a failure of the C_{2v} selection rules and a partial D_{5h} behavior. It is reasonable to think that this failure should become more evident on going from pyrrole to pyrrolyl anion.[15]

In the light of these considerations the above interpretation of the infrared spectrum of azaferrocene seems to be supported. In particular, when the five electrons of the pyrrolyl ring are symmetrically involved in the dπ–pπ bond with the iron atom in azaferrocene, the symmetry of the pyrrolyl ring should increase and the C_{2v} local symmetry should tend toward a D_{5h} one (C_{5v} when referred to the π-C_4H_4NFe moiety).

The infrared spectra of $(C_4H_4N)Mn(CO)_3$ and $(C_5H_5)Mn(CO)_3$ give additional support to the above arguments. The cyclopentadienyl compound has been widely studied by infrared and Raman spectroscopy; a rather complete vibrational assignment has been proposed[16] for the ring and for the inorganic grouping modes. When this spectrum is compared with the infrared one of $(C_4H_4N)Mn(CO)_3$ reported in ref 1, one can see that almost all the relevant infrared bands of the pyrrolylic complex correspond, at about the same frequency, to vibrational modes of the cyclopentadienylic compound.

The above points and the previously reported assignments[5,6] of ferrocene allow us to propose with some confidence an assignment of the infrared spectrum of azaferrocene (see Table II). The table shows that the present attributions follow Fritz's assignments for ferrocene, except for a few cases. In particular, for the ν_2, ν_3, ν_9, and ν_{10} modes, Lippincott's assignments have been preferred, since the frequency range seems to be more appropriate to the nature of the corresponding vibrations.

Mass Spectral Studies.—The most peculiar feature of the mass spectrum[3,4] of azaferrocene is the very low abundance of the $C_4H_4NFe^+$ fragment. The peaks corresponding to the parent ion and to $C_5H_5Fe^+$ are instead very intense.

It has been therefore possible to determine the appearance potential (AP) of $C_5H_5Fe^+$ ion and the ionization potential (IP) of azaferrocene. Table IV gives these values, compared with those for ferrocene.[17,18] For the fragmentation processes giving $C_5H_5Fe^+$ from azaferrocene, it is possible to write the equation

TABLE IV
IONIZATION POTENTIALS (IP) AND APPEARANCE POTENTIALS (AP) (EV)

	Azaferrocene	Ferrocene
IP	7.17 ± 0.1	6.99 ± 0.1,[a] 7.05 ± 0.1[b]
AP[$C_5H_5Fe^+$]	12.6 ± 0.2	12.8 ± 1,[a] 14.38 ± 0.3[b]

[a] Reference 17. [b] Reference 18.

$$\mathrm{AP}[C_5H_5Fe^+]^{\mathrm{I}} = \mathrm{IP}[C_5H_5Fe] + D[C_5H_5Fe\text{–pyrrolyl}] + \mathrm{EE}^{\mathrm{I}} \quad (1)$$

while in the case of the $C_5H_5Fe^+$ formation from ferrocene it can be written

$$\mathrm{AP}[C_5H_5Fe^+]^{\mathrm{II}} = \mathrm{IP}[C_5H_5Fe] + D[C_5H_5Fe\text{–}C_5H_5] + \mathrm{EE}^{\mathrm{II}} \quad (2)$$

By subtracting eq 1 from 2 one has

$$\mathrm{AP}[C_5H_5Fe^+]^{\mathrm{II}} - \mathrm{AP}[C_5H_5Fe^+]^{\mathrm{I}} = D[C_5H_5Fe\text{–}C_5H_5] - D[C_5H_5Fe\text{–pyrrolyl}] + (\mathrm{EE}^{\mathrm{II}} - \mathrm{EE}^{\mathrm{I}}) \quad (3)$$

Neglecting in eq 3 the term relative to the difference in the excess energy (EE) one can see that the difference of the AP's is equal to the difference of the bond dissociation energies reported in eq 3. The AP values of Table IV suggest therefore that the $D[C_5H_5Fe\text{–pyrrolyl}]$ is lower than the $D[C_5H_5Fe\text{–}C_5H_5]$. However, due to both the large error encountered in the AP measurements for ferrocene and the above approximation regarding the EE term, this result should be used with caution.

For the fragmentation processes giving $C_5H_5Fe^+$ from azaferrocene, one can also write

$$\mathrm{AP}[C_5H_5Fe^+] \geqslant \mathrm{IP}[\text{azaferrocene}] + D[C_5H_5Fe^+\text{–pyrrolyl}]$$

By using the AP and IP values from Table IV, a value $\geqslant 125$ kcal/mol for the $D[C_5H_5Fe^+\text{–pyrrolyl}]$ is found. Even allowing for some excess energy in the AP value, it is evident that this bond dissociation energy in azaferrocene cation is much greater than that for the corresponding bond in the neutral molecule. From the above conclusion indeed the $D[C_5H_5Fe\text{–pyrrolyl}]$ value cannot be certainly higher than 69.5 kcal/mol (thermochemical value[19] for $D[C_5H_5Fe\text{–}C_5H_5]$). So, as in ferrocene, the less firmly bound electron of azaferrocene is therefore an antibonding one. In fact it has to be said that a great excess energy term might be involved in the fragmentation process leading to $C_5H_5Fe^+$, since it could require a large activation energy owing to its multicenter nature. It seems, however, unlikely that such activation energy could reach the value of at least 60 kcal/mol, which would question the last conclusion.

[15] By using a $C_{2v} \rightarrow D_{5h}$ correlation table, the decrease of infrared activity on going from pyrrole to pyrrolyl anion can be easily explained.

[16] I. J. Hyams, R. T. Bailey, and E. R. Lippincott, *Spectrochim. Acta, Sect. A*, **23**, 273 (1967).

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Icosahedral Carboranes. XV. Monomeric Carboranylenesiloxanes[1,2]

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In recent years the chemistry of the icosahedral car-

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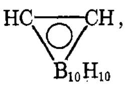
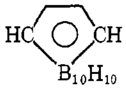
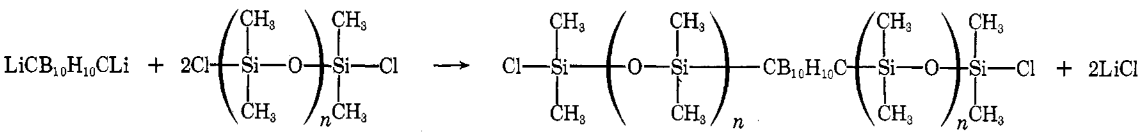
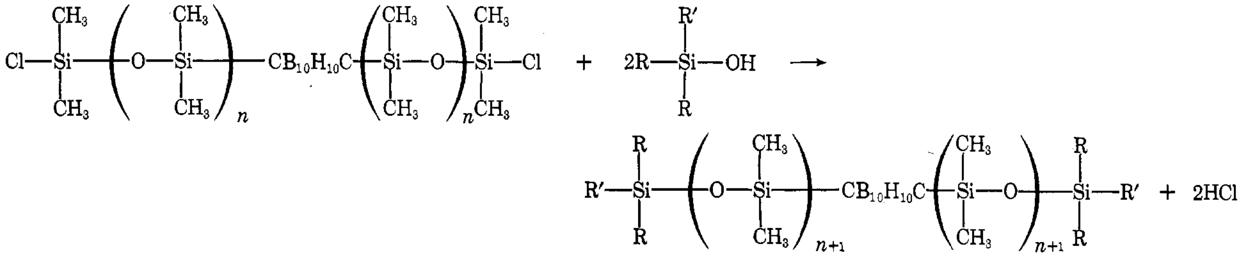
[1] Preceding communication: J. S. Roscoe, S. Kongpricha, and S. Papetti, *Inorg. Chem.*, **9**, 1561 (1970).

[2] Nomenclature of the closo boron–carbon hydrides is discussed by R. Adams, *ibid.*, **2**, 1087 (1963), and appropriate rules approved by the Council of the American Chemical Society are presented in *ibid.*, **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 in formulas, tables, etc.


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




$$\mathrm{LiCB_{10}H_{10}CLi} + 2\,\mathrm{Cl}\left(\mathrm{Si(CH_3)_2{-}O}\right)_n\mathrm{Si(CH_3)_2{-}Cl} \longrightarrow \mathrm{Cl{-}Si(CH_3)_2}\left(\mathrm{O{-}Si(CH_3)_2}\right)_n\mathrm{{-}CB_{10}H_{10}C}\left(\mathrm{Si(CH_3)_2{-}O}\right)_n\mathrm{Si(CH_3)_2{-}Cl} + 2\,\mathrm{LiCl} \quad (1)$$



$$\mathrm{Cl{-}Si(CH_3)_2}\left(\mathrm{O{-}Si(CH_3)_2}\right)_n\mathrm{{-}CB_{10}H_{10}C}\left(\mathrm{Si(CH_3)_2{-}O}\right)_n\mathrm{Si(CH_3)_2{-}Cl} + 2\,\mathrm{R{-}Si(R)(R'){-}OH} \longrightarrow \mathrm{R'{-}Si(R)_2}\left(\mathrm{O{-}Si(CH_3)_2}\right)_{n+1}\mathrm{{-}CB_{10}H_{10}C}\left(\mathrm{Si(CH_3)_2{-}O}\right)_{n+1}\mathrm{Si(R)_2{-}R'} + 2\,\mathrm{HCl} \quad (2)$$

$n = 1, 2$

boranes has been extensively investigated in our own laboratory and others and a large number of derivatives have been characterized.[3] A survey of the existing derivatives reveals a striking lack of liquid carborane compounds with the exception of certain monosubstituted alkyl derivatives such as *n*-hexyl-[4] or *n*-octyl-*o*-carborane[5] which have limited heat stability due to their long aliphatic side chains.

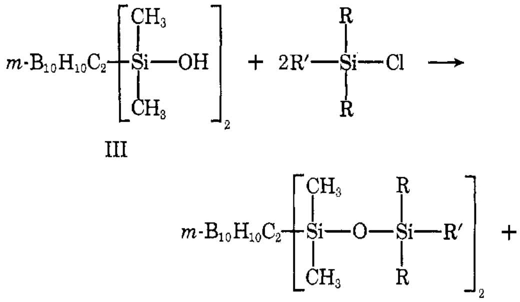
During the course of development work on the poly-*m*-carboranylenesiloxanes[6] it was noted that several of the carborane-containing intermediates were low-melting solids or liquids at room temperature. This observation prompted us to investigate this class of compounds, the monomeric carboranylenesiloxanes, with the objective of preparing new liquid carborane derivatives of high thermal stability with decomposition temperatures above those of existing silicone fluids. The latter materials are polymeric and thermal degradation results chiefly from depolymerization to form volatile cyclics.[7] In contrast, monomeric carborane derivatives with "short-chain" siloxane attachments should not be subject to this problem.

With the exception of 1,7-bis(chlorodimethylsilyl)-*m*-carborane[8] (I), 1,7-bis(3-chlorotetramethyldisiloxanyl)-*m*-carborane[9] (II), and 1,7-bis(hydroxydimethylsilyl)-*m*-carborane[8] (III) which had been prepared earlier for use as polymer intermediates, the carborane derivatives described herein are reported for the first time in the present work.

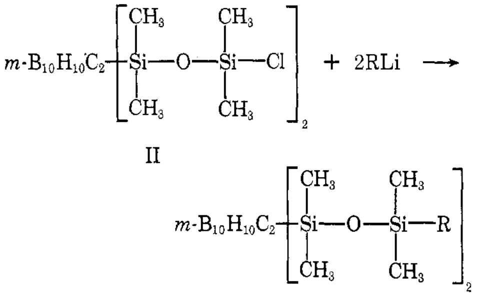
Results and Discussion

The tri- and tetrasiloxanyl carboranes were prepared by a two-step reaction sequence: first, synthesis of a chlorosiloxanyl carborane having one less Si in the side chain than the desired product and, second, condensation of this chloro compound with the appropriate silanol (see eq 1 and 2).

The disiloxanyl derivatives were prepared by two different routes, the first being a condensation reaction between III and a monochlorosilane and the second a metathesis reaction between II and phenyllithium or a monolithiocarborane



$$\underset{\mathrm{III}}{m\text{-}\mathrm{B_{10}H_{10}C_2}\left[\mathrm{Si(CH_3)_2{-}OH}\right]_2} + 2\,\mathrm{R'{-}Si(R)_2{-}Cl} \longrightarrow m\text{-}\mathrm{B_{10}H_{10}C_2}\left[\mathrm{Si(CH_3)_2{-}O{-}Si(R)_2{-}R'}\right]_2 + 2\,\mathrm{HCl} \quad (3)$$



$$\underset{\mathrm{II}}{m\text{-}\mathrm{B_{10}H_{10}C_2}\left[\mathrm{Si(CH_3)_2{-}O{-}Si(CH_3)_2{-}Cl}\right]_2} + 2\,\mathrm{RLi} \longrightarrow m\text{-}\mathrm{B_{10}H_{10}C_2}\left[\mathrm{Si(CH_3)_2{-}O{-}Si(CH_3)_2{-}R}\right]_2 + 2\,\mathrm{LiCl} \quad (4)$$

The structures, physical properties, and syntheses of the carboranylenesiloxanes are summarized in Table I. With the exception of the disiloxanyl derivatives XVII, XVIII, and XIX which are white crystalline solids, these compounds are colorless fairly high-boiling liquids which can be purified by distillation *in vacuo*. In general, the liquids exhibit low ASTM viscosity slopes, low pour points, and high spontaneous ignition temperatures and flash points. The structures proposed for these materials are consistent with their nmr (Table II) and ir spectra as well as osmometric molecular weights and elemental analyses (Table III). At present we can offer no simple explanation based on electronegativity considerations for the observed variations in the chemical shifts of the terminal $\mathrm{Si(CH_3)_3}$ groups and the $\mathrm{Si(CH_3)_2}$ groups adjacent to the carborane in compounds XVI, VIII, and X.

The results of thermal analyses and applications testing of these materials will be reported elsewhere.

[3] (a) H. A. Schroeder, *Inorg. Macromol. Rev.* **1**, 45 (1970). (b) V. I. Bregadze and O. Uu. Okholbystin, *Russ. Chem. Rev.*, **37** (3), 173 (1968), and references contained therein.

[4] T. L. Heying, J. W. Ager, Jr., S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, *Inorg. Chem.*, **2**, 1089 (1963).

[5] R. P. Alexander and H. A. Schroeder, unpublished results.

[6] DEXSIL polymers.

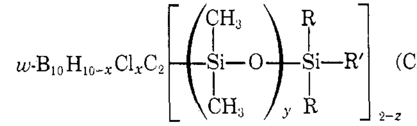
[7] J. B. Carmichael and R. J. Winger, *J. Polym. Sci., Part A*, **3**, 971 (1965).

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

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

TABLE I

STRUCTURES AND PROPERTIES OF MONOMERIC CARBORANYLENESILOXANES



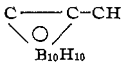
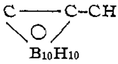
$$w\text{-}B_{10}H_{10-x}Cl_xC_2\left[\left(\begin{array}{c}CH_3\\ |\\ -Si-O-\\ |\\ CH_3\end{array}\right)_y \begin{array}{c}R\\ |\\ Si-R'\\ |\\ R\end{array}\right]_{2-z}(CH_3)_z$$

Compound	R	R′	*w*	*x*	*y*	*z*	% yield	Bp,[a] °C (mm)	Mp,[a] °C	$n^{25}D$	d^{25}, g/cm³
VIII	CH_3	CH_3	*m*	0	2	0	80[b]	175–180 (2.0)	. . .	1.4544	0.9377
IX	CH_3	CH_3	*m*	1	2	0	84[b]	184–186 (0.75)	. . .	1.4604	0.9742
X	CH_3	CH_3	*m*	0	3	0	47[b]	184–185 (0.07)	. . .	1.4434	. . .
XI	CH_3	CH_3	*o*	0	2	1	81[b]	129 (0.10)	. . .	1.4780	. . .
XII	CH_3	CH_3	*m*	0	2	1	70[b]	112 (0.08)	. . .	1.4680	. . .
XIII	CH_3	C_6H_5	*m*	0	2	0	43[b]	228–230 (0.07)	. . .	1.4990	1.0013
XIV	CH_3	C_6H_5	*m*	0	3	0	14[b]	245–247 (0.05)	. . .	1.4823	. . .
XV	CH_3	*p*-C_6H_4Cl	*m*	0	2	0	37[b]	262–264 (0.55)	. . .	1.5095	1.0554
XVI	CH_3	CH_3	*m*	0	1	0	52[c]	335 (760)	. . .	. . .	. . .
XVII	C_6H_5	CH_3	*m*	0	1	0	43[c]	. . .	91.5	. . .	. . .
XVIII	CH_3	*m*-$C_2B_{10}H_{10}CH_3$	*m*	0	1	0	78[d]	. . .	145–8	. . .	. . .
XIX	CH_3	*o*-$C_2B_{10}H_{10}CH_3$	*m*	0	1	0	. . .[d]	. . .	123–4	. . .	. . .
XX	CH_3	C_6H_5	*m*	0	1	0	39[d]	226 (0.18)	. . .	1.5276	. . .

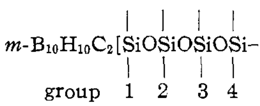
[a] Uncorrected. [b] *Via* condensation procedure A. [c] *Via* condensation procedure B. [d] *Via* metathesis reaction C.

TABLE II

PROTON MAGNETIC RESONANCE DATA[a] FOR MONOMERIC CARBORANYLENESILOXANES[b]

Compd	*n*	R	Assignment[c]			
			Group 1	Group 2	Group 3	Group 4
		m-$B_{10}H_{10}C_2[(Si(CH_3)_2O)_nSi(CH_3)_2R]_2$				
	0	CH_3	7.2			
XVI	1	CH_3	9.4	5.9		
VIII	2	CH_3	11.3	3.3	6.7	
X	3	CH_3	8.6	3.0	4.8	5.5
XVIII	1	$CB_{10}H_{10}C{-}CH_3$	14.1	14.1		
XIX	1	 C——C–CH_3 $B_{10}H_{10}$	17.1	26.0		
XX	1	C_6H_5	8.0	20.8		
XIII	2	C_6H_5	8.5	4.3	20.8	
XV	2	*p*-C_6H_4Cl	9.2	4.5	20.5	
		$R[Si(CH_3)_2O]_nSi(CH_3)_3$				
XI	2	 C——C–CH_3 $B_{10}H_{10}$	22.0	4.9	5.7	
XII	2	$CB_{10}H_{10}C{-}CH_3$	11.4	3.6	5.9	

[a] Chemical shifts (δ) in Hz downfield from TMS as internal standard at 60 MHz in $CDCl_3$ solution. [b] Only resonances arising from Si-bonded methyl groups are listed. [c] Group numbers are defined as follows



$$m\text{-}B_{10}H_{10}C_2[\underset{1}{Si}O\underset{2}{Si}O\underset{3}{Si}O\underset{4}{Si}\text{-}]_2$$

group 1 2 3 4

Experimental Section

All syntheses involving organolithium reagents and/or compounds bearing hydrolyzable chloro groups were performed in a nitrogen atmosphere under anhydrous conditions.

Reagents.—Unless specified otherwise, reagents were used as received from various commercial sources.

Diphenyltetramethyldisilazane.—A 3-l. flask was charged with 186.9 g (1.09 mol) of phenyldimethylchlorosilane and 650 ml of anhydrous diethyl ether. Ammonia was bubbled through the solution with constant stirring at 0° for 20.5 hr, at which point the reaction mixture was filtered. The filtrate was stripped of solvent and the residue was distilled *in vacuo* to give 101.6 g (65%) of diphenyltetramethyldisilazane; bp 130–131° (0.65 mm); $n^{24}D$ 1.5384.

Di-*p*-chlorophenyltetramethyldisilazane.—Using the procedure described above, the reaction of 663.5 g (3.24 mol) of dimethyl(*p*-chlorophenyl)chlorosilane[10] with gaseous ammonia yielded 421.4 g (73%) of the desired disilazane; bp 169–172° (0.2 mm); $n^{25}D$ 1.5511. *Anal.* Calcd for $C_{16}H_{21}Cl_2Si_2N$: C, 54.22; H, 5.97; N, 3.95; Cl, 20.01. Found: C, 54.12; H, 5.99; N, 4.07; Cl, 20.06.

Silanols.—The trimethyl-, phenyldimethyl-, and *p*-chlorophenyldimethylsilanols used in this work were prepared *via* acid hydrolysis of the corresponding disilazanes using the method of Sauer.[11]

1,7-Bis(chlorodimethylsilyl)-*m*-carborane (I).—Preparation was in accordance with that described by Papetti and Heying.[8]

1,7-Bis(3-chlorotetramethyldisiloxanyl)-*m*-carborane (II).—Preparation was in accordance with that described by Papetti, *et al.*[9]

1,7-Bis(hydroxydimethylsilyl)-*m*-carborane (III).—Preparation was in accordance with that described by Papetti and Heying.[8]

1,7-Bis(5-chlorohexamethyltrisiloxanyl)-*m*-carborane (IV).—The reaction of 1.04 mol of *C,C′*-dilithio-*m*-carborane with 2.29 mol of 1,5-dichlorohexamethyltrisiloxane at 0°, according to the procedure described for II, yielded 0.25 mol (25%) of the desired product; bp 170° (0.20 mm); $n^{25}D$ 1.4638. Proton nmr indicated the presence of three distinct types of CH_3 groups in the ratio 1:1:1. Singlets were observed at 13.0, 8.2, and 26.6 Hz. *Anal.* Calcd for $C_{14}H_{46}B_{10}Si_6O_4Cl_2$: C, 26.86; H, 7.41; Cl, 11.32. Found: C, 27.07; H, 7.41; Cl, 10.91.

1,7-Bis(3-chlorotetramethyldisiloxanyl)-9-chloro-*m*-carborane (V).—A 500-ml flask was charged with 63.4 g (0.132 mol) of II, 250 ml of carbon tetrachloride, and 4.0 g (0.030 mol) of aluminum trichloride. The reaction mixture was heated under reflux for 4 hr and stripped of solvent at reduced pressure; the residue was distilled *in vacuo* to yield 24.0 g (36%) of V; bp 172–174° (1.1 mm); $n^{25}D$ 1.4924. *Anal.* Calcd for $C_{10}H_{33}B_{10}Si_4O_2Cl_3$: C, 23.44; H, 6.51; B, 21.94; Si, 21.94; Cl, 20.76. Found: C, 24.48; H, 6.82; B, 21.01; Si, 21.56; Cl, 21.53.

1-Methyl-2-(3-chlorohexamethyldisiloxanyl)-*o*-carborane (VI).—The reaction of 0.632 mol of 1-lithio-2-methyl-*o*-carborane with 1.476 mol of 1,3-dichlorotetramethyldisiloxane, using the procedure described for II, yielded 84.1 g (41%) of VI; bp 135° (0.42 mm). *Anal.* Calcd for $B_{10}C_7H_{25}SiOCl$: B, 33.26; C,

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[10] V. Bazant, *et al.*, "Organosilicon Compounds," Vol. 2, Publishing House of the Czechoslovak Academy of Sciences, Prague, 1965, part 1, p 259.

[11] R. O. Sauer, *J. Amer. Chem. Soc.*, **66**, 1707 (1944).

TABLE III

ANALYTICAL DATA FOR MONOMERIC CARBORANYLENESILOXANES

Compound	% C		% H		% B		% Cl		% Si		Mol wt	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
VIII	32.84	32.32	8.95	8.53	18.47	17.91	...	...	28.79	27.75	585	585[a]
IX	31.01	30.91	8.30	8.33	17.45	17.10	5.72	5.92	...	...	619.7	...
X	32.75	32.92	8.79	8.69	14.74	14.53	...	...	32.75	32.92	733.5	701[b]
XI	31.71	31.69	9.05	9.02	28.54	28.43	...	...	...	...	378.8	...
XII	31.71	31.70	9.05	8.96	28.54	28.25	...	...	...	...	378.8	...
XIII	44.02	43.53	7.96	8.10	15.24	15.13	...	...	23.76	23.39	709.3	695[b]
XIV	42.01	41.32	7.91	7.70	12.61	12.75	...	...	...	...	857.7	834[b]
XV	40.13	40.08	6.99	6.98	13.89	13.58	9.11	9.81	...	...	778.2	804[b]
XVI	32.98	32.95	9.23	9.18	24.76	24.99	...	...	25.71	25.61	437	...
XVII	56.09	54.91	7.06	6.93	15.78	14.65	...	...	16.40	16.19	653.2	624[b]
XVIII	26.64	26.42	8.38	8.39	44.96	44.63	...	...	15.58	13.80	721.3	...
XIX	26.64	26.68	8.38	8.43	44.96	44.69	...	...	15.58	15.95	721.3	...
XX	47.10	46.83	7.90	7.88	19.27	18.77	...	...	...	...	561.1	579[b]

[a] By mass spectrometry. [b] By vapor pressure osmometry.

25.87; H, 7.75; Cl, 10.91. Found: B, 32.70; C, 26.03; H, 7.54; Cl, 9.89.

1-Methyl-7-(3-chlorohexamethyldisiloxanyl)-*m*-carborane (VII).—The reaction of 1.48 mol of monolithiomethyl-*m*-carborane with 2.96 mol of 1,3-dichlorotetramethyldisiloxane, using the procedure described for II, yielded 0.513 mol (35%) of VII; bp 130–131° (0.28 mm); $n^{25}D$ 1.4919. *Anal.* Calcd for $B_{10}C_7H_{25}Si_2OCl$: B, 33.26; C, 25.87; H, 7.75; Cl, 10.91. Found: B, 32.33; C, 26.04; H, 7.96; Cl, 11.26.

"End-Capping" Reactions.—The various "end-capped" carboranylenesiloxanes were prepared by one of three general methods illustrated below by specific examples.

(A) Condensation of Chlorosiloxanylcarboranes with Silanols. 1,7-Bis(heptamethyltrisiloxanyl)-*m*-carborane (VIII).—In a 500-ml flask equipped with condenser, nitrogen inlet, and magnetic stirrer were placed 151.0 g (1.67 mol) of trimethylsilanol and 200.0 g (0.418 mol) of II. After the initial, vigorous reaction had subsided, the reaction mixture was heated to reflux under nitrogen for 3 hr. After cooling, the mixture was diluted with 650 ml of diethyl ether and washed three times with 500-ml portions of distilled water. The organic layer was diluted with 650 ml of ether, dried over anhydrous sodium sulfate, and then stripped of solvent at reduced pressure; the residue was distilled *in vacuo* to yield 195.8 g (79.8%) of colorless liquid.

(B) Condensation of III with Chlorosilanes. 1,7-Bis(pentamethyldisiloxanyl)-*m*-carborane (XVI).—In a 250-ml flask equipped with magnetic stirring bar and condenser were placed 29.0 g (0.100 mol) of III and 43.48 g (0.400 mol) of trimethylchlorosilane. A 2-hr period of heating to reflux followed the initial exothermic reaction. The crude product, which was shown by vpc analysis to contain 71% of XVI, was distilled *in vacuo* to yield 22.7 g (52%) of colorless liquid.

(C) Metathesis Reactions. 1,7-Bis(3-[1-methyl-*m*-carboran-7-yl]tetramethyldisiloxanyl)-*m*-carborane (XVIII).—Dropwise addition of a solution of 0.316 mol of 1-methyl-7-lithio-*m*-carborane in 100 ml ether to an ice-cooled solution of (0.158 mol) of II in 100 ml of ether was followed by hydrolysis with 250 ml of distilled water. The white precipitate was collected by suction filtration and the organic and water phases of the filtrate separated. The residue obtained from evaporation of the ether solution was combined with the first precipitate. Recrystallization of the crude product was from petroleum ether (bp 30–60°); yield 78.2 g (69%); mp 145–148°.

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The Systems Xenon Hexafluoride–Tantalum Pentafluoride, Xenon Hexafluoride–Manganese Fluoride, Xenon Hexafluoride–Uranium Hexafluoride

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Xenon hexafluoride combines with a number of other fluorides to give complex compounds considered to be of two types. In the substances[2] $2NaF \cdot XeF_6$, $2KF \cdot XeF_6$, $CsF \cdot XeF_6$, $2CsF \cdot XeF_6$, $RbF \cdot XeF_6$, and $2RbF \cdot XeF_6$ it is believed that XeF_6 combines with F^- to give an anion of the type XeF_7^- or XeF_8^{2-}. Perhaps the substance $2NOF \cdot XeF_6$[3] is also of this type. Other compounds, including $XeF_6 \cdot BF_3$,[4] $4XeF_6 \cdot SnF_4$,[5] $4XeF_6 \cdot GeF_4$,[6] $2XeF_6 \cdot GeF_4$,[6] $XeF_6 \cdot GeF_4$,[6] $2XeF_6 \cdot PF_5$,[7] $XeF_6 \cdot AsF_5$, $2XeF_6 \cdot AsF_5$,[7] $2XeF_6 \cdot SbF_5$,[8] $XeF_6 \cdot SbF_5$,[8] $XeF_6 \cdot 2SbF_5$,[8] $XeF_6 \cdot VF_5$,[9] $XeF_6 \cdot PtF_5$,[10,11] and $2XeF_6 \cdot PtF_5$,[10] probably involve donation of fluoride from XeF_6 to leave XeF_5^+ or $Xe_2F_{11}^+$.

It has now been found that the reaction of XeF_6 in excess with TaF_5 proceeds readily at 60° to yield $2XeF_6 \cdot TaF_5$ which decomposes under vacuum at 20° to give XeF_6 and $XeF_6 \cdot TaF_5$. These complex compounds probably are of the second type mentioned above.

A compound which appears to be either $4XeF_6 \cdot MnF_4$ or $4XeF_6 \cdot MnF_3$ is formed when Mn is heated with excess Xe and F_2 under pressure. The reactants Mn,

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