TABLE III

ANALYTICAL DATA FOR MONOMERIC CARBORANYLENESILOXANES

	% C		% H		% B		% Cl		% Si		Mol wt	
Compound	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); $n^{25}\text{D}$ 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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XeF_6, and F_2 may also be used. The experimental data do not allow one to decide which oxidation state, III or IV, for manganese is correct. If the compound involves formation of XeF_7^- ions, one would expect manganese to be in the IV state. If the manganese accepts F^- from XeF_6, it is reasonable that the resulting ions should be $Xe_2F_{11}^+$ and MnF_6^{2-}, again requiring Mn(IV). It also seems possible that $4XeF_6 \cdot MnF_3$ could exist with either MnF_5^{2-} or MnF_6^{3-} ions being present. When the compound is held under vacuum at 40° or more, it loses XeF_6.

No evidence for combination was found when UF_6 and XeF_6 were mixed and held together at 70 or 100°.

Experimental Section

Apparatus.—All reactions were run in a metal vacuum line made largely from 6.35-mm o.d. copper tubing. Metal valves with Teflon packing were used and soldering was done with silver solder. The reactors were made from 6.35-mm o.d. Monel tubing welded at one end and attached to a stainless steel valve at the other end. It should have been safe to use such a reactor at pressures up to 500 atm at 200°. The valve could be removed to allow the reactor to be opened. Pressure of gas in the vacuum line was measured with a precision of 5 mm by a Bourdon gauge.

Reagents.—Fluorine, xenon, tantalum, and uranium were industrial products of good quality. They were used without refining. Manganese was also of good quality. It had been reduced to the metallic form by electrolysis. Xenon hexafluoride was prepared by holding a mixture of xenon with a large excess of fluorine at a pressure of about 300 atm and a temperature of about 225° for a period of 2 days or more. The reactor was then cooled below its valve to −183° and the unreacted fluorine was pumped away. The material remaining in the reactor was nearly pure xenon hexafluoride.

Tantalum pentafluoride was prepared in the same reactor to be used later for combining TaF_5 with XeF_6. Tantalum powder was placed in the reactor and was dried by pumping away vapors. Fluorine was then introduced, and the vessel was heated to approximately 120° for about 15 min. Even though fluorine was present at a pressure of nearly 25 atm, only a part of the tantalum was consumed. The reaction stopped, because of a protective coating formed on the metal. At this stage, the vessel was chilled to −183° and fluorine was pumped away. The valve was then closed and the bottom of the reactor was warmed enough to distil TaF_5 away from the tantalum and into the upper part of the reactor. By adding more fluorine and repeating partial reactions of this sort from six to ten times, it was possible to convert all of the tantalum to TaF_5.

Uranium hexafluoride was produced from the metal by using an excess of fluorine and holding the reactor near 160° for about 12 hr. Only one step was needed to consume all of the metal. The uranium hexafluoride was purified by sublimation, the product being collected by condensation in a trap at −60°.

When powdered manganese was exposed to fluorine at 200° and about 185 atm pressure for 16 hr, the metal was only partially converted to fluoride. Because of this, adducts of XeF_6 to manganese fluoride were produced starting with manganese, xenon, and fluorine or with manganese, xenon hexafluoride, and fluorine but not with MnF_3.

System XeF_6–TaF_5.—A 0.2040-g sample of tantalum (1.127 mg-aoms) was converted to the pentafluoride in a Monel reactor. Xenon hexafluoride (3.65 mmol) was distilled into the reactor and the vessel was then held at 60° for 65 hr. Following this, the vessel was held at 0° while xenon hexafluoride was pumped away and condensed in a cold trap. From time to time the reactor was removed from the vacuum line and weighed. The change in the remaining ratio of XeF_6 to TaF_5 is shown in Figure 1. The ratio fell rapidly due to removal of excess XeF_6 until the ratio 1.995 was reached. From this point on, loss of XeF_6 was slow. This indicates existence of a solid compound $2XeF_6 \cdot TaF_5$. When the reactor was then held at 100° and pumping was continued, there was a loss of XeF_6 until the ratio 1.0 was reached. The remaining solid was $XeF_6 \cdot TaF_5$. Other runs with different initial rates of XeF_6 to TaF_5, different reaction conditions, and different temperatures while pumping away XeF_6 confirmed the two compounds $2XeF_6 \cdot TaF_5$ and $XFe_6 \cdot TaF_5$ but gave no indication of other complex compounds. No evidence was found for a compound having an XeF_6:TaF_5 ratio greater than 2. The compound $2XeF_6 \cdot TaF_5$ also was obtained by mixing TaF_5, Xe, and a large excess of F_2 in a Monel reactor which was then held at about 225°.

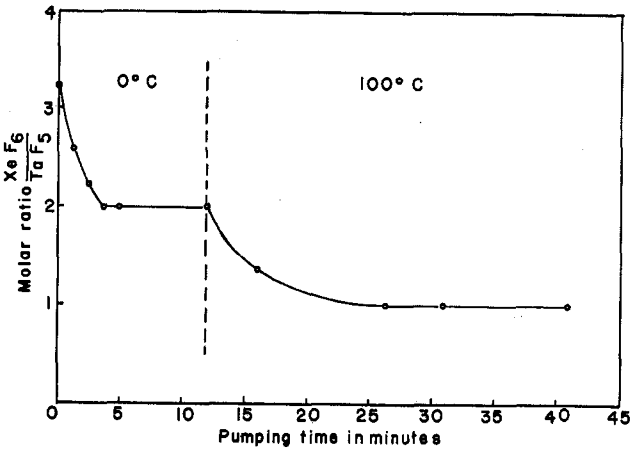

Figure 1.—Removal of XeF_6 under vacuum.

$2XeF_6 \cdot TaF_5$ is a white solid at 25° which reacts vigorously and rapidly with water. It reacts slowly with concentrated H_3PO_4 giving a gas and a precipitate but dissolves in H_2SO_4 without evolution of gas. The latter solution when added in a small amount to KI solution gives I_2. Adding more of the sulfuric acid solution causes the color of iodine to vanish, presumably because of formation of the IO_3^-. $2XeF_6 \cdot TaF_5$ can be stored in glass for at least several days. It reacts with flame with trichloroethylene and slowly with CCl_4. The reaction with hexafluorobenzene is rapid, but with trifluoroacetic anhydride or with $(CF_2CFCl)_n$ polymer, reaction is slow.

$XeF_6 \cdot TaF_5$ is a white solid at 25°. It reacts with water, but more slowly than $2XeF_6 \cdot TaF_5$. Its behavior with phosphoric and sulfuric acids is like that of $2XeF_6 \cdot TaF_5$. With CCl_4 it reacts slowly at 60° but apparently not at 25°. Its reaction with hexafluorobenzene is vigorous, but with trifluoroacetic anhydride reaction is slow. The solid seems neither to react with nor to dissolve in $(CF_2CFCl)_n$ polymer oil.

X-Ray powder patterns were obtained for powdered materials held in Pyrex-glass capillaries. These were filled and sealed in a manner which rigorously excluded water vapor. The capillaries were held in a 114.6-mm diameter Hull–Debye–Scherrer powder camera and were irradiated with nickel-filtered copper radiation (λ 1.5418 Å). *d* spacings are given in Table I for TaF_5, $XeF_6 \cdot TaF_5$, and $2XeF_6 \cdot TaF_5$. Each of the solids has its own characteristic set of lines. The visually estimated relative intensity of each line is listed as very strong (vs), strong (s), medium (m), weak (w), or very weak (vw).

System XeF_6–Manganese Fluoride.—Because of the time schedule of J. A. the study of this system had to be discontinued before it reached completion. The description of an experiment will now be given.

Manganese powder (1.006 mg-atoms), Xe (6.167 mg-atoms), and F_2 (53.2 mmol) were placed together in a Monel metal reactor having a volume of 4.6 ml. The vessel was then held at about 225° for 65 hr. These reaction conditions allowed substantially complete conversion of xenon to XeF_6 or a complex compound of XeF_6. All of the manganese metal reacted (found later when the vessel was opened). The vessel was then cooled below its

TABLE I

X-RAY POWDER DIFFRACTION DATA

TaF_5		$TaF_5 \cdot XeF_6$		$TaF_5 \cdot 2XeF_6$	
d, Å	Intens	*d*, Å	Intens	*d*, Å	Intens
5.05	w	4.70	vs	5.08	vs
4.44	w	4.17	s	4.48	s
4.32	w	4.07	s	4.10	vs
4.06	s	3.77	vs	3.91	s
3.96	s	3.13	vs	3.78	s
3.59	w	2.86	w	3.60	vs
3.35	s	2.68	m	3.07	m
2.74	w	2.52	w	2.94	m
2.38	m	2.40	m	2.78	w
2.26	w	2.34	m	2.70	vw
2.13	m	2.26	m	2.55	vw
2.02	m	2.23	vw	2.46	vw
1.99	vw	2.154	m	2.28	s
1.97	vw	2.090	m	2.16	vw
1.890	w	1.984	m	2.12	s
1.838	w	1.945	m	2.08	s
1.779	w	1.912	w	2.06	vw
1.729	w	1.836	w	1.94	vw
1.684	w	1.796	s	1.88	vw
1.607	w	1.701	vw	1.84	vw
1.481	w	1.684	vw	1.802	m
1.460	w	1.638	w	1.698	m
		1.622	vw	1.610	w
		1.573	w	1.577	w
		1.555	vw	1.537	m
		1.538	vw	1.500	m
		1.504	vw	1.419	w
		1.455	vw	1.363	m
		1.439	w		

valve to −183° and unreacted F_2 was removed. This step was followed by pumping for a few minutes with the vessel at −60°. The weight of product, 1.6381 g, corresponded to the weight remaining in the reactor of 6.167 mmol of XeF_6 and 1.006 mmol of $MnF_{3.67}$. (In another similar run a ratio of F/Mn of 3.25 was found.) These data suggest that the manganese was either in the III or the IV oxidation state. Experimental error (mainly a loss of a small amount of XeF_6 remaining in the valve and removed by pumping while the tube was cold) could easily have been large enough to allow either number to be correct. The vessel was then held at 0° while XeF_6 was removed by pumping. From time to time, the vessel was removed and weighed. Figure 2 shows the relationship between time of pumping and weight of product remaining in the reactor. The weight fell rapidly until the ratio of XeF_6 to MnF_3 (or MnF_4) was a little less than 4; then the weight remained about constant. This indicated existence of a compound which was either $4XeF_6 \cdot MnF_3$ or $4XeF_6 \cdot MnF_4$. Pumping was then continued at 40, 50, 60, and finally 70° as shown in Figure 2. During these operations xenon hexafluoride was removed at a decreasing rate, as shown in the figure, until a constant weight of 0.4070 g was reached at an Xe:Mn ratio a little greater than 1. The product was found by analysis to contain about 10.7 g-atoms of F/g-atom of Mn (average of two determinations, 10.4 and 11.1). It also reacted with potassium iodide solution liberating 4.0 mol of I_2/g-atom of Mn (average of two determinations, 3.95 and 4.05).

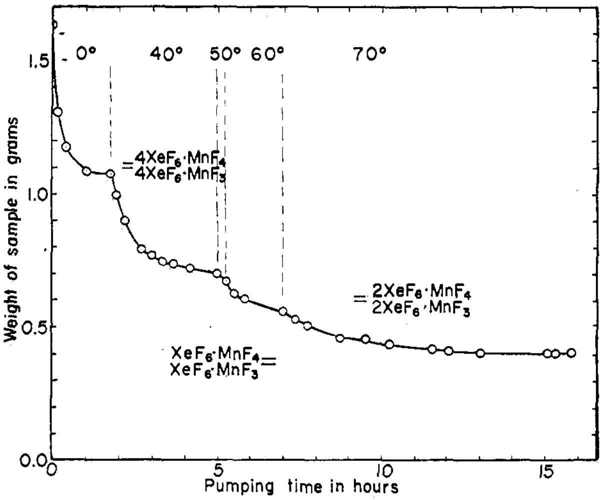

Figure 2.—Removal of XeF_6 under vacuum.

Other experiments gave results similar to the above. One of the runs involved the use of Mn, XeF_6, and F_2. While the formulas for the compounds have not been definitely established, the authors feel strongly that the first compound is $4XeF_6 \cdot MnF_4$ and that this decomposes when heated under vacuum to give XeF_6 and a product of composition close to $XeF_6 \cdot MnF_4$. The final material was found to be pink (suggesting the presence of MnF_5^-) and to react vigorously at 25° with water but not with $(CF_2CFCl)_n$ polymer oil. It could be stored without decomposition under nitrogen in glass but became brown in air containing water vapor. Data regarding the X-ray powder pattern can be furnished by the authors.

System XeF_6–UF_6.—A mixture of XeF_6 with UF_6 in the molar ratio 6.66 was held at 70° in a Monel metal reactor for 65 hr. A second mixture in the ratio 4.79 was held in another reactor for 17 hr at 100°. In each case subsequent pumping from the reactor when held at 0° allowed one to draw a smooth curve for weight of sample *vs.* time. No plateau existed in the curve. The whole sample was pumped away. These experiments gave no indication of compound formation by combination of the two hexafluorides.

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Perhaloalkyl Hydrochlorites and Pentafluorosulfur Hypochlorite. III. Lewis Acid Catalyzed Synthesis

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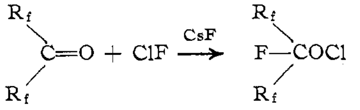
Recent publications have described the synthesis of perfluoroalkyl hypochlorites, R_fOCl, a new class of compounds prepared by the metal fluoride catalyzed addition of chlorine monofluoride to perfluorinated carbonyl compounds[1-3]



$$(R_f)_2C{=}O + ClF \xrightarrow{CsF} (R_f)_2CF{-}OCl \qquad (1)$$

These may be regarded as base-catalyzed oxidative additions to the carbonyl group, where the first step

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