total of 5.6 g of precipitate was isolated. After washing with water to a negative halide test and recrystallization from *o*-xylene, a total of 2.2 g of polydisulfide was isolated; mp 315–317°. *Anal.* Calcd for $Cl(SCB_{10}H_{10}CS)_{12}Cl$: C, 11.31; H, 4.75; B, 50.94; Cl, 2.78; S, 30.21. Found: C, 12.72; H, 5.01; B, 50.37; Cl, 2.86; S, 28.2.

(3) From Dilithio-*m*-carborane and Sulfur Dichloride.—A slurry of 0.1 mol (from 14.4 g *m*-carborane) of *m*-$B_{10}H_{10}C_2Li_2$ in 200 ml of diethyl ether was added slowly to a solution of SCl_2 (22.7 g, 0.22 mol) in ether (100 ml) while the temperature was maintained at −10°. After the addition was complete, the reaction mixture was stirred at ambient temperature for 60 min and then hydrolyzed with ice water. The suspension was filtered and the precipitate was dried *in vacuo*. This material was recrystallized from ethylene dichloride to yield 7.0 g (34%) of a white product (mp 231–233°) of molecular weight 1265 (osmometry), which corresponds to 6 repeating units. *Anal.* Calcd for $Cl(SCB_{10}H_{10}CS)_6Cl$ (1309): C, 11.01; H, 4.62; B, 49.58; S, 29.38; Cl, 5.41. Found: C, 11.59; H, 4.89; B, 50.11; S, 28.20; Cl, 5.42.

Poly-*m*-carboranylene Thiolsulfinate.—A total of 5.54 g (0.02 mol) of *m*-$B_{10}H_{10}C_2(SCl)_2$ was suspended in 50 ml of water, first refluxed periodically over a 4-hr period, and then kept at room temperature for another 20 hr. Next, the suspension was filtered, and the residue was washed successively with water and ether and dried *in vacuo* to yield 4.70 g (100%) of a white polymer. Recrystallization of a portion of this product from benzene–heptane yielded pure $Cl[SCB_{10}H_{10}CS(O)]_{11}Cl$, mp 281–285°. The molecular weight found by osmometry was 2525. *Anal.* Calcd for $Cl[SCB_{10}H_{10}CS(O)]_{11}Cl$ (2516.6): C, 10.50; H, 4.41; B, 47.25; Cl, 2.82; S, 28.03. Found: C, 11.03; H, 4.68; B, 47.84; Cl, 2.3; S, 27.72.

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Icosahedral Carboranes. XI. Germanium and Tin Derivatives of *o*-, *m*-, and *p*-Carborane and Their Polymers[1-3]

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The dilithio salts of *o*-, *m*-, and *p*-carborane were allowed to react with selected chloro derivatives of germanium and tin. In the germanium series, disubstituted *o*-carborane derivatives were formed as in the similar silicon chemistry, but the germanium *m*- and *p*-carborane products obtained were mixtures of disubstituted monomers and related polymers. In analogous reactions of the *m*- and *p*-dilithio salts with various substituted dichlorotin derivatives, it was found that the tendency toward polymerization is much more pronounced although the substituents still have a marked influence on the type of product formed. With regard to preparing high-melting linear polymers, homopolymers based on *p*-carborane nuclei linked by tin with softening points up to 420° could be obtained; in addition, related random copolymers having melting ranges between 350 and 400° were prepared.

A prime objective of this research program has been the incorporation of the $B_{10}C_2$ carborane nuclei into the backbone of essentially inorganic polymers. To this end, we have conducted studies to determine which elements or groups of elements are most suitable for linking these icosahedra. Our recent success with either dimethylsiloxy groups[4,5] or carbon,[6] phosphorus,[7] and sulfur bridges[1] prompted extension of this work to other elements, and the results wherein germanium and tin derivatives were explored are reported here.

Until this investigation was nearly completed, no such derivatives had been described. Recently, however, the syntheses of several series of such monomers[8,9] and polymers[10-13] based on *o*- and *m*-carborane but not the *para* species have been reported. Consequently, *o*- and *m*-carborane derivatives will be de-

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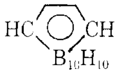
[1] Preceding communication: N. S. Semenuk, S. Papetti, and H. Schroeder, *Angew. Chem., Intern. Ed. Engl.*, **6**, 997 (1967); *Inorg. Chem.*, **8**, 2441 (1969).

[2] Presented at the 3rd International Symposium of Metal Organic Chemistry, Munich, Sept 1967.

[3] Nomenclature of the *closo* boron-carbon hydrides was discussed by R. Adams, *Inorg. Chem.*, **2**, 1087 (1963), and appropriate rules approved by the Council of the American Chemical Society are presented in *Inorg. Chem.*, **7**, 1945 (1968). The terms *o*-, *m*-, and *p*-carborane are used to designate 1,2-, 1,7-, and 1,12-dicarba-*closo*-dodecaborane. In accord with current practice, the following symbols are employed for representation of these isomers


$HCB_{10}H_{10}CH$,


[4] S. Papetti, B. B. Schaeffer, A. P. Gray, and T. L. Heying, *J. Polymer Sci., A-1*, **4**, 1623 (1966).

[5] H. Schroeder, O. G. Schaffling, T. B. Larchar, F. F. Frulla, and T. L. Heying, *Rubber Chem. Technol.*, **39**, 1184 (1966).

[6] J. R. Reiner, R. P. Alexander, and H. Schroeder, *Inorg. Chem.*, **5**, 1460 (1966).

[7] R. P. Alexander and H. Schroeder, *ibid.*, **5**, 493 (1966).

[8] L. I. Zakharkin, V. I. Bregadze, and O. Yu. Okhlobystin, *J. Organometal. Chem.* (Amsterdam), **4**, 211 (1965).

[9] S. Bresadola, F. Rossetto, and G. Tagliavani, *Ann. Chim.* (Rome), **58**, 597 (1968).

[10] S. Bresadola, F. Rossetto, and G. Tagliavini, *Chem. Commun.*, 673 (1966).

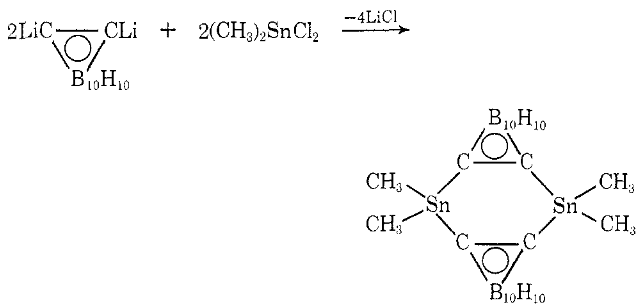
[11] S. Bresadola, F. Rossetto, and G. Tagliavini, *Chim. Ind.* (Milan), **49**, 531 (1967).

[12] S. Bresadola, F. Rossetto, and G. Tagliavini, *European Polymer J.*, **4**, 75 (1968).

[13] S. Bresadola, F. Rossetto, and G. Tagliavini, *Chim. Ind.* (Milan), **50**, 452 (1968).

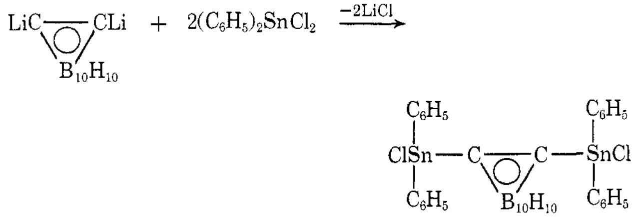
scribed herein only as far as new or supplementary results are concerned, or in order to demonstrate reaction schemes depending on substituents and, to a lesser degree, on solvents.

Tin–Carborane Derivatives.—In an attempt to obtain o-$B_{10}H_{10}C_2(Sn(CH_3)_2 \cdot Cl)_2$ as a difunctional derivative for use in further reactions, o-$B_{10}H_{10}C_2Li_2$ and 2 molar equiv of $(CH_3)_2SnCl_2$ were allowed to interact in ether solution, but the following reaction occurred

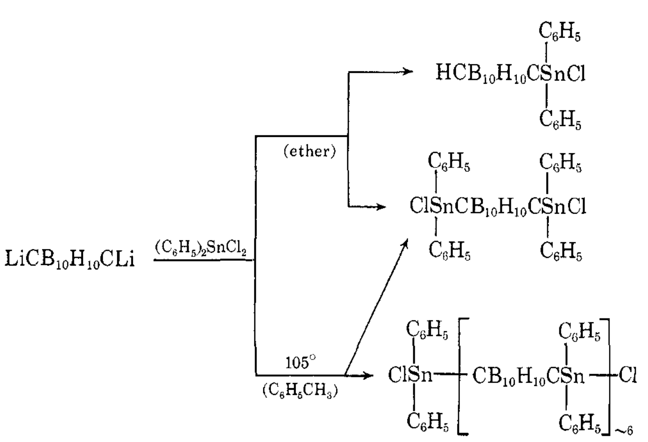


The cyclic compound containing a distannocyclohexane skeleton[14] was obtained quantitatively. The formation of this type of six-membered ring compound directly from o-$B_{10}H_{10}C_2Li_2$ had previously occurred only with PCl_3[15] and $COCl_2$[6] but had not been observed with $SiCl_4$[16], the related group IV representative.

Employment of an aryl- instead of an alkyl-substituted dichlorotin derivative in this reaction, however, resulted in a noncyclic and difunctional compound as desired

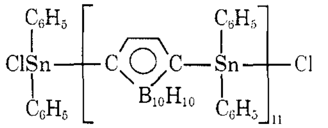


Pursuing this further, it is interesting to note that in the reaction of $(C_6H_5)_2SnCl_2$ with m-$B_{10}H_{10}C_2Li_2$ under the same conditions (ether solution and ambient temperature), metathesis of either one or both lithium atoms occurs;[17] when refluxing toluene was the reaction medium, a mixture of disubstituted as well as polymeric material was obtained



The latter product is similar to that obtained exclusively in THF solution by Bresadola, *et al.*[10,12] The same team[9] also prepared a number of monomeric m-carborane–tin compounds starting from either m-$B_{10}H_{10}C_2Li_2$, m-$B_{10}H_{10}C_2(CH_3)Li$, or m-$B_{10}H_{10}C_2(C_6H_5)Li$ and attaching tin to the carborane carbons *via* a common metathesis reaction.

In the reaction of $(C_6H_5)_2SnCl_2$ with p-$B_{10}H_{10}C_2Li_2$, however, polymeric material was obtained exclusively, even in ether solution. The chain length of the highest molecular weight fraction, approximately 11 repeating units as illustrated below, was still not significantly greater than that of the corresponding m-carborane derivative.



In returning to the alkyl-substituted dichlorotin derivative, which in the *ortho* system had led to products entirely different from those obtained by use of the corresponding aryltin compound, $(CH_3)_2SnCl_2$ and m-$B_{10}H_{10}C_2Li_2$ were found, even with the former in large excess, to undergo polycondensation only. In an effort to achieve maximum chain length, the polymerization was conducted in different solvents at reflux and the results of this study are summarized in Table I. All products obtained could be recrystallized; the molecular weights were determined in o-dichlorobenzene at 100°. Bresadola, *et al.*,[12] have reported extensive studies with the same polymer using THF and benzene as solvents, attaining their highest melting material (mp 205°) in the latter. They were also able to extend this polymerization reaction to $(CH_3)_2SiCl_2$ by the use of THF, whereas Papetti and Heying[18] had obtained in diethyl ether the difunctional monomer m-$B_{10}H_{10}C_2((CH_3)_2SiCl)_2$.

As for our objective, even our best product with a softening point around 250°, prepared in decaline, did not approach expectation for a polymer to be used at high temperatures. Therefore, structural changes were required to improve the desired property.

It is known that direct halogenation of o-carborane occurs first at the 9,12 borons[19] and, except for fluorine, produces derivatives with extremely stable boron–halogen bonds.[20] Since 9-bromo-m-carborane is easily prepared,[21] the dilithio derivative of this heavy-atom-substituted compound was selected for participation in

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(14) Zakharkin, *et al.*,[8] reported the synthesis of the corresponding t-butyl-substituted derivative.

(15) R. P. Alexander and H. Schroeder, *Inorg. Chem.*, **2**, 1107 (1963).

(16) S. Papetti and T. L. Heying, *ibid.*, **2**, 1105 (1963).

(17) Bresadola, *et al.*,[9] reported the difunctional compound as the only product from the reaction under these conditions; we were able to isolate the monofunctional compound by fractional distillation of the reaction mixture.

(18) S. Papetti and T. L. Heying, *Inorg. Chem.*, **3**, 1448 (1964).

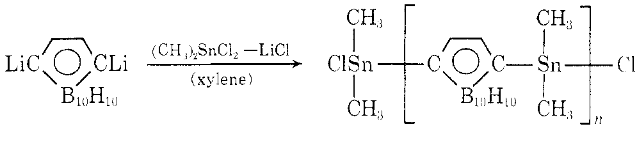
(19) J. A. Potenza, W. N. Lipscomb, G. D. Vickers, and H. Schroeder, *J. Am. Chem. Soc.*, **88**, 628 (1966).

(20) S. Kongpricha and H. Schroeder, *Inorg. Chem.*, **8**, 2449 (1969).

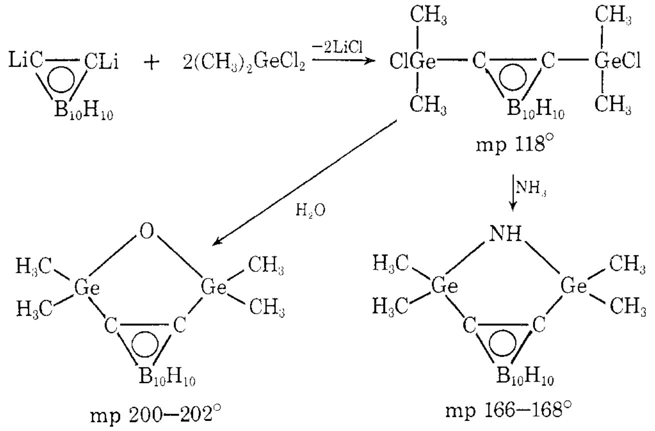
(21) H. D. Smith, T. A. Knowles, and H. Schroeder, *ibid.*, **4**, 107 (1965).

the usual polycondensation hoping to obtain a higher melting product. Polymerization proceeded as expected producing in 73% yield a polymer with low solubility, melting 130° higher than the best nonbrominated polymer. As apparent from Figure 1, the bromine atoms extend out from the cages in positions as remote from the polymer chain axis as possible.

The concluding step in this series was the combination of *p*-carborane nuclei and methyl substituents on the tin bridges. To this end, *p*-$B_{10}H_{10}C_2Li_2$ and $(CH_3)_2SnCl_2$ were allowed to interact first in ether and then in xylene. While polycondensation in the former solvent provided a product melting around 370°, employment of the latter medium resulted in the desired type of truly high-melting material. The polymer obtained in ~70% yield was insoluble in common organic solvents and softened only above 420°. When heated above this temperature in air, both tga and dta measurements show exothermal decomposition starting at 425°. In comparison, the diphenyltin species in the *meta* series showed similar weight loss between 300 and 350°.[12]



Germanium–Carborane Derivatives.—The contrasting results between the silicon and tin systems aroused interest to establish the chemical behavior of the respective compounds of germanium, the element between them in the fourth group of the periodic table. Zakharkin, *et al.*,[8] had shown in the germanium–*o*-carborane series that treatment of $GeCl_4$ with *o*-$B_{10}H_{10}C_2(C_6H_5)Li$ results in the displacement of only two chlorines to give bis(1-phenyl-*o*-carboranyl)dichlorogermane. We extended these studies and found such reactions in general to proceed in a manner identical with those encountered in silicon–*o*-carborane chemistry.[16] The following scheme illustrates the experiments performed.

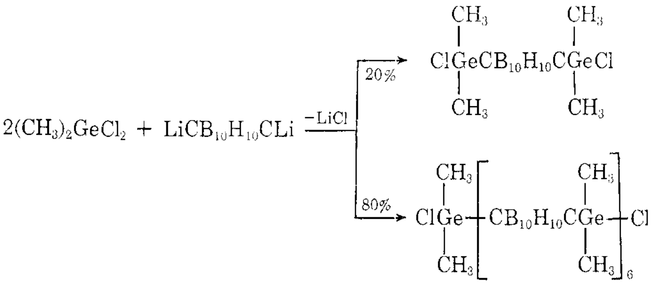


The dichloro compound as well as the cyclic derivatives were obtained in excellent yields and their structures were proven by elemental and infrared analysis in combination with mass spectroscopy. As in the case of silicon, but in contrast to tin, no dimeric material was formed in the upper reaction.

The intermediate position of germanium between silicon and tin became apparent, however, on allowing its chlorine-containing derivatives to react with *m*-$B_{10}H_{10}C_2Li_2$. While $GeCl_4$ behaved as does $SiCl_4$[16] with formation of a hexachloro compound

$$GeCl_4 + LiCB_{10}H_{10}CLi \xrightarrow{-2LiCl} Cl_3GeCB_{10}H_{10}CGeCl_3$$

the reaction between $(CH_3)_2GeCl_2$ and *m*-$B_{10}H_{10}C_2Li_2$ in the stoichiometric ratio 2:1 in ether solution produced not only the dichloro monomer "in the silicon fashion" but in addition, and to a considerably greater extent, a germanium-linked polymer "in the tin fashion"

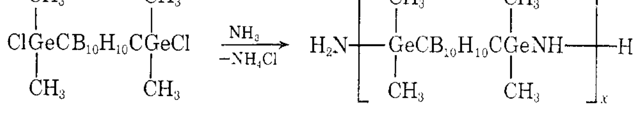


$$2(CH_3)_2GeCl_2 + LiCB_{10}H_{10}CLi \xrightarrow{-LiCl} \begin{cases} \xrightarrow{20\%} ClGe(CH_3)_2CB_{10}H_{10}CGe(CH_3)_2Cl \\ \xrightarrow{80\%} ClGe(CH_3)_2\left[CB_{10}H_{10}CGe(CH_3)_2\right]_6Cl \end{cases}$$

Adjusting the reactant ratio to a 1:1 proportion resulted in the exclusive formation of a polymeric product again with approximately 6 repeating units. The chain length has not been increased by conducting the polymerization in other solvents such as hexane. These results are very similar to those by Bresadola, *et al.*,[12] using the diphenyl-substituted dichlorogermanium compound in polymer preparation. Their products average 4–5 and in one case 10 repeating units.

Attempts to obtain a higher molecular weight material by incorporating *p*-carborane in the polymer backbone did not produce the desired results. The reaction of *p*-$B_{10}H_{10}C_2Li_2$ with $(CH_3)_2GeCl_2$ again gave only an oligomer which contained approximately 5 repeating units.

A significant difference in the behavior of analogous silicon and germanium derivatives of *m*-carborane became apparent when *m*-$B_{10}H_{10}C_2(Ge(CH_3)_2Cl)_2$ was found to serve as a polymer intermediate. Whereas ammonolysis of *m*-$B_{10}H_{10}C_2(Si(CH_3)_2Cl_2)$ had furnished the respective diamino compound in good yield,[18] in the case of the difunctional germanium compound, displacement of chlorine by ammonia also took place but was accompanied with the formation of the polymer as in



$$ClGe(CH_3)_2CB_{10}H_{10}CGe(CH_3)_2Cl \xrightarrow[-NH_4Cl]{NH_3} H_2N\left[Ge(CH_3)_2CB_{10}H_{10}CGe(CH_3)_2NH\right]_xH$$

This carborane–metal–imino bonded polymer consisting of about 7 repeating units was exclusively ob-

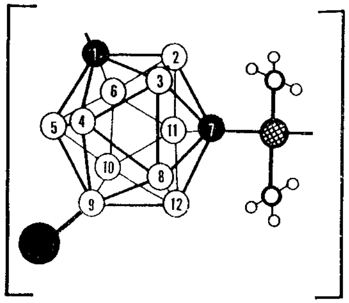
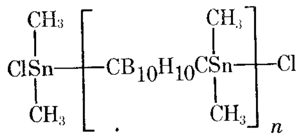


Figure 1.—Dimethyltin bromo-*m*-carborane polymer (mp 380–383°).

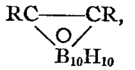
TABLE I
EFFECT OF POLYMERIZATION MEDIUM ON CHAIN LENGTH OF



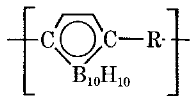
$ClSn(CH_3)_2-[CB_{10}H_{10}CSn(CH_3)_2]_n-Cl$

Solvent	Recrystallized from	Mp, °C	Mol wt	No. of repeating units
Ether	Benzene	217–221	2563	8
Xylene	Xylene	236–243	7060	24
Hexane	Xylene	240–244	8405	28
Decalin	*o*-Dichloro-benzene	250–255	9020	30

TABLE II
MONOMERIC AND POLYMERIC ICOSAHEDRAL CARBORANE DERIVATIVES



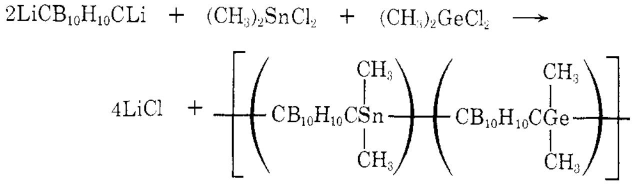
$\underset{B_{10}H_{10}}{RC—CR}$, $RCB_{10}H_{10}CR$

Carborane isomer	R	Mp, °C	Yield, %	Solvent	Recrystallized from	Formula	Mol wt found	% carbon		% hydrogen		% boron		% chlorine		% tin (or Ge)	
								Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
o	$ClSn(C_6H_5)_2$	143–144	17.5	Ether	Heptane	$C_{26}H_{30}B_{10}Cl_2Sn_2$	...	41.14	42.43	3.98	4.33	14.25	13.98	9.34	9.20	31.28	29.90
o	$ClGe(CH_3)_2$	118	42	Ether	Hexane	$C_6H_{22}B_{10}Cl_2Ge_2$	...	17.22	17.30	5.30	5.42	25.85	25.44	16.94	17.00	34.69	34.15
m	$ClGe(CH_3)_2$	59–61	20	Ether	*a*	$C_6H_{22}B_{10}Cl_2Ge_2$	...	17.22	17.06	5.30	5.45	25.85	25.56	16.94	17.40	...	...
m	Cl_3Ge	...	34	Ether	*b*	$C_2H_{10}B_{10}Cl_6Ge_2$	...	4.80	4.89	2.01	2.10	21.63	21.69	42.53	42.55	29.03	29.09
						$-\!(CB_{10}H_{10}C—R)\!-$,											
m	$Sn(C_6H_5)_2$	235–240	30	Toluene	Insol	$C_{82}H_{110}B_{50}Cl_2Sn_6$	2360[c]	40.75	40.36	4.55	4.63	22.36	21.84	2.93	3.18	...	...
m	$Sn(CH_3)_2$	217–221	42	Ether	Benzene	$C_{34}H_{134}B_{80}Cl_2Sn_9$	2563	16.03	16.70	5.30	5.60	33.97	35.43	2.78	2.30	...	...
m (9-Br)	$Sn(CH_3)_2$	380–383	73	Ether	*o*-Dichloro-benzene	$(C_4H_{15}B_{10}BrSn)_n$	...	12.98	13.11	4.09	4.21	29.24	28.58	21.60[e]	21.35	32.08	31.50
p	$Sn(C_6H_5)_2$	404–412[f]	13	Ether	Benzene–heptane	$C_{166}H_{230}B_{110}Cl_2Sn_{12}$	4780	40.62	40.55	4.68	4.68	24.23	24.48	1.44	1.43	...	...
p	$Sn(CH_3)_2$	365–375	50	Ether	*o*-Dichloro-benzene	$(C_4H_{16}B_{10}Sn)_n$	6050[d]	16.51	16.32	5.54	5.56	37.17	36.72	...	...	40.78	40.28
m	$Ge(CH_3)_2$	*g*		Ether	CCl_4	$C_{26}H_{102}B_{60}Cl_2Ge_7$	1755	19.01	17.99	6.26	6.60	39.84	38.22	4.32	3.90	30.93	31.90
p	$Ge(CH_3)_2$	460–480[h]	12	Ether	*o*-Dichloro-benzene	$C_{22}H_{86}B_{50}Cl_2Ge_6$	1470	18.91	18.11	6.16	6.00	38.69	38.37	...	...	31.18	30.49
m	$Sn(CH_3)_2$, $Ge(CH_3)_2$	350–355	44	Ether	Insol	$(C_8H_{32}B_{20}GeSn)_n$	...	17.92	17.16	6.02	6.12	40.37	39.42	...	...	22.14[i] 13.54[j]	23.10[i] 13.07[j]
m, *p*	$Sn(CH_3)_2$	370–375	62	Ether	Insol	$(C_4H_{16}B_{10}Sn)_n$	...	16.51	16.53	5.54	5.49	37.17	36.61	...	...	40.78	40.50

[a] Vacuum distilled (bp 130–132° (0.05 mm)). [b] Vacuum distilled (bp 124–126° (0.2 mm)). [c] In *o*-dichlorobenzene at 100°. [d] Product prepared in xylene; mp >420°; too insoluble for molecular weight determination. [e] Bromine analysis. [f] Softens at 360–390°. [g] Softens above 95° over a wide temperature range; no major decomposition up to 500°. [h] With decomposition. [i] Tin analysis. [j] Germanium analysis.

tained regardless of reaction conditions, even when an ethereal solution of the dichloro compound was added to a large excess of liquid ammonia. Unfortunately, this type of reaction cannot be extended to the tin–*m*-carborane series since, as pointed out above, the monomeric dichlorotin compound cannot be obtained by conventional methods because of immediate polymerization.

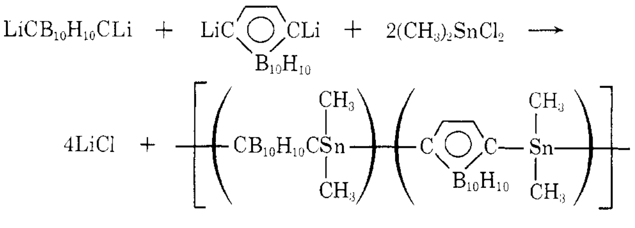
Random Copolymers.—Whereas homopolymers in the tin series containing either *m*- or *p*-carborane nuclei had appreciable molecular weights and, in the latter case, in addition a high-melting range, comparable results in the germanium series had not been realized. For this reason, the condensation polymerization used in all previous reactions was then applied for the preparation of a copolymer with random tin and germanium links between *m*-carborane moieties



$$2LiCB_{10}H_{10}CLi + (CH_3)_2SnCl_2 + (CH_3)_2GeCl_2 \longrightarrow 4LiCl + \left[\left(CB_{10}H_{10}C\overset{CH_3}{\underset{CH_3}{Sn}}\right)\left(CB_{10}H_{10}C\overset{CH_3}{\underset{CH_3}{Ge}}\right)\right]$$

mp 350–355°

The considerable increase in the melting temperature prompted us to synthesize another random copolymer, this time connecting both *m*- and *p*-carborane units by tin atoms



mp 370–375°
(shrinks at
340°)

The above approach bears promise for the preparation of a wide variety of related copolymers.

Experimental Section[22]

Starting Materials.—*o*-Carborane was used as received from the pilot plant without further purification; *m*-carborane was prepared from crude *o*-carborane *via* a continuous-flow process[23] and refined by vacuum sublimation; *p*-carborane was made by the same flow process but purified by elution chromatography on basic alumina.[24] Dimethyltin dichloride (Metal & Thermit Corp.), diphenyltin dichloride (Peninsular ChemResearch, Inc.), and diphenyl- and dimethylgermanium dichloride (Alfa Inorganics, Inc.) were used as received.

The following example is representative for the preparation of C,C′-disubstituted *o*- and *m*-carborane derivatives.

1,2-Bis(chlorodimethylgermanyl)-*o*-carborane.—A 1,2-dilithio-*o*-carborane slurry in ether was prepared[25] from 9.36 g (0.0649 mol) of *o*-carborane and 0.144 mol of butyllithium and slowly added to a stirred ethereal solution of 25.0 g (0.144 mol) of dichlorodimethylgermane cooled in an ice bath. After addition was complete, the mixture was stirred for 2 more hr and filtered. The filtrate was evaporated to dryness, and the residue was recrystallized from hexane. Physical data and yields as well as results of elemental analyses of this and other compounds are compiled in Table II.

1,2-(1′,1′,3′,3′-Tetramethyldigermanaoxanyl-1′,3′)-*o*-carborane.—This compound was readily prepared by adding excess water to an acetone solution of bis(chlorodimethylgermanyl)-*o*-carborane at room temperature. The resulting solution was evaporated to dryness and the residue was recrystallized from high-boiling petroleum ether. The product (mp 200–202°) was obtained practically in quantitative yield. *Anal.* Calcd for $C_6H_{16}B_{10}Ge_2O$ (357.6): C, 19.82; H, 6.10; B, 29.75; Ge, 39.93. Found: C, 19.88; H, 6.08; B, 29.86; Ge, 40.10.

1,2-(1′,1′,3′,3′-Tetramethyldigermanaazanyl-1,3′)-*o*-carborane.—Bis(chlorodimethylgermanyl)-*o*-carborane (2.0 g) was dissolved in 40 ml of ethyl ether. Ammonia was passed through at a rapid rate for 30 min, during which time a precipitate formed. The mixture was filtered and the filtrate was evaporated to dryness. The residue so formed was recrystallized from high-boiling petroleum ether to give essentially quantitative yield of product (mp 166–168°). *Anal.* Calcd for $C_6H_{17}B_{10}Ge_2N$ (356.6): C, 19.87; H, 6.39; B, 29.85; Ge, 40.04; N, 3.86. Found: C, 19.97; H, 6.45; B, 29.61; Ge, 39.81; N, 3.52.

Dimeric Dimethyltin *o*-Carborane.—A slurry of 0.071 mol (from 10.0 g of *o*-carborane) of 1,2-dilithio-*o*-carborane in 200 ml of diethyl ether was added, with stirring in an ice bath, to a solution of 55 g (0.25 mol) of dimethyltin dichloride in 500 ml of diethyl ether. The resulting slurry was refluxed for 1 hr and then stirred overnight at room temperature. A white solid was removed from the reaction mixture by filtration and recrystallization from benzene to give 8.4 g (21%) of product, mp 352–354°. *Anal.* Calcd for $C_8H_{32}B_{20}Sn_2$ (830.4): C, 16.51; H, 5.54; B, 37.17; Sn, 40.78. Found: C, 16.53; H, 5.44; B, 37.13; Sn, 39.78.

1-Chlorodiphenyltin *m*-Carborane.—A slurry of 0.05 mol (from 7.2 g of *m*-carborane) of 1,7-dilithio-*m*-carborane in 500 ml of diethyl ether was added, with stirring and cooling in an ice bath, to a solution of 37.8 g (0.11 mol) of diphenyltin dichloride in 500 ml of diethyl ether. The resulting white slurry was stirred overnight at room temperature, and then the mixture was filtered. The solvent was removed from the filtrate by distillation under vacuum leaving a pale yellow oil. This material was distilled *in vacuo* to give 12.9 g of product, mp 72–73°. The distillation residue contained $m\text{-}B_{10}H_{10}C_2((C_6H_5)_2SnCl)_2$.[9] *Anal.* Calcd for $C_{14}H_{21}B_{10}ClSn$ (451.4): C, 37.23; H, 4.69; B, 23.95; Cl, 7.85. Found: C, 37.62; H, 4.62; B, 23.81; Cl, 8.20.

Polymer Preparation.—Two illustrative examples are given below, describing the employment of either *m*- or *p*-carborane as well as a mixture of the two in the synthesis of a random copolymer. Pertinent data of all products obtained are contained in Table II.

Dimethyltin Carborane Polymers.—A 1,7-dilithio-*m*-carborane slurry in ether (500 ml) was prepared from 7.2 g (0.05 mol of *m*-carborane and 0.11 mol of butyllithium and added, with stirring, at 0° to a solution of 11.0 g (0.05 mol) of dimethyltin dichloride in 500 ml of diethyl ether. The resulting slurry was stirred overnight at reflux, and then the ether was removed by distillation. The resulting white solid was washed with 1 l. of water and dried *in vacuo* over P_2O_5. After recrystallization from benzene, 6.0 g (42%) of polymer, $ClSn(CH_3)_2\text{-}(\text{-}CB_{10}H_{10}CSn(CH_3)_2\text{-})_8\text{-}Cl$, was obtained, mp 217–221°.

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[22] Melting points are uncorrected (Mel-Temp apparatus); elemental analyses were by the Olin Microchemical Section under the supervision of Dr. R. C. Rittner; the molecular weights were determined using a Mechrolab vapor pressure osmometer, Model 301. Measurements in each case were conducted at four different concentrations ranging between 5 and 25 g/l.

[23] S. Papetti, C. Obenland, and T. L. Heying, *Ind. Eng. Chem., Prod. Res. Develop.*, **5**, 334 (1966).

[24] J. F. Sieckhaus, N. S. Semenuk, T. A. Knowles, and H. Schroeder, *Inorg. Chem.*, **8**, 2452 (1969).

[25] For details of preparing ethereal slurries of *o*- and *m*-carborane see ref 15 and 18.

1,12-Dilithio-*p*-carborane, prepared from *p*-carborane (10.0 g; 0.07 mol) and butyllithium (0.15 mol), was washed with petroleum ether (bp 30–60°) and then slurried with 75 ml of xylene. A solution of dimethyltin dichloride (16.74 g; 0.07623 mol) in 100 ml of xylene was added dropwise, at ambient temperature, to the *p*-$B_{10}H_{10}C_2Li_2$ suspension. The resulting slurry was heated at reflux for 6 hr and then cooled to ambient temperature. Filtration of the reaction mixture provided a precipitate which was washed successively with water, acetone, and ether to yield 14 g (69%) of product, mp 420–430°.

Dimethyltin *m*-Carborane–Dimethyltin *p*-Carborane Copolymer.—A slurry of dilithio-*m*- and -*p*-carborane in ether (100 ml) was prepared from 7.2 g (0.05 mol) of *m*-carborane, 7.2 g (0.05 mol) of *p*-carborane, and 0.22 mol of butyllithium. To this slurry was added, with ice cooling, a solution of dimethyltin dichloride (24.17 g; 0.11 mol) in ether (250 ml). The reaction mixture was then refluxed for 5 hr. After cooling to ambient temperature, the precipitate was collected by filtration and washed successively with water, acetone, and ether to provide 18 g (62%) of product, mp 370–375°, insoluble in common organic solvents.

Germanium Imino-*m*-carborane Polymer.—1,7-Bis(chlorodimethylgermanyl)-*m*-carborane (2.0 g) was dissolved in 50 ml of ethyl ether and cooled in an ice–water bath. Ammonia was passed through at a rapid rate for 30 min, during which time a precipitate formed. The mixture was filtered and the filtrate was evaporated to dryness. The residue so formed was recrystallized from high-boiling petroleum ether to give a polymeric material (molecular weight 1800). *Anal.* Calcd for $C_{30}H_{118}B_{50}Ge_{10}N_6$ (1830.2): C, 19.69; H, 6.50; B, 29.56; Ge, 39.66; N, 4.59. Found: C, 20.10; H, 6.83; B, 28.60; Ge, 40.02; N, 4.19.

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Icosahedral Carboranes. XII. Direct Fluorination of *o*-, *m*-, and *p*-Carborane[1-3]

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Reaction of the parent carboranes with excess elemental fluorine in liquid hydrogen fluoride resulted in *o*-, *m*-, and *p*-$B_{10}F_{10}C_2H_2$ in yields of 30, 60, and 85%, respectively. Replacement of carbon-bonded hydrogen did not occur; however, perfluoro-*m*-carborane was obtained by direct fluorination of *m*-$B_{10}H_{10}C_2F_2$. All three B-decafluorocarboranes will hydrolyze either on immersion in water or exposure to moist air contrasting the hydrolytic stability of all other B-polyhalocarborane species.

The preponderance of studies of the icosahedral carboranes concerns substitution at the two structural carbon atoms which is easily achieved *via* metathesis and insertion reactions involving the C,C′-dilithiocarboranes.[4] Replacement of hydrogen attached to the cage borons, on the other hand, is still limited to a few representatives[5] except for extensive studies of direct chlorination,[6-9] bromination,[9-11] and iodination[9,12,13] of *o*-, *m*-, and *p*-carborane. Some of these reaction products served in X-ray diffraction studies to elucidate the respective carborane structures.[14-16]

As a rule, only boron-attached hydrogens are replaced in such halogenation reactions.[7] In general, C,C′-dihalocarboranes can only be prepared by treatment of the respective dilithio salts with elemental halogen.[17-19]

Recently, we set out to prepare representatives of the heretofore unknown class of B-polyfluorocarboranes. Since halogen exchange in *o*-$B_{10}Cl_{10}C_2H_2$ by means of Swart's mixture[6] or fluoride salts such as AgF and KF had been unsuccessful, initial attempts concerned the action of chlorine monofluoride on *o*- or *m*-carborane suspensions in liquid HF. This pro-

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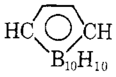
[1] Preceding communication: H. Schroeder, S. Papetti, R. P. Alexander, J. F. Sieckhaus, and T. L. Heying, *Inorg. Chem.*, **8**, 2444 (1969).

[2] Presented at the 4th International Symposium on Fluorine Chemistry, Estes Park, Colo., July 1967.

[3] Nomenclature of the *closo* boron–carbon hydrides is discussed by R. Adams, *Inorg. Chem.*, **2**, 1087 (1963), and appropriate rules approved by the Council of the American Chemical Society are presented in *Inorg. Chem.*, **7**, 1945 (1968). The terms *o*-, *m*-, and *p*-carborane are used to designate 1,2-, 1,7-, and 1,12-dicarba-*closo*-dodecaborane. In accord with current practice, the following symbols are employed for representation of these isomers

$HCB_{10}H_{10}CH$,



[4] For a general review see: T. Onak, *Advan. Organometal. Chem.*, **3**, 263 (1965).

[5] Pertinent literature references on aryl-, alkyl-, alkoxy-, hydroxy-, and amino-B-substituted compounds are given by J. S. Roscoe, S. Kongpricha, and S. Papetti, *Inorg. Chem.*, in press.

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