

## The Structure of Bis(2,4-pentanediono)diacetatosilicon(IV)

Sir:

In a recent communication<sup>1</sup> the preparation and identification of bis(2,4-pentanediono)diacetatosilicon(IV) was reported. Infrared and ultraviolet spectroscopic evidence was presented in support of the bidentate nature of the acetylacetonate ligands and consequent hexacoordination of the silicon atom. It was therefore of interest to examine the nmr spectrum of this material. Studies of a similar nature in other systems had shown this technique to be of value in determining structure and rates of ligand exchange.<sup>2</sup>

In the present work solutions for spectroscopy were prepared in a drybox using carefully dried solvents (chloroform and methylene chloride fractionated over phosphorus pentoxide under a dry nitrogen atmosphere). The nmr spectra were obtained on a Varian A-60 instrument and the results are summarized in Table I and Figure 1. The most striking feature

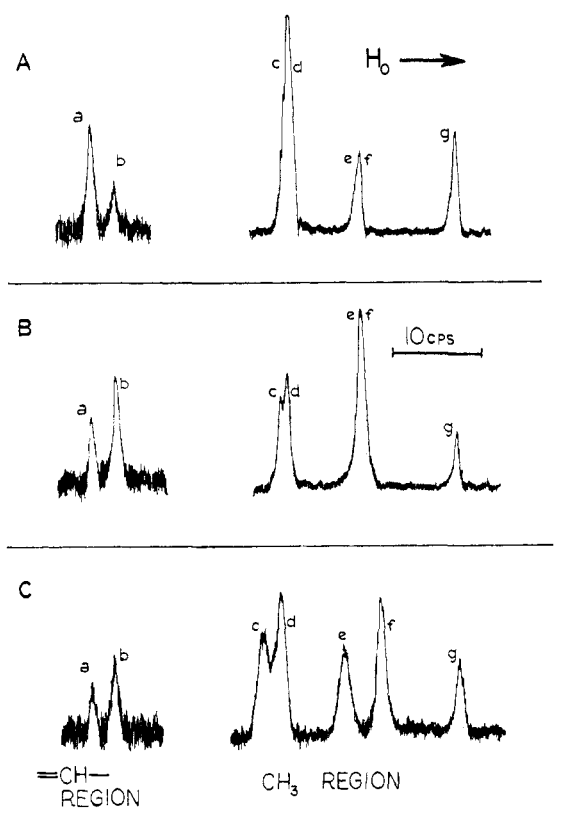


Figure 1. Nmr spectra of  $\text{Si}(\text{acac})_2(\text{C}_2\text{H}_3\text{O}_2)_2$ : (A) fresh solution in  $\text{CHCl}_3$ , (B) aged solution in  $\text{CHCl}_3$ , (C) aged solution in  $\text{CH}_2\text{Cl}_2$ .

observed was the change of the spectrum with time. Thus a few minutes after the preparation of the solution, spectrum A of Figure 1 was obtained. On standing for half an hour the solution exhibited spectrum B. Using methylene chloride as solvent gave a better separation of the peaks (spectrum C). There were essen-

(1) R. M. Pike and R. R. Luongo, *J. Am. Chem. Soc.*, **87**, 1403 (1965).

(2) D. C. Bradley and C. E. Holloway, *Chem. Commun.*, 284 (1965); J. A. S. Smith and E. J. Wilkins, *ibid.*, 381 (1965).

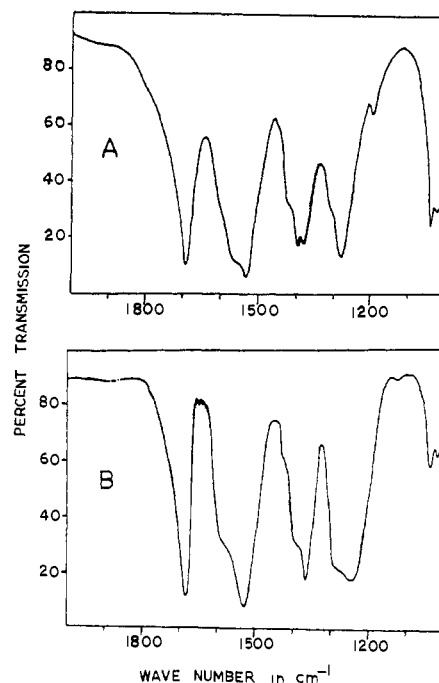


Figure 2. Infrared spectra of  $\text{Si}(\text{acac})_2(\text{C}_2\text{H}_3\text{O}_2)_2$ : (A) solid as KBr disk, (B) solution in  $\text{CH}_2\text{Cl}_2$ .

tially no further changes in spectra B and C with time. Preparation of a solution in the immediate vicinity of the nmr probe, by adding chloroform to the silicon compound by syringe through the sealed cap of an nmr cell, enabled the change through spectrum A to spectrum B to be followed from within 15 sec of solution. The initial spectrum consisted of intense peaks in positions a, d, and g, a small peak in position e, f, and a barely perceptible peak in position b.

Table I. Nmr Chemical Shifts<sup>a</sup>

Isomer	Group	$\text{CHCl}_3$ soln	$\text{CH}_2\text{Cl}_2$ soln	Designation in Figure 1
<i>trans</i>	Acetate	-1.82	-1.92	g
<i>trans</i>	acac:CH <sub>3</sub>	-2.13	-2.25	d
<i>trans</i>	acac:CH	-6.12	-6.00	a
<i>cis</i>	Acetate	-2.00	-2.05	f
<i>cis</i>	acac:CH <sub>3</sub> (1)	-2.00	-2.14	e
	acac:CH <sub>3</sub> (2)	-2.16	-2.27	c
<i>cis</i>	acac:CH	-6.08	-5.97	b
Integrated areas (relative)		$(a + b):(c + d + e + f + g) = 0.85:9.00$ ; required 1.00:9.00		
		$\text{CH}_2\text{Cl}_2$ soln		
		$g:f:e:(d + c) = 1.00:1.61:1.65:3.61$ ; required $f = e$ , and $(d + c + e) = 2(f + g)$		

<sup>a</sup> In ppm relative to TMS as internal standard.

Assignment of the peaks was made with the aid of previous work<sup>2</sup> and confirmed by integration of peak areas where possible (Table I). The time dependence was accounted for in terms of a *cis-trans* isomerization. Thus the material is predominantly *trans* in the solid

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  $\text{cm}^{-1}$ , characteristic of the chelated acetylacetone group,<sup>3</sup> 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- $\text{cm}^{-1}$  region.<sup>4</sup> The increase in complexity of the acetate C–O stretching region, 1240–1280  $\text{cm}^{-1}$ , 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 anti-symmetric 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.

(3) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1965.

(4) R. West, *J. Am. Chem. Soc.*, **80**, 3246 (1958).

(5) Chemistry Department, University of Cincinnati, Cincinnati, Ohio.

Clive E. Holloway<sup>5</sup>

Department of Chemistry, University of Western Ontario  
London, Ontario

Ronald R. Luongo, Ronald M. Pike

Department of Chemistry, Lowell Technological Institute  
Lowell, Massachusetts

Received February 10, 1966

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

Sir:

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  $\text{C}_2\text{B}_4\text{H}_8$  and may be separated by means of gas chromatographic techniques.<sup>1</sup> Monoisotopic transformation procedures on the nearly identical mass spectra (Figure 1) coupled with the  $\text{B}^{11}$  nmr spectra at 12.8 Mc (Figure 2) established the empirical formulas  $\text{C}_2\text{B}_5\text{H}_{11}$  for all

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

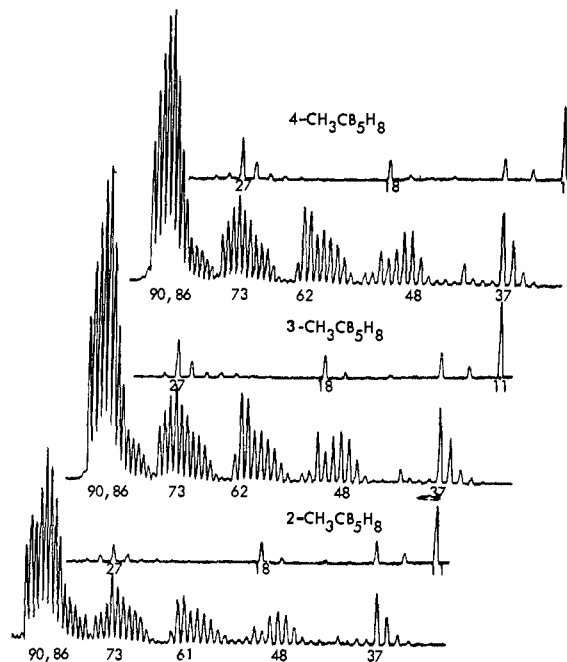


Figure 1. Mass spectra of the methyl derivatives of  $\text{CB}_5\text{H}_9$ . The parent peak in each case is  $m/e$  90. The other  $m/e$  values represent the most intense peak in each group.

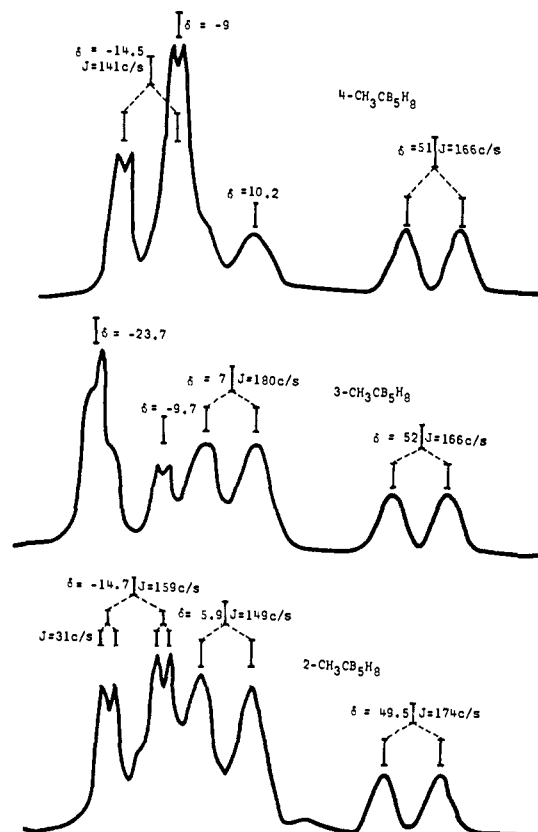


Figure 2.  $\text{B}^{11}$  nmr spectra at 12.8 Mc of the methyl derivatives of  $\text{CB}_5\text{H}_9$ . Chemical shifts are referred to  $\text{BF}_3 \cdot \text{OEt}_2$ .

three compounds. The  $\text{B}^{11}$  nmr spectra further indicate that they are methyl derivatives of 2-carbahexaborane(9),  $\text{CB}_5\text{H}_9$  (Figure 3b). The  $\text{H}^1$  nmr spectra which will be discussed in a subsequent publication show, in addition to the broad multiplets due to the