obtained on a Perkin–Elmer 337 instrument using balanced 0.25-mm path length KBr cells for a 3% w/v methylene chloride solution, and a pressed KBr disk for the solid material. The presence of strong absorptions in the region 1500–1600 cm^{-1}, characteristic of the chelated acetylacetone group,[3] confirms the bidentate nature of the acetylacetone in both the solid material and its solution, as does the absence of any new absorptions in the 1670–1700-cm^{-1} region.[4] The increase in complexity of the acetate C–O stretching region, 1240–1280 cm^{-1}, is consistent with a change from *trans* to *cis*. The coupling of the acetate C–O vibrations through the silicon atom leads to symmetric and antisymmetric stretching modes which should both be infrared active in the *cis* form. Only the antisymmetric mode is infrared active in the *trans* form.

It is hoped that further work with this and related complexes may reveal more about the relative stabilities of *cis* and *trans* forms and the mechanism of *cis* enantiomer isomerization. In the meantime the proposed behavior of the compound suggests that attempts to isolate the geometric and optical isomers would be unsuccessful.

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A New Class of Carboranes. Methyl Derivatives of 2-Carbahexaborane(9)

Sir:

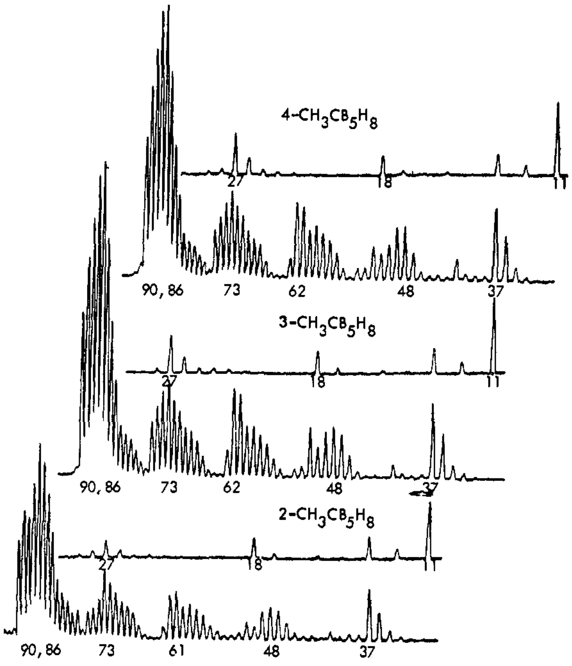

Figure 1. Masss pectra of the methyl derivatives of CB$_5$H$_9$. The parent peak in each case is *m/e* 90. The other *m/e* values represent the most intense peak in each group.

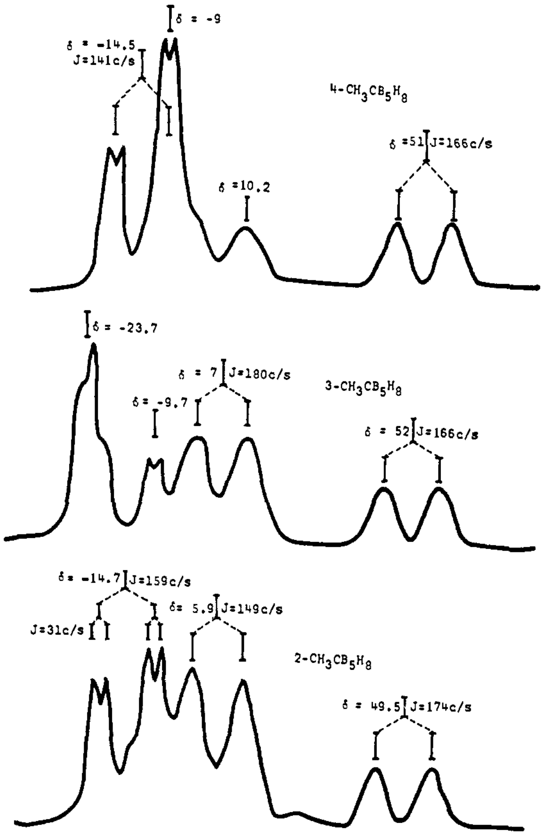

Figure 2. B^{11} nmr spectra at 12.8 Mc of the methyl derivatives of CB$_5$H$_9$. Chemical shifts are referred to BF$_3$·OEt$_2$.

Three new compounds have been isolated from the reaction of acetylene with pentaborane(9) at 215°. They are produced in low yield (1–2%) along with C$_2$B$_4$H$_8$ and may be separated by means of gas chromatographic techniques.[1] Monoisotopic transformation procedures on the nearly identical mass spectra (Figure 1) coupled with the B^{11} nmr spectra at 12.8 Mc (Figure 2) established the empirical formulas C$_2$B$_5$H$_{11}$ for all three compounds. The B^{11} nmr spectra further indicate that they are methyl derivatives of 2-carbahexaborane(9), CB$_5$H$_9$ (Figure 3b). The H^1 nmr spectra which will be discussed in a subsequent publication show, in addition to the broad multiplets due to the

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(1) T. P. Onak, R. P. Drake, and G. B. Dunks, *Inorg. Chem.*, **3**, 1686 (1964).

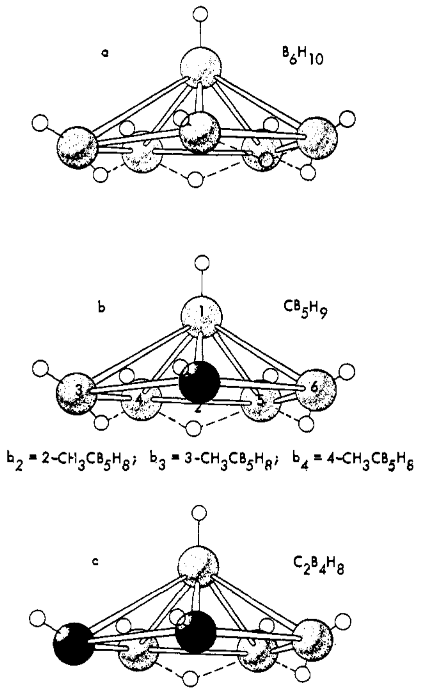

Figure 3. The structure of 2-carbahexaborane(9) and related species.

B–H components, a strong signal assigned to the CH_3 group at τ 8.3, 9.5, and 9.9 ppm for the 2-, 3-, and 4-methyl compounds, respectively. A less intense peak at τ 4.5 in the 3- and 4-methyl isomers represents the skeletal C–H group which is absent in the 2 isomer. This not only supports the proposed structure, but also eliminates an alternative structure for b_2 in Figure 3 which has a hydrogen atom as well as a CH_3 group on the skeletal carbon atom and one less bridge hydrogen atom.

A number of possible mechanisms should be considered to account for the formation of these compounds and the consequent proton and methyl group migrations. The constitution of the products suggests the initial formation of a vinylpentaborane intermediate followed by intramolecular hydroboration and rearrangement. Chemical and isotopic tracer experiments are presently underway to test this scheme as well as to reveal whether or not the 2-methyl isomer is the initial product which rearranges to the others (the 3-methyl isomer is the most abundant).

These derivatives of CB_5H_9 represent a new series of carboranes of the general formula CB_nH_{n+4} (one carbon atom, three bridge hydrogens) which may be added to the other classes of carboranes, *i.e.*, $C_2B_nH_{n+2}$ (two carbon atoms, no bridge hydrogens),[2,3] $C_2B_nH_{n+4}$ (two carbon atoms, two bridge hydrogen atoms),[4] and CB_nH_{n+2} (one carbon atom, one bridge hydrogen).[5] In Figure 3, the structural similarity of CB_5H_9 (b) to B_6H_{10} (a)[6] and $C_2B_4H_8$ (c) may be seen.

The two carboranes result from the successive substitution of BH_2 groups (one bridge and one terminal hydrogen atom) in B_6H_{10} by isoelectronic CH groups. It is apparent that similar substitution in other borane systems should result in additional series of carborane species.

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Regulation of Rate of Reaction of a Polyuridylic Acid Derivative by Use of Suppressor and Antisuppressor Molecules[1,2]

Sir:

It has been demonstrated that the rate of a reaction involving transformations of functional groups X and Y in RX and R′Y may be unusually high when R and R′ bear ionic charges of opposite sign.[1,3] This phenomenon may be attributed to the molecular organization effected by the attractive forces between R and R′. In the present communication it is shown that the rate of reaction in such systems may be controlled, that is, successively decreased and increased at will, by additions to the reaction medium of substances which are chemically inert in the usual sense yet in extremely low concentrations serve as rate regulators. The principle of controlling reaction rates by means of chemical regulators may prove useful in developing a chemistry of complex molecules which react sequentially in a highly selective manner, such as found in biological systems.

A nitrophenyl ester derivative of polyuridylic acid was selected as RX. In solution at pH 8.5 this polymer is negatively charged, and it possesses ester groups which on reaction with imidazole derivatives afford nitrophenoxide, easily detected by the ultraviolet spectrum. It was prepared by warming polyuridylic acid ammonium salt[4] with excess succinic anhydride and pyridine in formamide for 6 hr at 65°, isolating the succinoylated derivative by chromatography in water on Sephadex G-25 followed by lyophilization, and esterifying the succinate derivative with nitrophenol and dicyclohexylcarbodiimide in formamide and pyridine. The resulting polymer (I), purified by chromatography on Sephadex, contained 0.44 nitrophenyl group per uridine unit as indicated by the ultraviolet spectra before and after alkaline hydrolysis. From the method of preparation and the properties of the substance it is probable that the nitrophenyl succinate

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[1] Part V in the series on Selective Catalysis. Part IV: R. L. Letsinger and I. S. Klaus, *J. Am. Chem. Soc.*, **87**, 3380 (1965).

[2] This research was supported by the Division of General Medical Sciences, National Institutes of Health, Grant 10265, and by a Predoctoral Public Health Science Fellowship awarded to T. E. W. (1-Fl-GM-25, 197-01).

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