

THE SYNTHESIS AND REACTIONS OF  
THALLIUM AND DITHALLIUM DICARBOLLIDES

by

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Polytechnic Institute and State University in partial fulfillment  
of the requirements for the degree of

Master of Science

in

Chemistry

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Blacksburg, Virginia

To Patricia, Kofi, and Miesha Smith

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## Part I. Historical Introduction

The chemistry of carborane has had a rapid and continuing growth since the first reported synthesis in 1963 by Heying and coworkers.<sup>1</sup> A number of review articles and books are available which describe the progress through about 1975,<sup>2-4</sup> and the open literature from 1975 to the present contains numerous papers on all aspects of carborane chemistry. Also, in the Journal of Organometallic Chemistry, there are periodic reviews of the progress in carborane chemistry.

Heterocarborane chemistry is the most recent outgrowth of carborane research. Heterocarborane is a term used to describe any neutral species formally derived from a polyhedral borane in which both carbon and a heteroatom are integral parts of the skeletal framework. Also included in the definition of the term are species in which the heteroatom is bonded to the open face of a nido-carborane via a bridge bond.

This thesis discusses research on the thallium-carborane system which essentially involves the insertion of a thallium atom into an open-cage carborane species. A literature survey of some aspects of heterocarborane chemistry is presented in the following section.

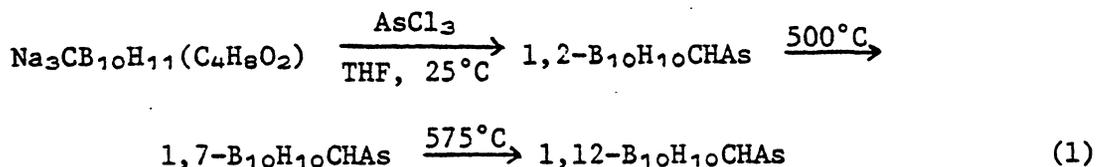
## Part II. Heterocarboranes--A Literature Review

Transition metal derivatives of carboranes are excluded from this discussion because these derivatives have been the subject of several recent articles.<sup>2-7</sup> Most of the compounds discussed here were prepared from carborane anions or nido-carboranes. Essentially, the following syntheses involve insertion of heteroatoms into open-cage carborane species such as  $C_2B_9H_{13}$ ,  $C_2B_9H_{11}^{2-}$ , or their mono-carbon analogs.

A. Icosahedral  $B_{10}CE$  Heterocarboranes (E = Main Group Atom): The insertion of phosphorus into an icosahedral carborane framework was the first reported example of a nontransition metal heterocarborane. This was accomplished by the addition of phosphorus trichloride to  $Na_3CB_{10}H_{11}(C_4H_8O)_2$  in heptane. The product 1,2- $B_{10}H_{10}CHP$  rearranges at 485°C to a second isomer 1,7- $B_{10}H_{10}CHP$ , which is an analog of the isostructural 1,7- $C_2B_{10}H_{12}$  (m-carborane). The addition of butyllithium followed by methyl iodide to 1,7- $B_{10}H_{10}CHP$  yields 1,7- $B_{10}H_{10}C(CH_3)P$ . The 1,2 isomer reacts with excess bromine and aluminum chloride to give 1,2- $B_{10}Br_3H_7CHP$ . The 1,7 isomer, however, can only be dibrominated, indicating a lower polarity than the 1,2 system.<sup>8</sup>

Todd et al.<sup>9</sup> later reported the synthesis and characterization of a number of other "phosphacarborane" derivatives as well as analogs containing antimony and arsenic.

The tetrahydrofuran adduct of  $\text{Na}_3\text{CB}_{10}\text{H}_{11}$  reacts with  $\text{AsCl}_3$  to yield closo-1,2-arsacarborane. Rearrangement to the 1,7-closo species occurs at  $500^\circ\text{C}$ . At  $575^\circ\text{C}$  1,7-closo-arsacarborane rearranges to 1,12-closo-arsacarborane, completing the analogy with the icosahedral  $\text{C}_2\text{B}_{10}\text{H}_{12}$  system.<sup>9</sup>

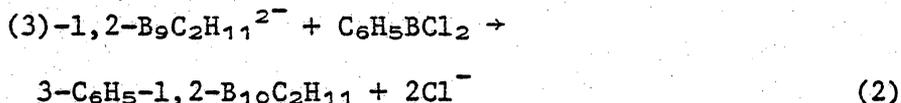


Like the analogous closo-phosphacarboranes, 1,2- and 1,7- $\text{B}_{10}\text{H}_{10}\text{CHAs}$  undergo base degradation to give the isomeric  $\text{B}_9\text{H}_{10}\text{CHAs}^-$  ions, which, based upon a metallocene crystal structure, are presumed to be highly distorted icosahedral fragments. The chemistry of these ions parallels the chemistry of the  $\text{B}_9\text{C}_2\text{H}_{11}^{2-}$  ions, forming arsenic boride ions in strong base and subsequently forming transition metal complexes.<sup>10</sup>

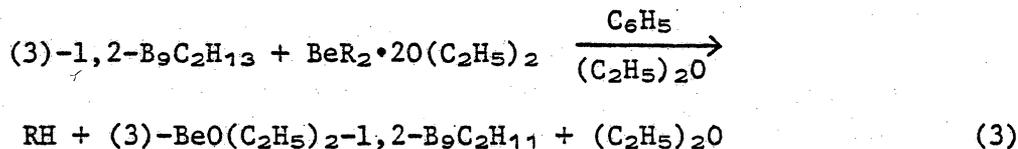
Zakharkin and coworkers<sup>11</sup> prepared methyl-mercury derivatives of 1,2- and 1,7-arsacarborane and phosphacarboranes and investigated the  $^1\text{H}$  NMR spectra. The electron acceptor character of the systems was found to increase in the series  $1,12\text{-B}_{10}\text{H}_{10}\text{C}_2\text{H}_2 < 1,12\text{-B}_{10}\text{H}_{10}\text{CHAs} < 1,12\text{-B}_{10}\text{H}_{10}\text{CHP}$  and  $1,7\text{-B}_{10}\text{H}_{10}\text{C}_2\text{H}_2 < 1,7\text{-B}_{10}\text{H}_{10}\text{CHAs} < 1,7\text{-B}_{10}\text{H}_{10}\text{CHP}$ . A nuclear quadrupole resonance study of  $^{75}\text{As}$  in 1,2-, 1,7-, and 1,12-arsacarborane also was carried out by Zakharkin. The NQR frequency of the 1,2-isomer was found to be substantially higher than that of the 1,7- and 1,12 isomers, reflecting the difference in the symmetry of the short-range surrounding of the arsenic atom in these compounds.

B. Icosahedral B<sub>9</sub>C<sub>2</sub>E Heterocarborane (E = Main Group

Atom): After the initial report by Hawthorne and Wagner on the reconstruction of the 1,2-dicarbido-closo-dodecaborane(12) icosahedron by the reaction of the (3)-1,2-dicarbollide ion, (3)-1,2-B<sub>9</sub>C<sub>2</sub>H<sub>11</sub><sup>2-</sup>, with RBCl<sub>2</sub> reagents,



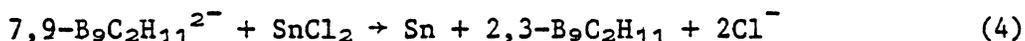
Popp and Hawthorne reported the successful synthesis of (3)-BeO(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>-1,2-B<sub>9</sub>C<sub>2</sub>H<sub>11</sub>.<sup>13</sup> Dimethylberyllium attacks (3)-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>13</sub> in ether to form a polyhedral cage structure containing beryllium at the originally vacant (3) position coordinated to an ether molecule.



Replacement of the ether with trimethylamine yields (3)-BeN(CH<sub>3</sub>)<sub>3</sub>-1,2-B<sub>9</sub>C<sub>2</sub>H<sub>11</sub>. Both complexes may be regarded as base-substituted derivatives of C<sub>2</sub>BeB<sub>9</sub>H<sub>12</sub><sup>-</sup> which is isoelectronic with CB<sub>11</sub>H<sub>12</sub><sup>-</sup> and C<sub>2</sub>B<sub>10</sub>H<sub>12</sub><sup>3-</sup>.

The reaction of trialkylaluminum and trialkylgallium with (3)-1,2-B<sub>9</sub>C<sub>2</sub>H<sub>13</sub> produces two series of derivatives: 1,2-B<sub>9</sub>C<sub>3</sub>H<sub>12</sub>ER<sub>2</sub> and 3-R-3E-1,2-B<sub>9</sub>C<sub>3</sub>H<sub>11</sub> (E = Al, R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>; E = Ga, R = C<sub>2</sub>H<sub>5</sub>). The former are tautomeric nido compounds containing bridging ER<sub>2</sub> groups, presumably attached through B-H-E bridges. Heating of the nido compounds in benzene yields the closo derivatives, 3-R-3E-1,2-B<sub>9</sub>C<sub>3</sub>H<sub>11</sub>.

Treatment of (3)-1,2- $B_9C_2H_{11}^{2-}$  with germanium, tin, and lead reagents leads to the formation of icosahedral tricarbaborane analogs,  $EC_2B_9H_{11}$  (E = Ge, Sn, Pb).<sup>14</sup> Rudolph et al.<sup>15</sup> found that treatment of the 7,9- $B_9C_2H_{11}^{2-}$  with  $SnCl_2$  produces an unexpected oxidative closure reaction. Since  $SnCl_2$  is not usually thought of as an oxidizing agent, the meta dicarbollide ion apparently is a relatively strong reducing agent.<sup>15</sup>



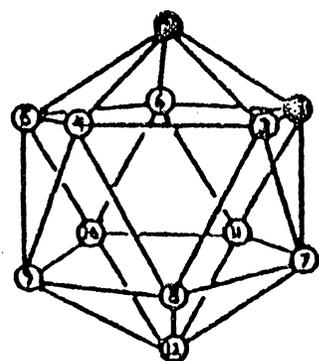
Spencer, Green, and Stone reported the synthesis of thallium derivatives of (3)-1,2- and (3)-1,7- $C_2B_9H_{11}^{2-}$  ions,  $Tl_2B_9C_2H_{11}$ .<sup>16</sup> One of the thallium atoms is readily replaced by other cations. This was interpreted to suggest the presence of the icosahedral ion  $TlB_9C_2H_{11}^-$ .

### Part III. Nomenclature

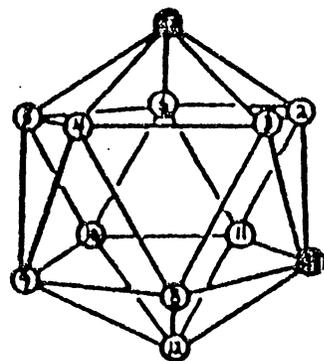
The systematic naming of polyhedral compounds presents unusual problems, and this is reflected by the lack of uniformity in the carborane literature.<sup>16-18</sup> No single universally accepted nomenclature exists for such compounds. The term "carborane" was originally introduced as the name given to compounds having the formula  $C_2B_nH_{n+2}$ . The term is generally used now to describe any polyhedral boron-carbon compound in which the carbon atoms occupy an integral position in the skeleton. The term also is widely used as the trivial name for the  $C_2B_{10}H_{12}$  compounds (three isomers) (Figure 1).

The introduction of atoms other than boron and carbon into polyhedral borane frameworks has considerably complicated the nomenclature picture. The most widely used and accepted nomenclature system for heterocarboranes is that of Hawthorne in which a combination of trivial and systematic nomenclature results in a much simplified scheme. The Hawthorne system was devised to simplify the naming of metal complexes of the  $B_9C_2H_{11}^{2-}$  ion (Figure 2). The term dicarbollide, introduced by Hawthorne, is now generally accepted as the trivial name for the  $B_9C_2H_{11}^{2-}$  species and in analogy to the cyclopentadienyl complexes, complexes of  $B_9C_2H_{11}^{2-}$  are called dicarbollyl complexes.

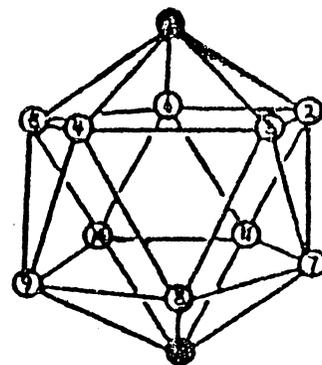
However, there is a system for the systematic naming of polyhedral compounds. The system was prepared by the Nomenclature Committee of the Division of Inorganic Chemistry of the American



1,2-  
(ortho)

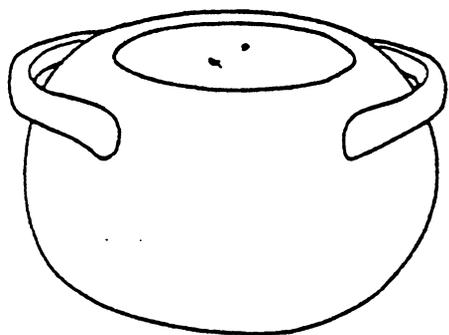


1,7-  
(meta)

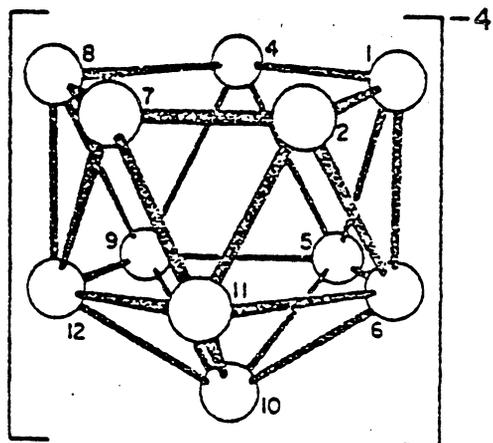


1,12-  
(para)

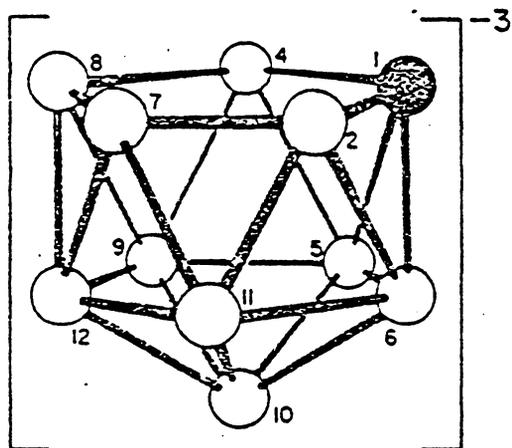
Figure 1. Icosahedral Carborane Configuration.



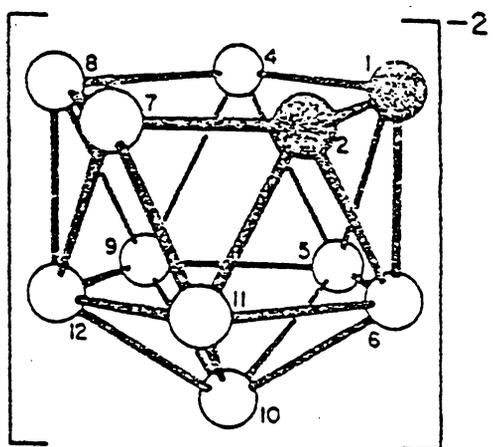
olla  
(Jar)



ollide  
( $B_{11}H_{11}^{-4}$ )



carbollide  
 $B_{10}CH_{11}^{-3}$



dicarbollide  
 $B_9C_2H_{11}^{-2}$

Figure 2. Hawthorne Nomenclature for the  $B_{11}H_{11}^{4-}$ ,  $B_9C_2H_{11}^{2-}$ , and  $B_{10}CH_{11}^{3-}$  Ions.

Chemical Society. In this scheme, a carborane is named as a borane in which one or more boron atoms have been replaced by carbon and the familiar oxa-aza convention of organic chemistry is followed. Closed-cage and open-cage systems are designated by the prefixes *closo-* and *nido-*, respectively, and the numbering of hydrogens is given in parentheses. Ions are given the ending *-borate* and the charge is enclosed in parentheses.<sup>3</sup> Examples of each are given below.

$C_2B_3H_5$       dicarba-*closo*-pentaborane(5)

$C_2B_4H_8$       dicarba-*nido*-hexaborane(8)

$C_2B_4H_7^-$       heptahydrodicarba-*nido*-hexaborate(1-)

Heterocarboranes derived from the dicarbollide ion can be named by using "carborane" interchangeably with dicarba-*closo*-dodecarborane(12). For example,  $CH_3AsB_9C_2H_{11}$  is named 3-methyl-3-arsa-1,2-dicarba-*closo*-dodecarborane(12). The thallacarborane,  $TlB_9C_2H_{12}$  is named 3-thalla-1,2-dicarba-*closo*-dodecarborane(12).

## Part IV. Experimental

### Material and Apparatus

All hydrocarbon and ether solvents used in this research were purified by distillation from calcium hydride. Analytical reagent-grade halogenated solvents were used as received from various commercial sources unless otherwise specified. Carborane was obtained from Olin Chemical Corporation. Thallium acetate was obtained from Alfa Inorganics.

For pyrolysis studies, a special reactor (Figure 3) was constructed from Pyrex glass. The reactor resembled a standard vacuum sublimator with the cold finger extending to approximately 1.25 inches above a flat bottom. The total volume of the reactor was approximately 125 mL. The top and bottom portions of the reactor were connected via a ground-glass flat surface. Attachment to the vacuum line was through a 2-mm vacuum stopcock with a standard ground-glass joint.

All operations were conducted under a chemically pure nitrogen atmosphere or in a standard high-vacuum glass vacuum line.

### Infrared Spectra

Infrared spectra were recorded with a Beckman IR 20A-X spectrometer. Solids were run as  $\text{CCl}_4$  or nujol mulls or neat.

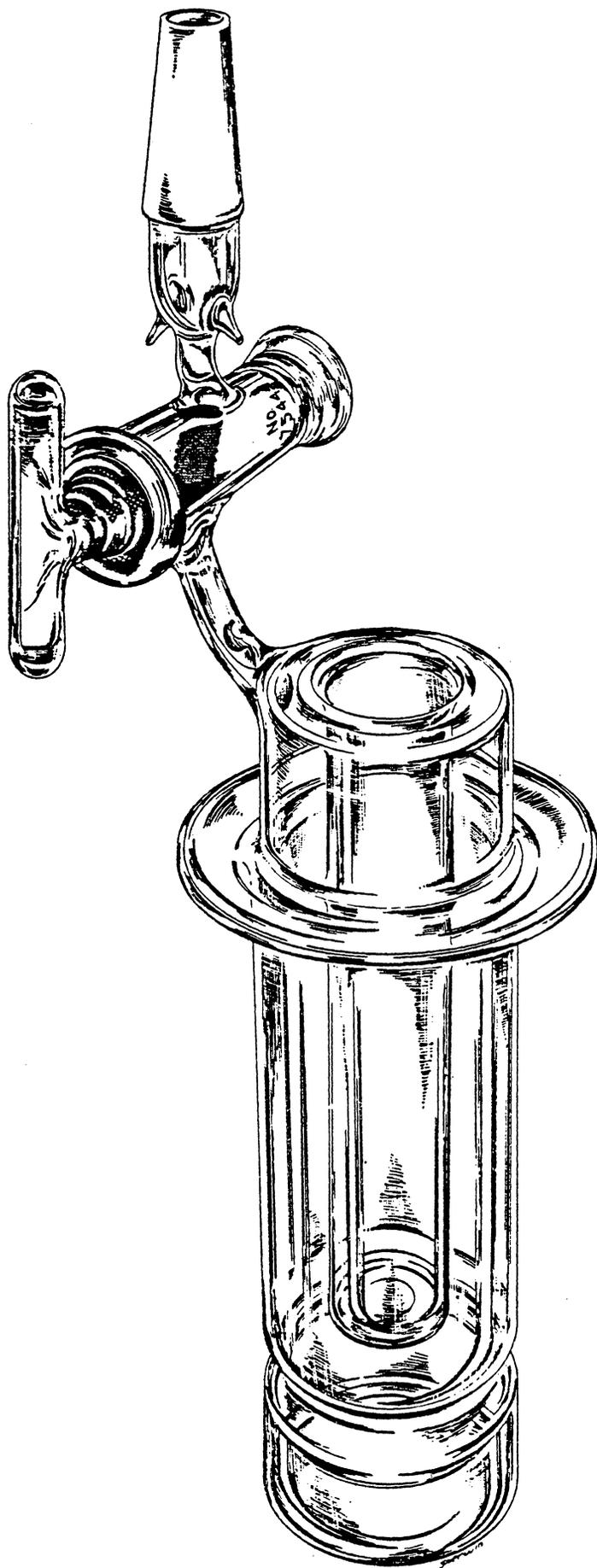


Figure 3. Special Reactor for Pyrolysis Studies.

### Nuclear Magnetic Resonance Spectra

Proton magnetic resonance data were recorded on a Jelco Model JNB-PS-100 MHz spectrometer by the analytical section of the chemistry department at VPI&SU.

The 80.5-MHz  $^{11}\text{B}$  NMR spectra were obtained on an instrument designed and built by Professor F.A.L. Anet and his research group at UCLA.

### Mass Spectra

Mass spectral data were obtained on a Perkin-Elmer RMU-7 spectrometer by Dr. Dillard and/or members of his research group in this department. Mass spectral data also were obtained through the biochemistry department at VPI&SU.

### Analyses

Carbon and hydrogen analyses were obtained through the analytical section of this department. Further elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee, and Schwarzkopt Microanalytical Laboratory, Inc., Woodside, New York.

### Purification of the Carboranes [o-Carborane, 1-Methyl-o-Carborane, 1,2-Dimethyl-o-Carborane]

The carborane was dissolved in hot petroleum ether. A small amount of carbon black was added to the hot solution, then the hot solution was filtered, reheated, and refiltered. The

carborane was crystallized by cooling the solution to  $-80^{\circ}\text{C}$  (acetone-dry ice slush). The crystals were filtered and dried on the vacuum line. The melting point and infrared data were compared with published data.

#### Dicarbollide Ions ( $\text{R}^1\text{R}^2\text{C}_2\text{B}_9\text{H}_{10}^{2-}$ )

Ions of the general formula  $\text{R}^1\text{R}^2\text{C}_2\text{B}_9\text{H}_{10}^{2-}$  ( $\text{R}^1=\text{R}^2=\text{H}$ ;  $\text{R}^1=\text{H}$ ,  $\text{R}^2=\text{CH}_3$ ;  $\text{R}^1=\text{R}^2=\text{CH}_3$ ) were prepared and purified by the general degradation and purification procedure of Hawthorne et al.<sup>16</sup>

#### Dithallium Dicarbollides ( $\text{Tl}_2\text{R}^1\text{R}^2\text{C}_2\text{B}_9\text{H}_9$ )

Compounds of the general formula  $\text{Tl}_2\text{R}^1\text{R}^2\text{C}_2\text{B}_9\text{H}_9$  ( $\text{R}^1=\text{R}^2=\text{H}$ ,  $\text{R}^1=\text{H}$ ,  $\text{R}^2=\text{CH}_3$ ;  $\text{R}^1=\text{R}^2=\text{CH}_3$ ) were prepared according to the method of Spencer, Green, and Stone.<sup>16</sup> The products were isolated via filtration; washed successively with distilled water, ethanol, and hexane; then dried on the vacuum line for approximately 12 hours. The products were powders and ranged in color from pale yellow to bright yellow ( $\text{R}^1=\text{R}^2=\text{H}$ , pale yellow;  $\text{R}^1=\text{H}$ ,  $\text{R}^2=\text{CH}_3$ , yellow;  $\text{R}^1=\text{R}^2=\text{CH}_3$ , bright yellow). As indicated by Stone et al.<sup>16</sup>, each salt was identified by its melting point (decomposition) and infrared spectrum. The infrared spectral data for each compound are recorded in Table I.

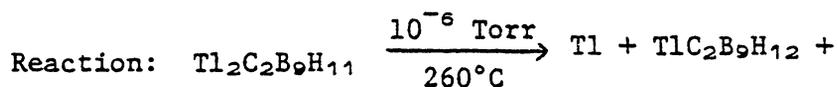
#### Pyrolysis of $\text{Tl}_2\text{C}_2\text{B}_9\text{H}_{11}$

All of the pyrolysis reactions were repeated a minimum of three times.

Table I. Infrared Spectra, <sup>a</sup> cm<sup>-1</sup> (Intensity)

TlC <sub>2</sub> B <sub>9</sub> H <sub>12</sub> <sup>b</sup>	2900 s, 2600-2380 s, mult, 1470 s, 1377 s, 1265 m, 1180 m, 1090 m, 1040 s, 1030 s, 985 m, 955 w, 912 m, 889 m, 880 w, 858 w, 820 w, 777 m, 746 m, 730 m, 723 m, 695 m
Tl(CH <sub>3</sub> )C <sub>2</sub> B <sub>9</sub> H <sub>11</sub> <sup>c</sup>	2960 m, 2940 m, 2915 m, 2880 m, 2855 m, 2540-2470 s, mult, 1457 m, 1488 m, 1377 w, 1273 w, 1155 w, 1125 w, 1087 w, 1060 w, 1030 s, 995 s, 960 w, 920 w, 898 w, 775 vs
Tl(CH <sub>3</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>9</sub> H <sub>10</sub> <sup>c</sup>	2975 m, 2940 m, 2880 m, 2580-2620 s, mult, 1455 s, 1390 m, 1380 m, 1260 w, 1205 m, 1110 m, 1070 m, 1027 s, 955 w, 922 m, 900 m, 890 m, 830 m, 775 vs, 685 w, 660 m, 630 m

<sup>a</sup>Key; s = strong; m = medium; w = weak; v = very; mult = multiplet. <sup>b</sup>Nujol mull. <sup>c</sup>Carbon tetrachloride mull.



decomposition products

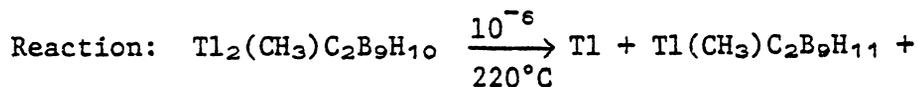
(5)

Two grams of  $\text{Tl}_2\text{C}_2\text{B}_9\text{H}_{12}$  was placed in the specially designed reactor and the reactor was attached to the high-vacuum line and evacuated to  $10^{-6}$  Torr. The reactor was slowly heated (oil bath) to  $100^\circ\text{C}$  at  $10^{-6}$  Torr. After approximately one hour at  $100^\circ\text{C}$ , the cold finger was filled with a dry ice-acetone slush ( $-80^\circ\text{C}$ ) and the reactor was quickly heated to  $260^\circ\text{C}$ . A vigorous reaction ensued, accompanied by bubbling of the melt. During the reaction the material volatile enough to pass the  $-80^\circ\text{C}$  cold finger was passed into a  $-196^\circ\text{C}$  (liquid nitrogen) trap. The reaction required approximately 2 hours and 45 minutes to go to completion. When the reaction was complete the cold finger was allowed to warm to room temperature. The reactor was removed from the vacuum line and transferred to the dry box (dry nitrogen filled) where the sublimate was removed and later identified as  $\text{TlC}_2\text{B}_9\text{H}_{12}$ . Analytical data are given in Table II.

The sublimate of the above reaction on the second run was extracted with hot benzene. The product was crystallized from a benzene-hexane mixture.

$\text{TlC}_2\text{B}_9\text{H}_{12}$  was found to be crystallizable from benzene-hexane, diethyl ether-hexane, benzene-chloroform, and water.

#### Pyrolysis of $\text{Tl}_2(\text{CH}_3)\text{C}_2\text{B}_9\text{H}_{10}$



decomposition products

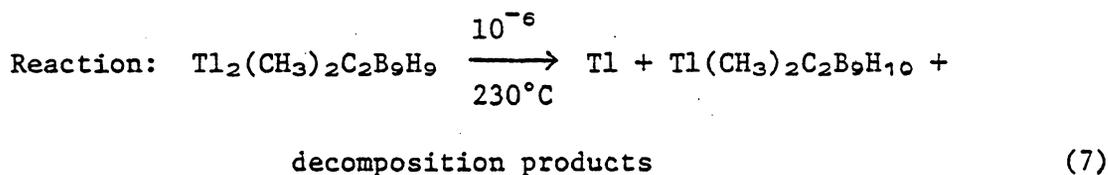
(6)

Table II. Analytical Data

	Mp (dec), °C	Elemental analysis (theory), %				Mol wt (calcd for monomer)		Mass spec cutoff (m/e at 34 and 70 eV)
		B	C	H	Tl	Benzene	Ethyl acetate	
TlC <sub>2</sub> B <sub>9</sub> H <sub>12</sub>	260	29.23 (28.75)	7.34 (7.13)	3.63 (3.56)	60.94 (60.51)			340
Tl(CH <sub>3</sub> )C <sub>2</sub> B <sub>9</sub> H <sub>11</sub>	295	27.51 (27.73)	10.41 (10.27)	3.89 (3.73)		697 (351.67)	374 (351.67)	354
Tl(CH <sub>3</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>9</sub> H <sub>10</sub>	290	25.00 (26.61)	13.54 (13.13)	5.00 (4.38)	55.72 (55.88)	534 (365.67)	362 (365.67)	368

The procedure was the same as that described for  $Tl_2C_2B_9H_{11}$ . The reaction required approximately two hours to go to completion. The reactor and cold finger were cooled to room temperature and the sublimate was extracted with dry, hot benzene. The product was crystallized from a benzene-hexane mixture. The crystals were identified as  $Tl(CH_3)_2C_2B_9H_{11}$ . Analytical data are given in Table II.

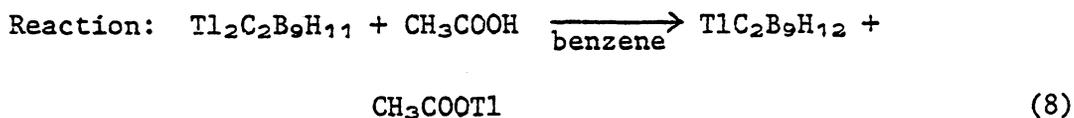
Pyrolysis of  $Tl_2(CH_3)_2C_2B_9H_9$

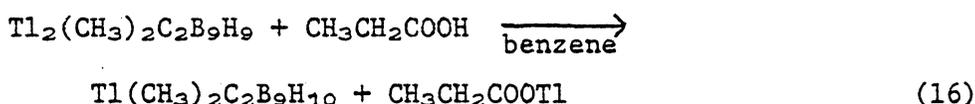
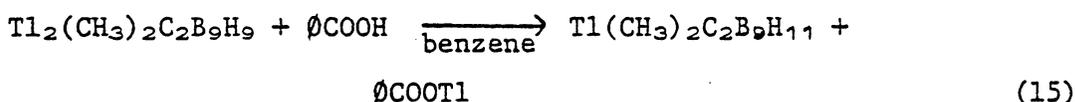
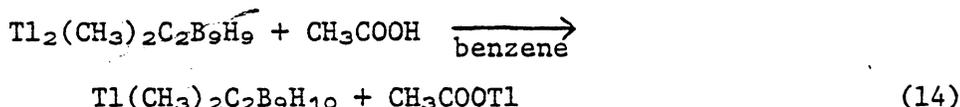
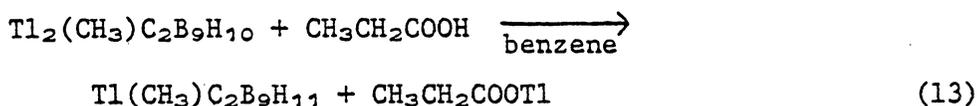
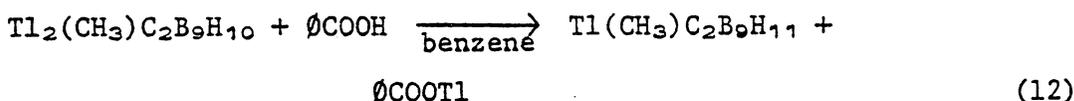
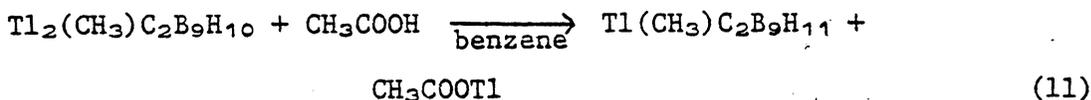
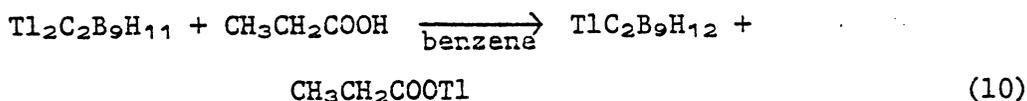
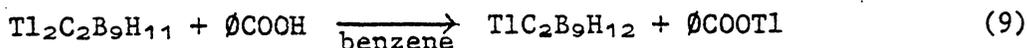


The procedure was the same as that described earlier. The reaction required approximately three hours to go to completion. The reactor was cooled to room temperature and the sublimate was extracted with dry, hot benzene. The product was crystallized from a benzene-hexane mixture. The resulting crystals were identified as  $Tl(CH_3)_2C_2B_9H_{10}$ . Analytical data are given in Table II.

Reaction of  $Tl_2R^1R^2C_2B_9H_9$  With Acid

Reaction of  $Tl_2R^1R^2C_2B_9H_9$  With Weak Acids: The procedure for the following weak acid reactions is the same as the one described below for  $Tl_2C_2B_9H_{11} + CH_3COOH$  unless otherwise specified. The reactions were repeated a minimum of three times.





Forty milliliters of benzene was placed in a 100-mL, two-necked, round-bottomed flask with magnetic stirrer. Glacial acetic acid (0.0037 mol) was added to the benzene. The flask was attached to the vacuum line by a standard adaptor.  $\text{Tl}_2\text{C}_2\text{B}_9\text{H}_{11}$  (0.0037 mol) was placed in a specially designed glass tube (Figure 4) and the tube attached to the two-necked flask. The tube design allowed the reactor and tube to be evacuated without mixing the  $\text{Tl}_2\text{C}_2\text{B}_9\text{H}_{11}$  with the benzene-acetic acid mixture. After the system was evacuated,  $\text{Tl}_2\text{C}_2\text{B}_9\text{H}_{11}$  was added to the reactor with stirring. The pale yellow powder turned to a white

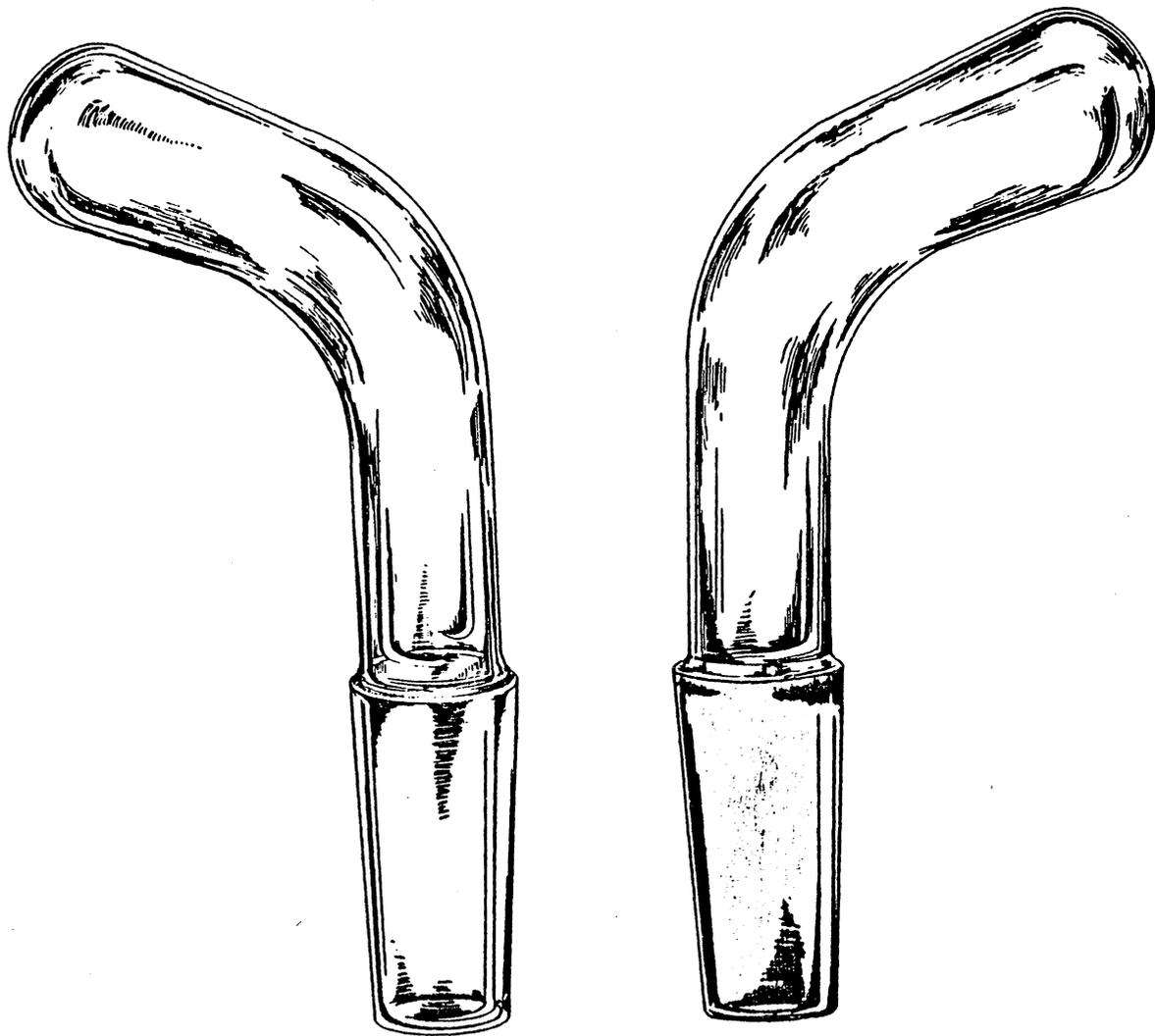
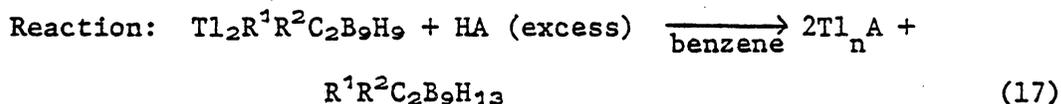


Figure 4. Special Designed Glass Tube.

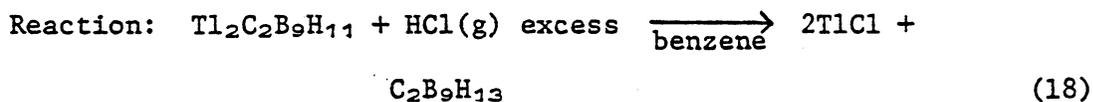
crystalline solid. The reaction required approximately 15 minutes to go to completion. The system was allowed to stand for 30 minutes, then nitrogen was added to the reactor through the vacuum line. A Schlenk tube was placed on the reactor, the entire system was removed from the vacuum line, and the insoluble product filtered and later identified as thallium acetate. The filtrate was stripped on the vacuum line and the residue extracted with hot benzene. The product was crystallized from a benzene-hexane mixture. Melting point, mass spectral, and infrared spectral data were used to identify the product.

Reaction of  $Tl_2R^1R^2C_2B_9H_9$  With Strong Acids



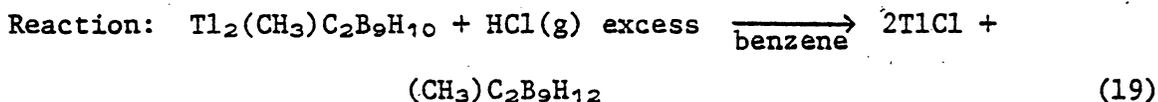
where  $HA = HCl, H_2SO_4, H_3PO_4$  and  $n = 1, 2, \text{ or } 3$ ).

The procedure for the following strong acid reactions is the same as the one described below for  $Tl_2C_2B_9H_{11} + HCl$  (excess), unless otherwise specified. The reactions of the strong acids were repeated a minimum of three times.

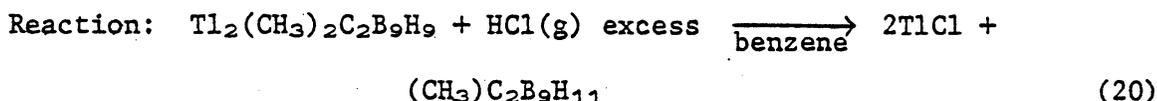


Approximately 1 g of  $Tl_2C_2B_9H_{11}$  was placed in a 250-mL, two-necked flask with a micro stirrer and 40 mL of benzene.  $HCl(g)$  was bubbled through the suspension with a fritted dispersion stick. The reactor was under an inert (nitrogen) atmosphere. After approximately 10 minutes the pale yellow precipitate turned to a white solid. The mixture was filtered under nitrogen and the benzene

solvent removed under vacuum (the filter cake was later identified as TlCl). The residue was a white crystalline solid identified by its mass spectrum as  $C_2B_9H_{12}$ .



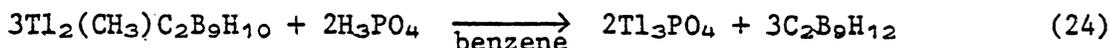
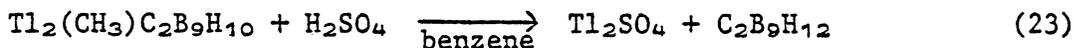
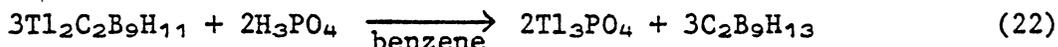
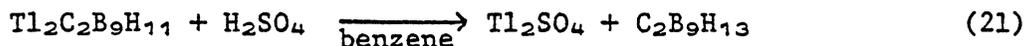
The methyl product was a colorless, moisture-sensitive semisolid, identified by its mass spectrum as  $(CH_3)C_2B_9H_{12}$  (m/e cutoff at 148 corresponding to parent minus two hydrogen atoms).

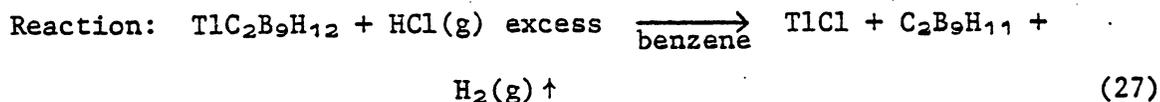
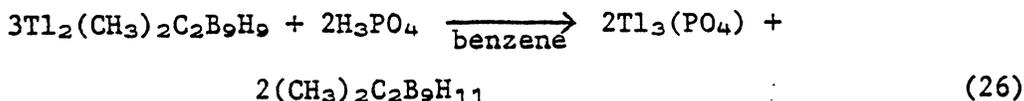
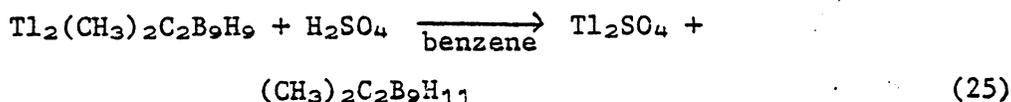


The dimethyl product,  $(CH_3)_2C_2B_9H_{11}$ , was a white crystalline solid identified by its mass spectrum, infrared spectrum, and melting point. The mass spectrum exhibited a cutoff at m/e 162. A small amount of the sample,  $(CH_3)_2C_2B_9H_{11}$  was heated in benzene under reflux conditions, hydrogen was evolved, and  $(CH_3)_2C_2B_9H_9$  was recovered.

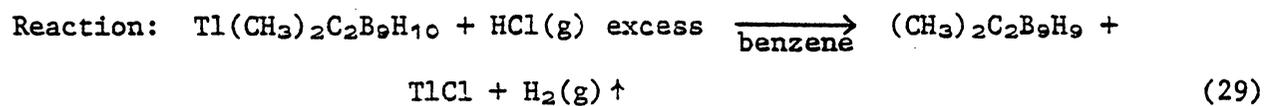
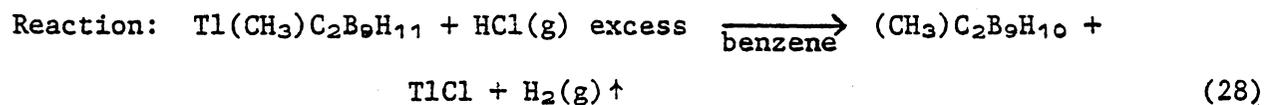
The procedures for the following strong acid reactions are similar to the ones for the weak acids.

Reactions:





One gram of  $\text{TlC}_2\text{B}_9\text{H}_{12}$  was placed in the specially designed sublimator (described in the pyrolysis procedure) which contained a micro stirring bar and approximately 15 mL of benzene. The sublimator was attached to the vacuum line and quickly evacuated and closed off. A  $\text{HCl(g)}$  cylinder was attached to the vacuum line by an inlet system and the system was evacuated. A section of the vacuum line was isolated and 0.104 g of  $\text{HCl(g)}$  was let into the isolated section of the vacuum line. The  $\text{HCl(g)}$  was condensed into the reactor by opening the reactor to the closed section of the vacuum line and cooling the reactor to  $-196^\circ\text{C}$ . The reactor was again closed to the vacuum line and allowed to warm to room temperature. A white precipitate immediately formed. The benzene was removed from the sublimator by the vacuum line. The cold finger was cooled to  $-80^\circ\text{C}$  and the reactor heated to  $110^\circ\text{C}$  for 25 minutes. The system was allowed to cool to room temperature, then nitrogen was let into the reactor through the vacuum line. The reactor was transferred to the dry box and the sublimate later identified as  $\text{C}_2\text{B}_9\text{H}_{11}$ .



The procedures for the above reactions were the same as those described for the  $\text{TlC}_2\text{B}_9\text{H}_{12}$ - $\text{HCl}(\text{g})$  system.

## Part V. Results and Discussion

The  $C_2B_9H_{11}^{2-}$  ion (dicarbollide ion, Figure 5) contains an open pentagonal face, incorporating two carbon and three boron atoms, which has five atomic orbitals directed towards the empty apical position.<sup>3</sup> Transition metal heterocarboranes derived from the dicarbollide ion have flourished in the literature since Hawthorne et al.<sup>17</sup> first reported the ferrocene analogs  $(C_2B_9H_{11})_2Fe^{2-}$  and  $(C_2B_9H_{11})Fe(C_5H_5)$  in 1965. However, only a limited number of nontransition metal heterocarboranes have been reported.

The reported preparation of a nontransition metal heterocarborane,  $Tl_2R^1R^2C_2B_9H_9$  ( $R^1=R^2=H$ ;  $R^1=H$ ,  $R^2=CH_3$ ;  $R^1=R^2=CH_3$ ) by Stone et al.,<sup>16</sup> suggested the intriguing possibility that one of the thallium atoms was covalently bonded to the pentagonal face of the dicarbollide ion.

Therefore, we have undertaken an investigation to understand the chemistry of thallium derivatives of carboranes. This thesis reports the synthesis and characterization of thallium-containing heterocarboranes formed by the vacuum pyrolysis of  $Tl_2R^1R^2C_2B_9H_9$  and the reaction of  $Tl_2R^1R^2C_2B_9H_9$  with weak acids.

The pyrolysis of the  $Tl_2R^1R^2C_2B_9H_9$  ( $R^1=R^2=H$ ;  $R^1=H$ ,  $R^2=CH_3$ ;  $R^1=R^2=CH_3$ ) compounds yielded thallium metal and the corresponding  $TlR^1R^2C_2B_9H_{10}$  compounds as the major products.

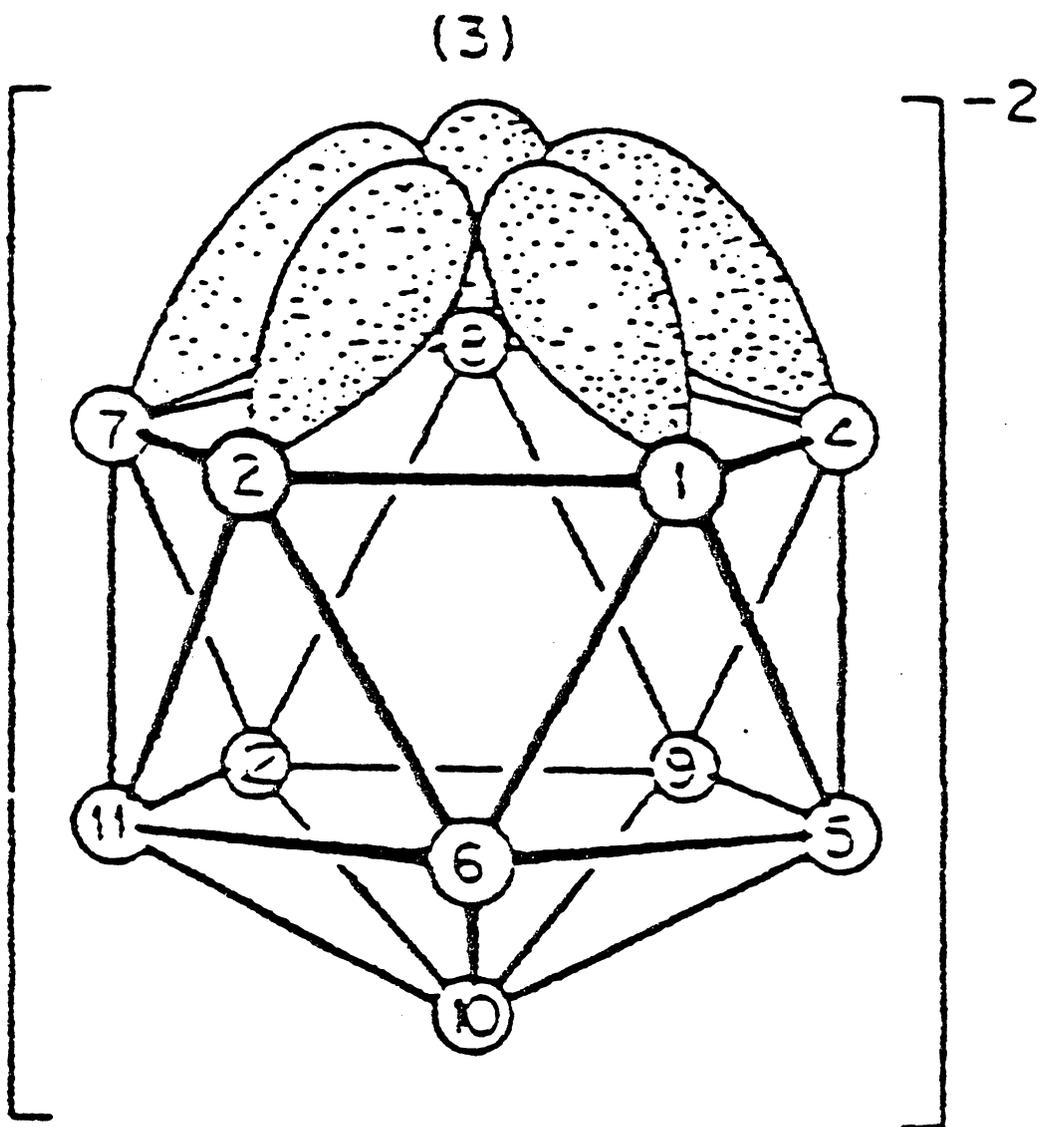
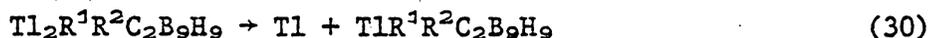


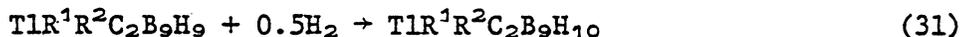
Figure 5.  $C_2B_9H_{11}^{2-}$  Ion (Dicarbollide Ion).

Hydrogen and the corresponding closo-carborane  $R^1R^2C_2B_9H_9$  were produced as minor products. An analysis of the thallium metal found it to be contaminated with approximately 3% boron, 0.3% hydrogen, and 0.7% carbon. The thallacarboranes,  $TlR^1R^2C_2B_9H_{10}$ , are all white, crystalline, relatively volatile, air-stable compounds. These compounds are soluble in benzene and other aromatic solvents, THF and diethyl ether (slightly) and insoluble in hydrocarbons ( $CS_2$ ,  $CCl_4$ , etc.).

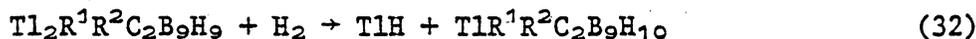
Our initial investigation of the pyrolysis of  $Tl_2R^1R^2C_2B_9H_9$  led us to believe that the thallacarborane should be formulated  $TlR^1R^2C_2B_9H_9$  and that the reaction was a disproportionation.



However, the formulation of the product as  $TlR^1R^2C_2B_9H_9$  requires that either thallium be considered formally  $Tl(II)$  or that the dicarbollide species be considered a monoanion. In either case the odd electron species should give an esr signal. No esr signal was detected. It is possible, however, that reaction 30 does occur as an immediate step. The  $TlR^1R^2C_2B_9H_9$  species then could react with hydrogen in the high-temperature melt.

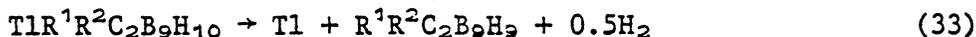


Another possibility is that  $Tl_2R^1R^2C_2B_9H_9$  reacts directly with the hydrogen at high temperatures.



The contamination of the thallium metal with small amounts of boron, carbon, and hydrogen suggests that the hydrogen is produced via initial decomposition of some of the starting material.

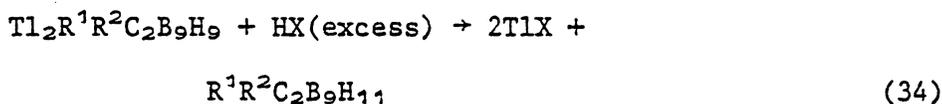
Furthermore, the presence of small amounts of the closo-carboranes  $R^1R^2C_2B_9H_9$  can only be attributed to further decomposition of  $TlR^1R^2C_2B_9H_{10}$  via an oxidative closure reaction.



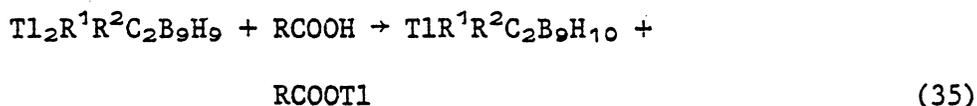
The oxidative closure reaction of  $TlR^1R^2C_2B_9H_{10}$  appears to be similar to the pyrolytic oxidative closure of (3)-Sn-7,9- $C_2B_9H_{11}$  reported by Rudolph et al.<sup>15</sup>

Because the overall pyrolysis of  $Tl_2R^1R^2C_2B_9H_9$  requires temperatures no higher than 325°C and because all of the thallacarboranes, though volatile at low pressures, readily dissociate at moderate temperatures, the oxidative closure reaction of  $TlR^1R^2C_2B_9H_{10}$  suggests a convenient route to the closo-carboranes  $R^1R^2C_2B_9H_9$  by the pyrolysis of  $Tl_2R^1R^2C_2B_9H_9$  species.

The reaction of  $Tl_2R^1R^2C_2B_9H_9$  with strong protic acids (HX, where  $X^- = Cl^-, H_2SO_4^-, H_2PO_4^-$ , etc.) produces the nido-carboranes  $R^1R^2C_2B_9H_{11}$  in analogy to the reactions of other metal dicarbollides.



In contrast to the action of strong protic acids, weak acids such as acetic and benzoic acids react according to the following equation:



The thallacarboranes produced by the action of weak acids are identical to those produced via pyrolysis. The action of the weak acids of the above equation was expected because one of the thallium atoms is covalently bonded to the dicarbollide ion. On the other hand, the strong protic acid could conceivably break the polar-covalent bond producing the nido carboranes. The nido-carboranes were readily identified by melting points, infrared spectra, and mass spectra.

The unsubstituted thallacarborane,  $\text{TlC}_2\text{B}_9\text{H}_{12}$ , was not sufficiently soluble in benzene to obtain molecular weight data.  $\text{TlC}_2\text{B}_9\text{H}_{12}$  is monomeric in ethyl acetate solution. The mass spectrum showed the anticipated parent ion ( $m/e$  340 corresponding to  $^{205}\text{Tl}^{12}\text{C}_2^{11}\text{B}_9^1\text{H}_{12}$ ). The  $^1\text{H}$  NMR spectrum of  $\text{TlC}_2\text{B}_9\text{H}_{12}$  showed the expected C-H resonance. The  $^{11}\text{B}$  NMR spectrum in benzene (poorly resolved) and in acetic acid was identical to the (3)-1,2- $\text{C}_2\text{B}_9\text{H}_{12}^-$  reported by Hawthorne et al. Our proposed icosahedral geometry of  $\text{TlC}_2\text{B}_9\text{H}_{12}$  is consistent with Hawthorne's characterization of (3)-1,2- $\text{C}_2\text{B}_9\text{H}_{12}^-$ . The molecular weight, mass spectral data, melting point, and elemental analyses are shown in Table III. The infrared spectrum is shown in Figure 6.

The monomethyl derivative,  $\text{Tl}(\text{CH}_3)\text{C}_2\text{B}_9\text{H}_{11}$ , exists principally as the dimer in benzene solution (molecular weight found: 695; calculated: 701.59). The mass spectrum of

Table III. Analytical Data, Thallo-carborane,  $TlC_2B_9H_{12}$

	Mp (dec), °C	Elemental analysis (theory), %				Mol wt (calcd for monomer)		Mass spec cutoff (m/e at 34 and 70 eV)
		B	C	H	Tl	Benzene	Ethyl acetate	
$TlC_2B_9H_{12}$	260	29.23 (28.75)	7.34 (7.13)	3.63 (3.56)	60.94 (60.51)			340

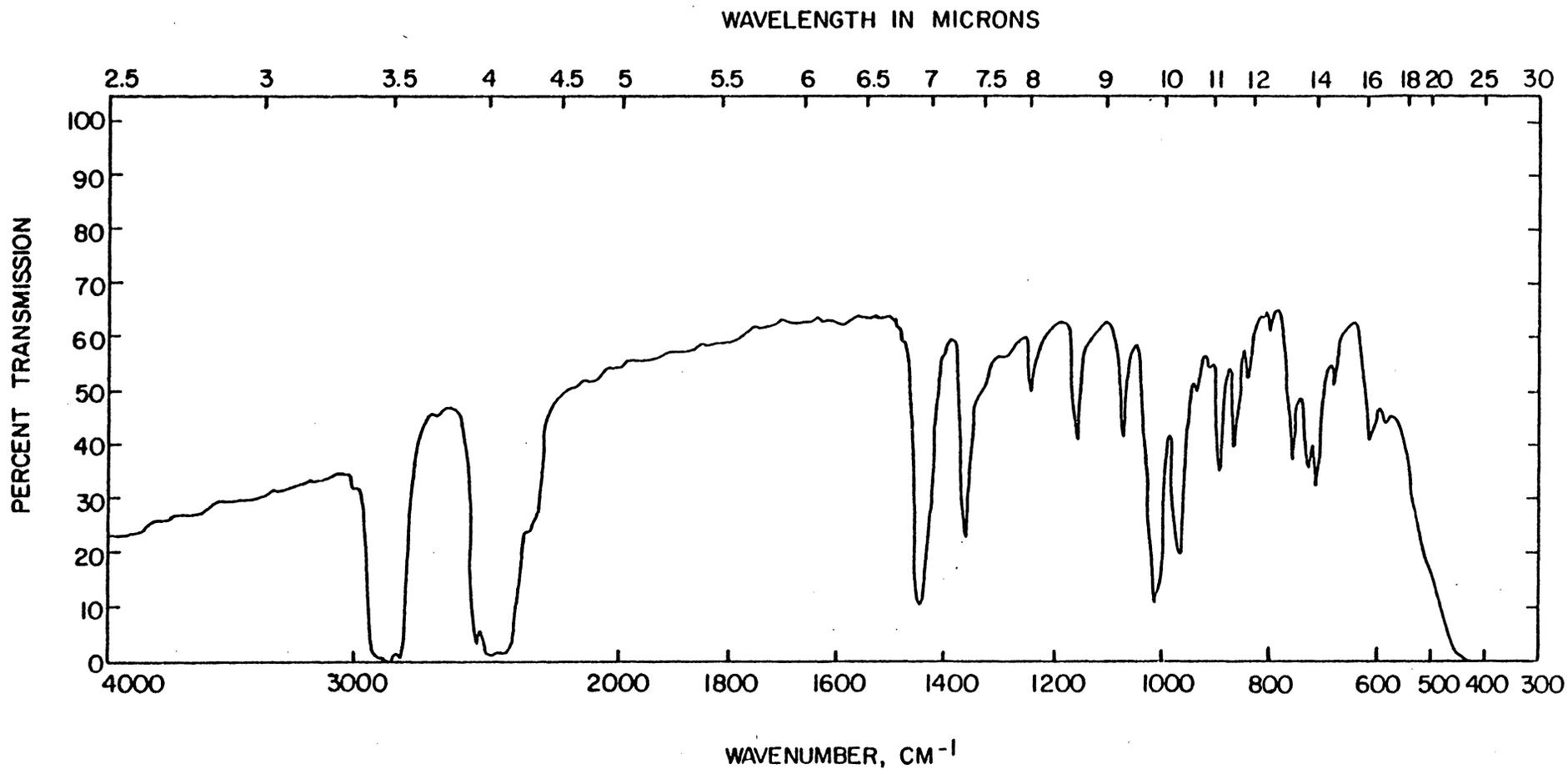


Figure 6. Infrared Spectrum,  $Tl_2C_2B_9H_{12}$ .

$\text{Tl}(\text{CH}_3)_2\text{C}_2\text{B}_9\text{H}_{11}$  did not show the anticipated ion  $m/e$  708 corresponding to  $^{205}\text{Tl}_2^{11}\text{B}_{18}^{12}\text{C}_6^{1}\text{H}_{28}$ . Instead, a weak ion appeared at 354 (calculated for  $^{205}\text{Tl}^{11}\text{B}_9^{12}\text{C}_3^{1}\text{H}_{14}^+$ ) and a strong ion appeared at 294 corresponding to a coupled species  $[(^{12}\text{C}^1\text{H}_3)^{12}\text{C}_2^{11}\text{B}_9^1\text{H}_9]_2^+$ . Boranes are known to lose  $\text{H}_2$  during the ionization process; therefore, the loss of hydrogen is not surprising for the coupled ion. A plausible explanation for the coupled ion formation is that the structure of the thallium monomethyl derivative is such that the Tl atoms are easily removed in the ionization process. This would suggest that the structure is such that the carborane portions are attached to each other in a manner other than through a Tl-Tl linkage.

The  $^1\text{H}$  NMR spectrum showed the expected C-H and C-attached methyl resonance at  $\tau$ 7.74 and  $\tau$ 8.26, respectively (Figure 7). The  $^{11}\text{B}$  NMR spectrum (Figure 8) indicates eight distinct boron resonances, seven of unit area and one of area two. The fine structure on the doublet at 33.4 ppm suggests a B-H-B bridge. The spectrum is consistent with that expected for an asymmetrically substituted ortho  $\text{C}_2\text{B}_9$  icosahedral fragment with accidental equivalence of two resonances. The spectrum measured in benzene was nearly identical with the spectrum in THF, but not as clearly resolved. The molecular weight, mass spectral data, melting point, and elemental analyses are shown in Table IV. The infrared spectrum is shown in Figure 9.

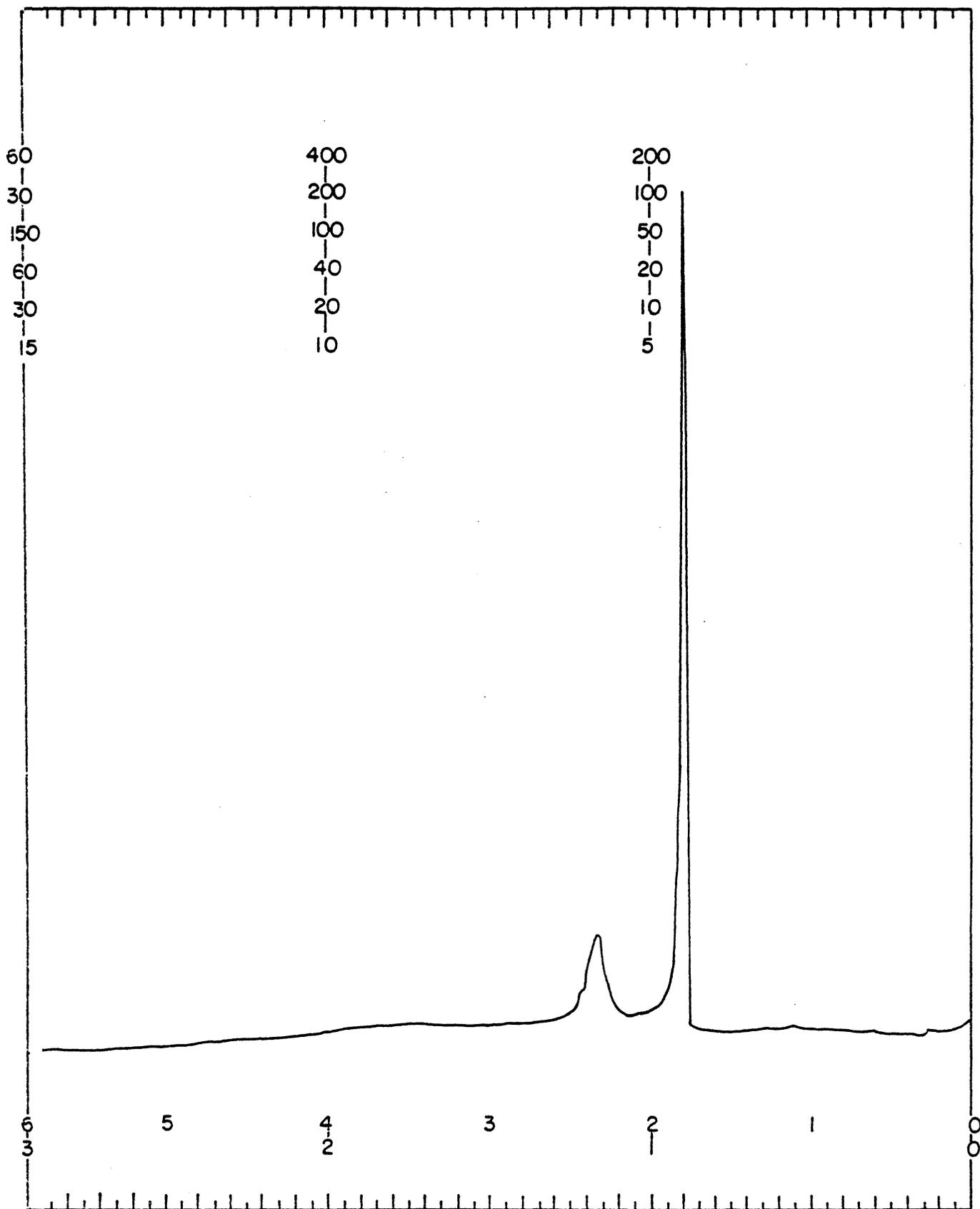


Figure 7.  $^1\text{H}$  NMR Spectrum,  $\text{Tl}(\text{CH}_3)\text{C}_2\text{B}_9\text{H}_{11}$ .

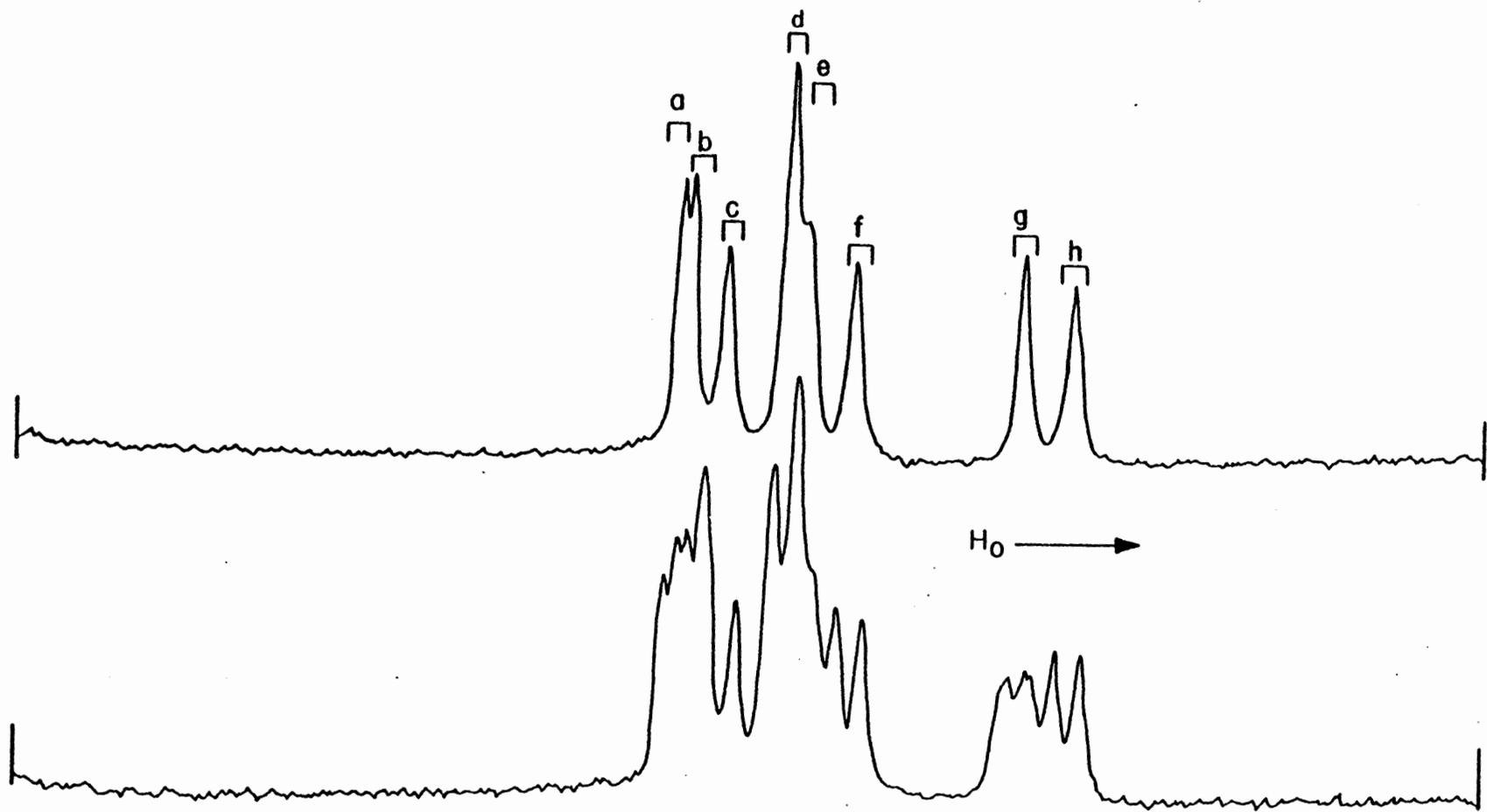


Figure 8.  $^{11}\text{B}$  NMR Spectrum,  $\text{Tl}(\text{CH}_3)\text{C}_2\text{B}_9\text{H}_{11}$ .

Table IV. Monomethyl Derivative,  $\text{Tl}(\text{CH}_3)\text{C}_2\text{B}_9\text{H}_{11}$

	Mp (dec), °C	Elemental analysis (theory), %				Mol wt (calcd for monomer)		Mass spec cutoff (m/e at 34 and 70. eV)
		B	C	H	Tl	Benzene	Ethyl acetate	
$\text{Tl}(\text{CH}_3)\text{C}_2\text{B}_9\text{H}_{11}$	295	27.51 (27.73)	10.41 (10.27)	3.89 (3.73)		697 (351.67)	374 (351.67)	354

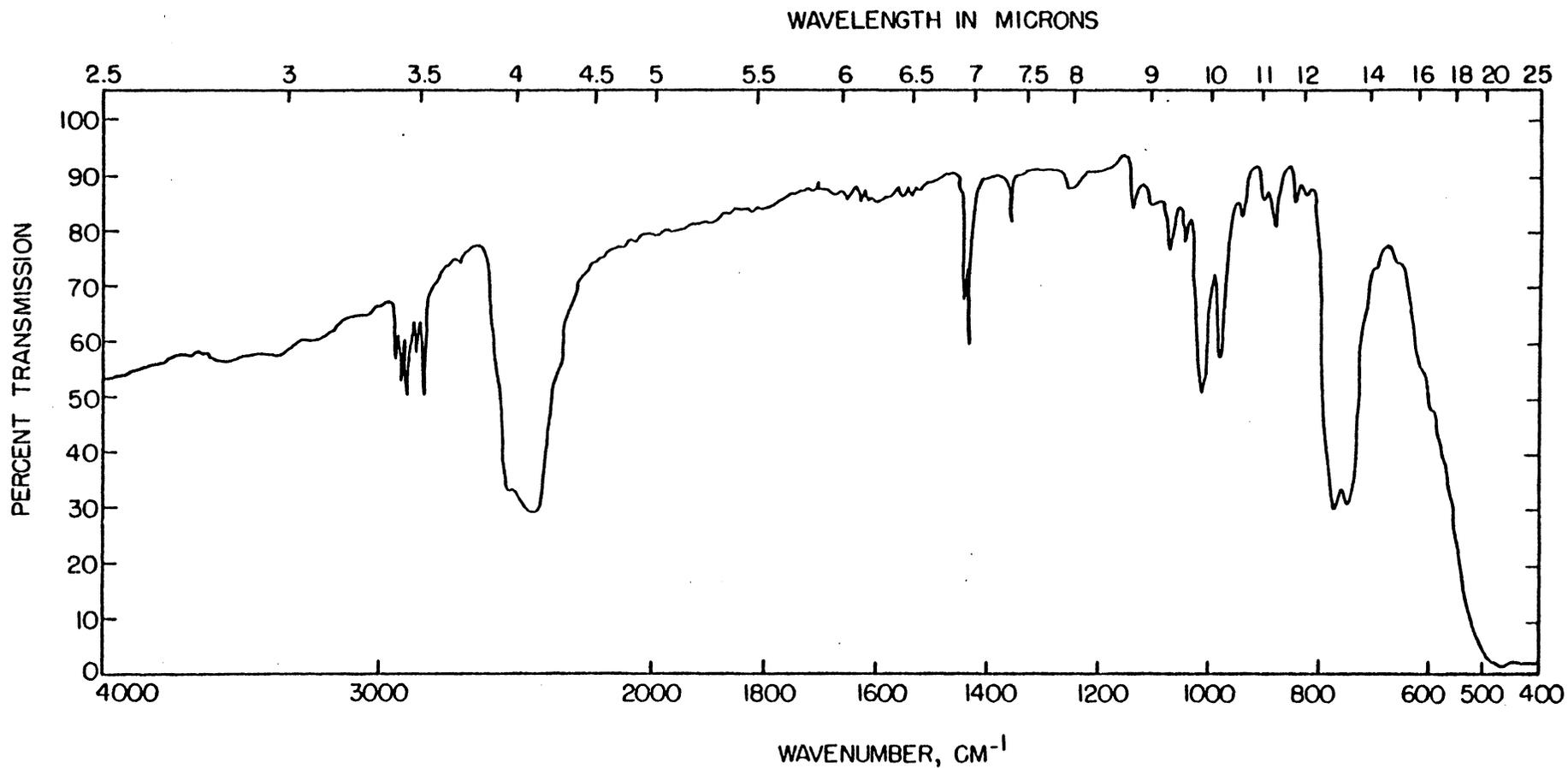


Figure 9. Infrared Spectrum,  $Tl(CH_3)C_2B_9H_{11}$  ( $CCl_4$  Mull).

The proposed static structure for  $[\text{Tl}(\text{CH}_3)\text{C}_2\text{B}_9\text{H}_{11}]_2$  (Figure 10) is consistent with the data reported, although not proven by the data. The fine structure on the doublet at 33.4 ppm, which is attributed to bridge hydrogen coupling, can be rationalized using a model similar to the one suggested by Hawthorne,<sup>21</sup> in which tautomerization of the bridge hydrogens between the boron atom of the pentagonal face occurs.

The dimethyl derivative,  $\text{Tl}(\text{CH}_3)_2\text{C}_2\text{B}_9\text{H}_{10}$ , shows appreciable association in benzene (molecular weight found: 534; calculated: 365.67). The mass spectrum showed the expected cutoff cluster corresponding to the  $^{205}\text{Tl}^{11}\text{B}_9^{12}\text{C}_4\text{H}_{16}^+$  ion (m/e 368). The  $^{11}\text{B}$  NMR spectrum (Figure 11) showed three clusters of peak, which on proton decoupling yielded four distinct resonances with integrated areas of 3:4:1:1. The spectrum is consistent with that expected for an asymmetrically substituted ortho  $\text{C}_2\text{B}_9$  icosahedral fragment with equivalence of two resonances. The molecular weight, mass spectral data, melting point, and elemental analyses are shown in Table V. The infrared spectrum is shown in Figure 12.

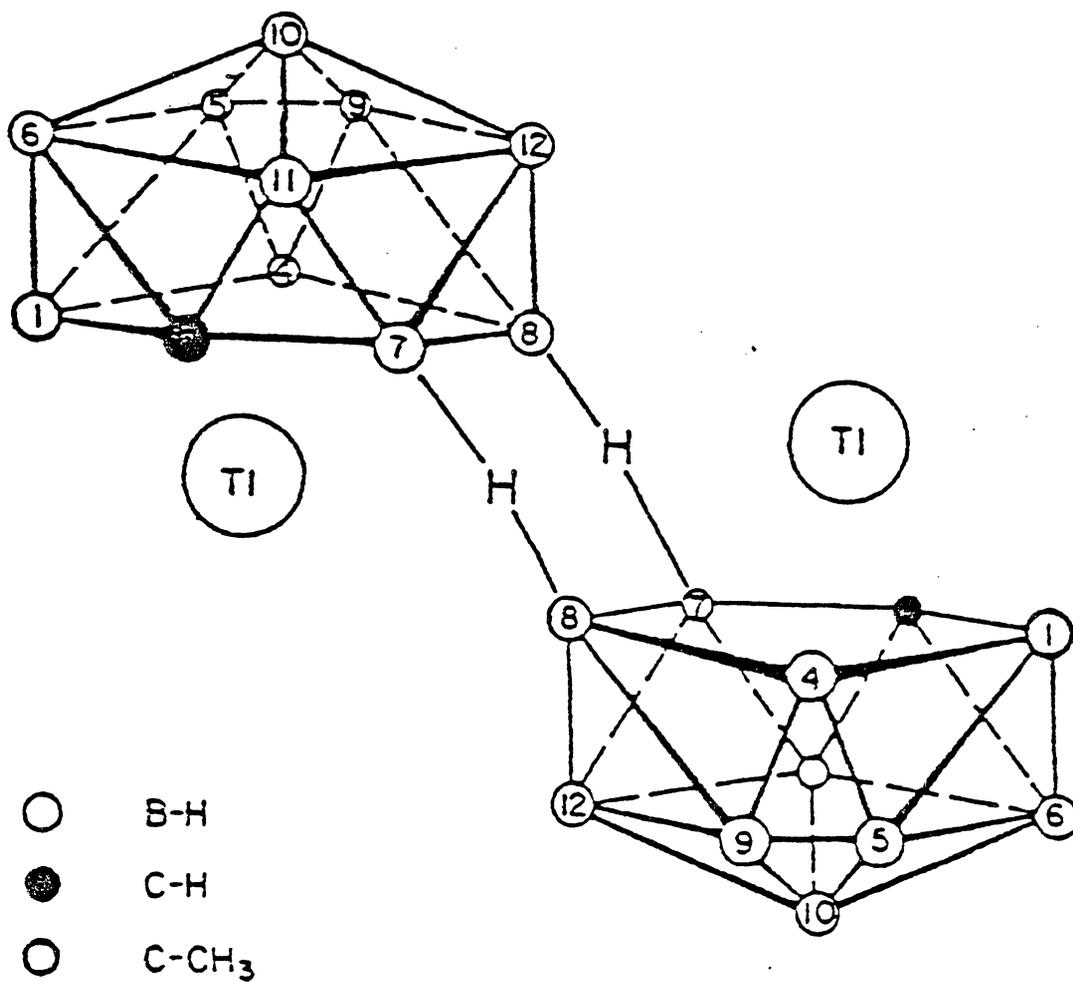


Figure 10. Proposed Static Structure,  $[\text{Tl}(\text{CH}_3)\text{C}_2\text{B}_9\text{H}_9]_2$ .

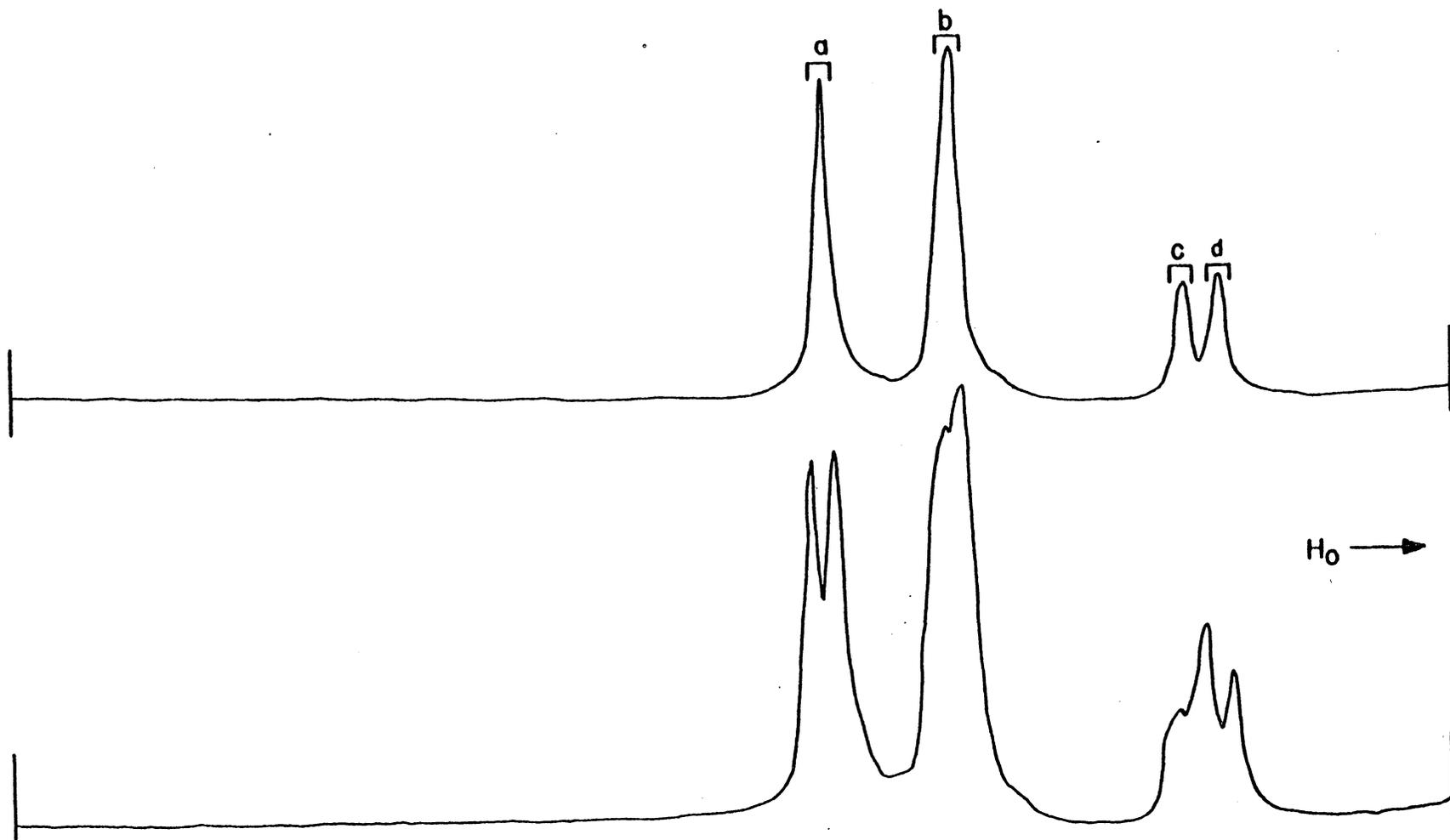


Figure 11.  $^{11}\text{B}$  NMR Spectrum,  $\text{Tl}(\text{CH}_3)_2\text{B}_9\text{H}_{10}$ .

Table V. Dimethyl Derivative,  $\text{Tl}(\text{CH}_3)_2\text{C}_2\text{B}_9\text{H}_{10}$

	Mp (dec), °C	Elemental analysis (theory), %				Mol wt (calcd for monomer)		Mass spec cutoff (m/e at 34 and 70 eV)
		B	C	H	Tl	Benzene	Ethyl acetate	
$\text{Tl}(\text{CH}_3)_2\text{C}_2\text{B}_9\text{H}_{10}$	290	25.00 (26.61)	13.54 (13.13)	5.00 (4.38)	55.72 (55.88)	534 (365.67)	362 (365.67)	368

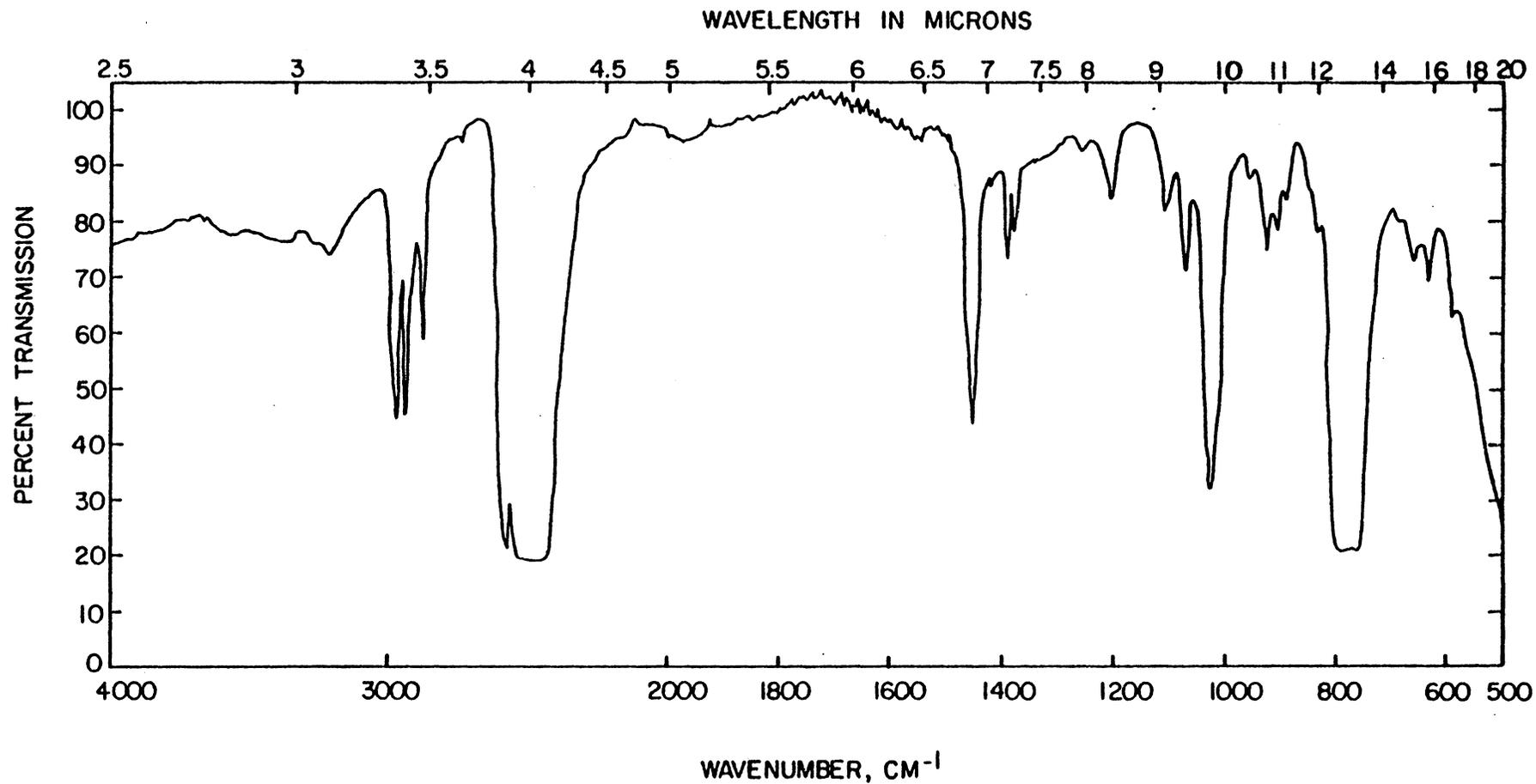


Figure 12. Infrared Spectrum,  $Tl(CH_3)_2C_2B_9H_{10}$ .

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THE SYNTHESSES AND REACTIONS OF  
THALLIUM AND DITHALLIUM DICARBOLLIDES

by

Johnny Smith

ABSTRACT

The vacuum pyrolysis of  $Tl_2R^1R^2C_2B_9H_9$  ( $R^1=R^2=H$ ;  $R^1=H$ ,  $R^2=CH_3$ ;  $R^1R^2=CH_3$ ) species yielded some interesting thallium-containing heterocarboranes. The major pyrolysis products are thallium metal and  $TlR^1R^2C_2B_9H_{10}$ . Hydrogen and the corresponding closo-carboranes,  $R^1R^2C_2B_9H_9$ , were produced as minor products.

The reactions of  $Tl_2R^1R^2C_2B_9H_9$  compounds with weak organic acids yielded the identical  $TlR^1R^2C_2B_9H_{10}$  products that were produced by vacuum pyrolysis. The action of strong protic acids on  $Tl_2R^1R^2C_2B_9H_9$  produced the nido-carboranes,  $R^1R^2C_2B_9H_9$ .

The mechanism of the pyrolysis reaction and the proposed structures of the  $TlR^1R^2C_2B_9H_{10}$  compounds are discussed. The compounds were identified by  $^1H$  and  $^{11}B$  NMR, IR, mass spectrometry, and elemental analysis.