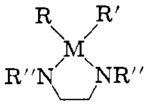
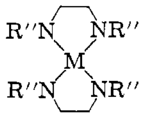
TABLE I

INFRARED SPECTRAL PARAMETERS OF GROUP IV *gem*-DIAMINES

M	R	R′	R″	$\nu_{M-N} \pm 5$ cm^{-1}	$\nu_{ring} \pm 5$ cm^{-1}
			$RR'M(NR''_2)_2$		
Si	CH_3	CH_3	C_2H_5	931	
Si	CH_3	C_6H_5	C_2H_5	934	
Si	C_6H_5	C_6H_5	CH_3	995	
Ge	CH_3	CH_3	C_2H_5	896	
Sn	CH_3	CH_3	C_2H_5	880	
					
Si	CH_3	CH_3	CH_3	933	1342
Si	CH_3	CH_3	C_2H_5	951	1330
Si	CH_3	CH_3	C_3H_7	963	*a*
Si	CH_3	CH_3	$C_6H_4CH_3$	962	*a*
Si	CH_3	CH_3	$C_6H_4OCH_3$	959	*a*
Si	CH_3	C_6H_5	CH_3	931	1340
Si	CH_3	C_6H_5	C_2H_5	952	1331
Si	C_6H_5	C_6H_5	CH_3	932	1344
Ge	CH_3	CH_3	CH_3	907	1333
Ge	C_6H_5	C_6H_5	CH_3	907	*b*
					
Si			CH_3	943	1349
Si			C_2H_5	967	1333
Si			$C_6H_4CH_3$	965	*a*
Ge			CH_3	910	1342
Ge			C_2H_5	926	1331

[a] Region obscured. [b] Weak.

have assigned the absorption at 880 cm^{-1} in the spectrum of bis(diethylamino)tin dimethyl to the tin–nitrogen asymmetric stretch. This is in agreement with the assignment based on a study of isotopomeric N^{14}- and N^{15}-trimethylstannylaniline of 843 ± 1 cm^{-1} for the $Sn-N^{14}$ stretch in this compound.[2,7]

The data of Table I show the silicon and germanium nitrogen stretching frequencies to be virtually independent of the group attached to these elements. The insulating effect of silicon toward changes in infrared absorption has been noted in numerous systems.[8] On the other hand, stretching frequencies and ring vibrations are rather dependent upon the group attached to nitrogen. The silicon–nitrogen stretch shifts to higher frequency in changing N-methyl for N-phenyl or larger N-alkyl groups while ring frequency decreases from N-methyl to N-ethyl.

Experimental Section

The preparation of the carbon,[9] silicon,[10] and germanium[11] imidazolidines, the spiro silicon and germanium imidazolidines,[12] and bis(diethylamino)dialkylgermanes[9,11] has been reported previously. Preparation of the bis(diethylamino)dialkylsilanes and stannanes followed procedures reported by Henglein and Lienhard[3] and Jones and Lappert,[13] respectively.

The infrared spectra of the compounds as liquid smears were recorded on a Perkin-Elmer infracord in the 4000–650-cm^{-1} range. All spectra were calibrated with polystyrene.

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[7] Assignment of $\nu_{asym}(Sn-N)$ has been the subject of some controversy. A band at 510 cm^{-1} in the spectrum of N′,N′-dimethyl-N-phenylureidotin trimethyl has been assigned to $\nu(Sn-N)$ on the basis of the similarity of mass of the Sn–N and Sn–C groups in four-coordinate tin compounds: T. A. George, K. Jones, and M. F. Lappert, *J. Chem. Soc.*, 2157 (1965). Infrared spectra of tris(tri-*n*-alkyltin)amines containing methyl, ethyl, and propyl groups yielded an assignment of $\nu_{asym}(Sn-N)$ at 728, 712, and 712 cm^{-1}, respectively: K. Sisido and S. Kojima, *J. Org. Chem.*, **29**, 907 (1964). More recently infrared and Raman spectra of tris(trimethyltin)amine and tetrakis(dimethylamino)tin have yielded assignments of $\nu_{sym}(Sn_3-N)$ at 514, $\nu_{asym}(Sn_3-N)$ at 672, and $\nu_{asym}(Sn-N_4)$ at 538 cm^{-1} in the two compounds [R. E. Hester and K. Jones, *Chem. Commun.*, 317 (1966)]. Bands in these regions, although present in the spectrum of N-trimethylstannylaniline, failed to shift to lower frequencies on N^{15} substitution.[2]

[8] A. L. Smith, *Spectrochim. Acta*, **16**, 87 (1960).

[9] C. H. Yoder and J. J. Zuckerman, *J. Am. Chem. Soc.*, **88**, 4831 (1966).

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The Reaction of Xenon Hexafluoride with Stannic Fluoride

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Xenon hexafluoride is known to form the following compounds by combination with the appropriate reactants: $XeF_6 \cdot AsF_5$,[1] $XeF_6 \cdot BF_3$,[1] $XeF_6 \cdot 2SbF_5$,[2] $XeF_6 \cdot SbF_5$,[2] $2XeF_6 \cdot SbF_5$,[2] $CsF \cdot XeF_6$,[3] $2CsF \cdot XeF_6$,[3] $RbF \cdot XeF_6$,[3] $2RbF \cdot XeF_6$,[3] $2KF \cdot XeF_6$,[3] and $2NaF \cdot XeF_6$.[3] The reaction of excess XeF_6 with SnF_4 has now been found to proceed readily to yield the compound $4XeF_6 \cdot SnF_4$. When this compound is heated to about 50° while under vacuum, XeF_6 is slowly lost. The rate of loss of XeF_6 decreases somewhat when the molar ratio of XeF_6 to SnF_4 becomes less than 2.0. Below a molar ratio of 1.3 XeF_6 is lost only very slowly even when the solid is held at 110° under vacuum. While XeF_6 is being removed, the X-ray powder pattern of the solid remains substantially unchanged down to a molar ratio approaching 2.0. At molar ratios somewhat below 2.0 the powder pattern contains lines that can be attributed to uncombined SnF_4. Other lines that do not belong to either $4XeF_6 \cdot SnF_4$ or SnF_4 are also present and in some cases diffuse broad diffraction halos possibly due to extremely small crystallites are observed. Stoichiometric proportions of any compound(s) having molar ratio(s) of XeF_6 to SnF_4 less than 4.0 have not been established.

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[1] H. Selig, *Science*, **144**, 537 (1964).

[2] G. L. Gard and G. H. Cady, *Inorg. Chem.*, **3**, 1745 (1964).

[3] R. D. Peacock, H. Selig, and I. Sheft, *Proc. Chem. Soc.*, 285 (1964).

The 4:1 compound hydrolyzes to give a nearly quantitative yield of xenon(VI) in solution. When heated to about 100° in a glass vessel, the solid dissociates sufficiently to allow one to see a yellow vapor, presumably XeF_6. The density of the solid is 4.18 ± 0.04 g/cm^3 at 0°.

Experimental Section

Reagents.—Xenon hexafluoride was prepared by the combination of the elements under pressure at about 225°. Stannic fluoride was obtained from Alfa Inorganics Inc. Prior to use, an atmosphere of fluorine was placed over the stannic fluoride for a few hours.

Preparation of $4XeF_6 \cdot SnF_4$.—A Monel metal reactor equipped with a brass Hoke valve was used for the reactions. The reactor could be opened to allow solid to be added or removed. In a typical preparation 0.0914 g (0.469 mmole) of SnF_4 powder was transferred in a drybox to the reactor. The vessel was then attached to a metal vacuum line and 0.5494 g (2.24 mmoles) of XeF_6 was added by distillation (molar ratio 1:4.8). The vessel was then held at 57° for 6 hr. After pumping away the unreacted XeF_6 at room temperature, the product weighed 0.5176 g, corresponding to a composition of $3.70XeF_6 \cdot SnF_4$. Since the reaction was incomplete (possibly owing to too short a reaction time), an additional 0.3090 g (1.26 mmoles) of XeF_6 was distilled into the vessel, and the reaction was allowed to proceed for another 4 hr at 57°. The unreacted XeF_6 was then removed by pumping at room temperature for 7 min. The weight of the product, 0.5546 g, corresponded to a composition of $4.02XeF_6 \cdot SnF_4$. Pumping for another 10 min resulted in about a 1-mg weight loss and a drop in the composition to $4.01XeF_6 \cdot SnF_4$. An additional pumping time of 30 min produced only a 2-mg weight loss or a composition of $3.99XeF_6 \cdot SnF_4$.

Chemical Properties.—The substance was found to be a powerful oxidizing and fluorinating agent. It attacked dry glass only very slowly, but traces of moisture greatly accelerated the attack. About 1 mg of the compound readily ignited acetone in air.

A 0.1700-g sample of $4XeF_6 \cdot SnF_4$ was transferred to a glass bulb equipped with a Fischer and Porter 4-mm Lab-Crest threaded glass valve having a Teflon stem. When water was added through the valve, a vigorous reaction occurred, but only a little O_2 was formed, indicating that most of the oxidizing power remained in solution as Xe(VI). The addition of a solution of KI resulted in the liberation of I_2 and Xe. The I_2 was titrated with a solution of sodium thiosulfate. A total of 23.0 equiv of I_2/mole of $4XeF_6 \cdot SnF_4$ was found (theoretical 24.0). The result is somewhat low, at least in part, because some O_2 was produced.

X-Ray Powder Patterns.—The X-ray powder photographs were taken on samples contained in 0.2-mm Lindemann glass capillaries and 0.5-mm Pyrex glass capillaries. Because of the extremely hygroscopic nature of $4XeF_6 \cdot SnF_4$, the capillaries were filled in a drybox. Satisfactory results were obtained only when moisture was rigorously excluded from the system. The capillaries were then filled and temporarily sealed with a waxy polymer of chlorotrifluoroethylene. Outside of the drybox the capillaries were sealed with a microtorch. The capillaries were loaded into a 114.6-mm diameter Debye–Scherrer powder camera. Nickel-filtered copper radiation (λ 1.5418 A) was used, and exposures of 4–8 hr were taken.

The *d* spacings found for $4XeF_6 \cdot SnF_4$ are given in Table I. The visually estimated relative intensity of each measured line is listed as strong (s), medium (m), or weak (w).

When $4XeF_6 \cdot SnF_4$ was pumped on at about 50°, XeF_6 was slowly lost. Lowering the XeF_6 to SnF_4 ratio did not produce any noticeable changes in the powder pattern over a surprisingly long range. The same powder pattern was observed from a composition of molar ratio of XeF_6 to SnF_4 of 4:1 down to 2.29:1.

Thermal Decomposition.—Thermal decomposition of $4XeF_6 \cdot SnF_4$ under vacuum was studied by heating the solid and pumping away the XeF_6. A plot of composition against pumping time is given in Figure 1. The leveling of the curve at a molar ratio of XeF_6 to SnF_4 of about 1.3 and the change in slope at a molar ratio of 2.0 suggest the presence of other compounds. In general, some X-ray powder pattern lines characteristic of neither $4XeF_6 \cdot SnF_4$ nor SnF_4 were observed at XeF_6 to SnF_4 molar ratios between 1.0 and 2.0, but these lines were not consistently reproducible at any certain composition. The presence of uncombined SnF_4 was also detected. No other compounds, therefore, were identified.

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR $4XeF_6 \cdot SnF_4$

d, A	Intens	*d*, A	Intens	*d*, A	Intens
10.3	w	2.72	m	1.75	m
9.7	w	2.68	w	1.711	m
9.2	w	2.63	w	1.672	m
8.8	w	2.59	w	1.642	w
5.37	w	2.55	w	1.607	w
5.20	w	2.50	w	1.593	w
4.85	m	2.44	w	1.564	w
4.43	s	2.40	w	1.547	w
4.33	s	2.32	w	1.526	w
4.19	s	2.26	m	1.503	w
4.03	w	2.20	w	1.489	m
3.93	s	2.17	m	1.471	w
3.82	m	2.13	w	1.436	m
3.69	m	2.11	m	1.399	m
3.55	m	2.08	m	1.377	w
3.43	m	2.04	w	1.359	w
3.34	w	2.00	w	1.335	w
3.23	w	1.96	m	1.315	m
3.13	m	1.93	w	1.291	w
3.07	m	1.90	m	1.271	w
2.98	m	1.87	m	1.259	w
2.90	m	1.85	w	1.244	m
2.85	w	1.83	m	1.230	w
2.79	m	1.79	m	1.205	w

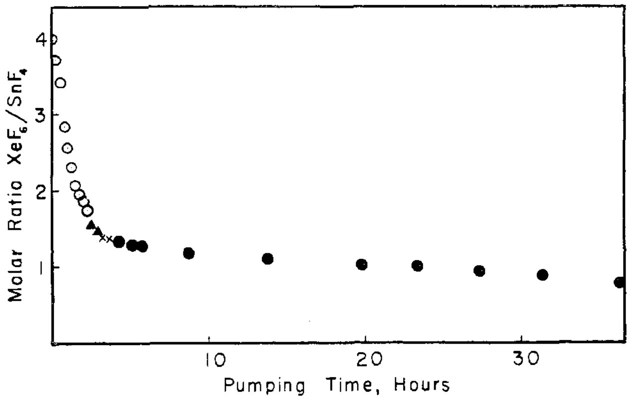

Figure 1.—Thermal decomposition of $4XeF_6 \cdot SnF_4$ under vacuum. The sample was held at: 50°, ○; 62°, ▲; 75°, ×; and 105°, ●.

An attempt was made to measure a melting point of $4XeF_6 \cdot SnF_4$ in a Pyrex glass tube of 3-mm o.d. Several milligrams of the solid was added to a tube in a drybox, and the open end was plugged with a waxy polymer of chlorotrifluoroethylene. No melting was observed, but at about 100° a yellow vapor (presumably XeF_6) could be seen above the white solid. At somewhat higher temperatures attack on the glass was considerable.

Density.—The density was measured in a small Pyrex pycnometer of about 0.2-cm^3 volume. A Fischer and Porter Lab-Crest valve equipped with a Teflon stem was attached to the pycnometer. About 0.2 g of $4XeF_6 \cdot SnF_4$ was added to the apparatus. Enough perfluoromethylcyclohexane was then distilled into the pycnometer to fill the apparatus, and the volume displaced by the $4XeF_6 \cdot SnF_4$ was calculated. The $4XeF_6 \cdot SnF_4$ neither reacted with nor was soluble in the perfluoromethylcyclohexane. The value of the density determined by this method was 4.18 ± 0.04 g/cm^3 at 0°.

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Temperature-Dependent Nuclear Magnetic Resonance Spectrum of Cyclooctatetraenecyclopentadienylcobalt

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Rapid valence tautomerism of cyclooctatetraenetricarbonyliron (**1**) is known to occur in solution.[1-3] The X-ray[1] and the infrared[2] analyses of **1** indicated that the tautomers have the 1,3-butadienetricarbonyliron-type structure. Valence tautomerism in **1** is very rapid even at −60° as evidenced by the appearance of a single, sharp nmr peak.[4]

In the related cobalt complex, cyclooctatetraenecyclopentadienylcobalt (**2**), the cyclooctatetraene coordinates to cobalt as 1,5-diene as indicated by the nmr spectrum having three peaks in a ratio of 4:5:4.[5] A marked difference in the modes of bonding of the cyclooctatetraene (COT) moiety to the metals is thus apparent.

There are some examples[6] of diolefincyclopentadienylcobalt complexes involving 1,3-diene coordination. Hence, the valence tautomers of **2** might contain the 1,3-diene coordination group at higher temperatures, at least as a transient species. The nmr spectrum of **2** at 70° gave rise to only a minor change as compared to the room-temperature spectrum. Line broadening of the peaks due to the COT protons was observed. At 100°, this broadening became very extensive and the peaks were almost disappearing.

These peaks reappeared on lowering the temperature to 70° and approximate to the uppermost curve as shown in Figure 1. This clearly assures the reversibility of the line broadening. The spectrum at 133° showed peaks at τ 4.36, 5.12, 5.36, 5.70, and 5.90, in approximate relative intensity of 7:15:10:9:7, respectively. The peaks at τ 5.70 and 5.90 can be assigned as due to the C_5H_5 and C_8H_8 protons of $[(C_5H_5)Co)_2C_8H_8$ (**3**), respectively (lit.[7] τ 6.1, 6.3).

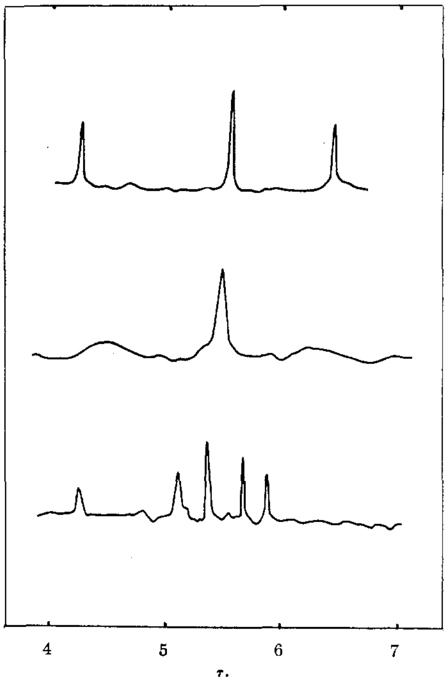

Figure 1.—Nmr spectrum of $(C_5H_5)Co(C_8H_8)$: top curve, room temperature; middle curve, 100°; bottom curve, 133°.

The formation of this binuclear compound (**3**) is not unexpected since the disproportionation of **2** was observed under the condition of the nmr measurement. A similar disproportionation was recently reported for tetracarbonylcyclooctatetraenemolybdenum.[8]

The peaks at τ 5.36 are due to C_5H_5 protons of **2**. New appearance of the peak at τ 5.12 and absence of the peaks at τ 4.25 and 6.48, originally present in the room-temperature spectrum of **2**, indicate the valence tautomerism to be occurring at 133° as expected. The position of the new peak is found quite near the average position (τ 5.17) of the two room-temperature peaks if the correction of the downfield shift (τ 0.22)[9] is made for raising the temperature (see Table I). The peak at τ 4.36 may be due to free C_8H_8 (lit.[7] τ 4.2) released by the reaction forming $[(C_5H_5)Co]_2C_8H_8$. This nmr observation is believed to be the first one of the valence tautomerism in COT complexes having a 1,5-diene as a coordinating site. Possibly the valence tautomerism occurs between the two different 1,5-diene structures only. Alternatively, the tautomerism may involve 1,3-diene coordination as an intermediate for the two 1,5-diene forms as mentioned above. However, no distinction between the two possibilities can be made from the present nmr information.

TABLE I
NMR DATA FOR $(C_5H_5)Co(C_8H_8)$ IN τ VALUES

	C_8H_8 protons	C_5H_5 protons
Room temperature	4.25, 6.48	5.58
133°	512	5.36
		$\Delta\tau$ 0.22

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[1] B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 2084 (1962).

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[8] H. D. Kaesz, S. Winstein, and C. G. Kreiter, *J. Am. Chem. Soc.*, **88**, 1319 (1966); see footnote 8 of that paper.

[9] The reason for this temperature shift could not be ascertained.