M, acidity in the range 3 M to pH 9, and with irradiation times of 2 h in seven experiments and 24 h in one.

The N_2 gas derived from irradiated azide in all these experiments showed no significant increase over the 25% ^{15}N level, indicating no scrambling of N atoms. The only significant departure from the unscrambled composition observed in N_2O product occurred at high acidity and consisted of an increase at mass 46, giving N_2O of ^{15}N content greater than 25%, opposite to the trend predicted for N scrambling. (The probable reason for this is the presence of a small residual of photolysis product.)

The irradiation experiments lend no support to the cyclic azide hypothesis but do not rule out the possibility of formation of such an intermediate species in the reaction sequence eq 1 and 2. While we have observed isotopic evidence in apparently close support of the hypothesis (experiments 6–8; Table IV), these data can be interpreted in an alternative way that seems to provide a more satisfactory view of the entire range of stoichiometries represented in Table IV. In summary, the evidence presented here must be taken as more con than pro cyclic azide.

Acknowledgment. We are grateful to Dr. M. J. Akhtar for assistance with mass spectrometry and Dr. G. Stedman for helpful discussions.

Registry No. HNO_2, 7782-77-6; $N_2H_5^+$, 18500-32-8.

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Direct Fluorination of Hexamethyldigermane and Hexamethyldisilane

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The low-temperature direct fluorination of hexamethyldigermane and hexamethyldisilane resulted in cleavage of the metal–metal bond in both compounds. From hexamethyldisilane, partially fluorinated derivatives of trimethylsilyl fluoride were obtained. The reaction of fluorine with hexamethyldigermane gave tris(trifluoromethyl)germanium fluoride in 66% yield.

Introduction

Controlled direct fluorination at low temperatures with careful manipulation of temperature and fluorine dilution is capable of preserving molecular structures that would normally be destroyed. As a result, a wide variety of organic, inorganic, and organometallic compounds have been synthesized.[1–6] The preservation of germanium and silicon carbon bonds during fluorination[7] earlier suggested the possibility that this technique might be capable of effecting fluorination while preserving metal–metal bonds in compounds such as hexamethyldigermane and hexamethyldisilane.

The reaction scheme followed is illustrated in Figure 1.

Experimental Section

The fluorine apparatus was described previously.[1] Specific reaction conditions were chosen to minimize breakage of metal–carbon bonds while at the same time replacing the maximum amount of hydrogen with fluorine. Procedures found most suitable for the silane and germane are presented in Tables I and II.

Mass spectra were measured on a CEC 491 spectrometer at 70 eV. Proton NMR spectra were measured on Varian HA-100 and N-T 200 spectrometers. The fluorine NMR spectra were taken on Varian Em-390 and Bruker WH-90 spectrometers. Infrared spectra were obtained in the gas phase on a Beckman IR 20A spectrophotometer. Gas chromatographic separation of the products was done on a Bendix gas chromatograph equipped with a cryogenic controller and a thermal conductivity detector. A 25 ft × $^3/_8$ in. column with

Table I. Fluorination of Hexamethyldigermane[a]

temp, °C	time, h	temp, °C	time, h
−100	48	−50	23
−90	25	−40	24
−80	24	−30	11
−70	21	−20	15
−60	24	amb	24

[a] Helium flow rate 60 cm^3/min throughout; fluorine flow rate 1.0 cm^3/min, except at ambient temperature when it was stopped.

Table II. Fluorination of Hexamethyldisilane[a]

temp, °C	time, h	temp, °C	time, h
−150	20	−120	10
−140	5.5	−110	9
−130	15	−100	15

[a] Helium flow rate 60 cm^3/min throughout; fluorine flow rate 1 cm^3/min throughout.

Table III. Gas Chromatographic Separation Program for Partially Fluorinated Tris(trimethylsilyl) Fluorides

temp, °C		time, min
0		30
	increase at 1.5 °C/min to 40 °C	
40		30
	increase at 1.0 °C/min to 60 °C	
60		60
	increase at 5 °C/min to 185 °C	

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(1) N. J. Maraschin, B. D. Catsikis, L. H. Davis, G. Jarvinen, and R. J. Lagow, *J. Am. Chem. Soc.*, **97**, 513 (1975).
(2) J. L. Adcock and R. J. Lagow, *J. Am. Chem. Soc.*, **96**, 7588 (1974).
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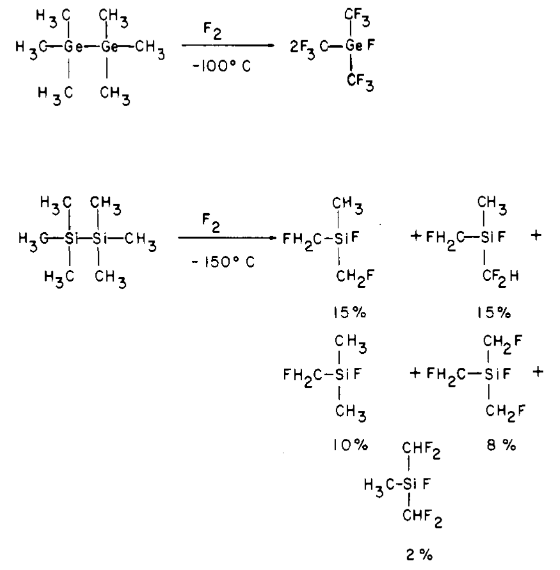

Figure 1. Cryogenic reaction of hexamethyldigermane and hexamethyldisilane with elemental fluorine.

Table IV. Infrared Spectra of Partially Fluorinated Methylsilyl Fluorides (cm^{-1})

$Si(CH_3)(CH_2F)_2F$	2940, 2930, 1260, 1005, 900, 840, 800, 725
$Si(CH_3)(CH_2F)(CF_2H)F$	2920, 1320, 1265, 1090, 1010, 910, 800, 830
$Si(CH_3)_2(CH_2F)F$	2980, 2930, 1270, 1025, 1015, 905, 855, 815, 735
$Si(CH_2F)_3F$	2925, 2900, 925, 825, 730, 700, 645
$Si(CH_2F)_2(CH_3)F$	2920, 1315, 1260, 1090, 1025, 905, 795, 725

fluorosilicone on chromosorb P was used for separations.

Fluorination of $Ge_2(CH)_6$. The fluorination system was purged with helium for 24 h, followed by cooling of the reactor to −100 °C. Hexamethyldigermane (Larame Chem. Co.) (1.2 g) was injected into the first zone of the reactor. Fluorine flow was initiated, and the temperature was slowly raised until the product, a volatile white solid, was trapped downstream with liquid nitrogen. Under the optimized fluorination reaction conditions delineated in Table I, 1.93 g (66% yield) of tris(trifluoromethyl)germanium fluoride was recovered. More rapid reactions with fluorine resulted in increased amounts of carbon and germanium tetrafluoride in the product mixture. On the other hand, milder conditions gave complex mixtures of partially fluorinated trimethylgermanium fluorides. $(P - F)^+$ and $(P - CF_3)^+$ were readily identified in the mass spectra due to the complex isotope pattern evident for germanium: mass spectrum, m/e 281 $(P - F)^+$, 231 $(P - CF_3)^+$, 181, 119, 93, 69; IR 1260 (s), 1175 (vs), 723 (s) cm^{-1}; ^{19}F NMR (rel ext CF_3COOH) 142.6 (GeF), −22.1 (CF_3) ppm.

Fluorination of $Si_2(CH_3)_6$. The fluorination system was pacified with fluorine and then purged with helium for 24 h. The reactor was cooled to −150 °C. Subsequently, hexamethyldisilane (1.35 g) was injected. Fluorine flow and temperature conditions presented in Table II were followed. Products from the reaction were fractionated on a vacuum line at −78, −131, and −196 °C. Only a trace of partially fluorinated material stopped at −78 °C. The majority of the material stopped in traps at −131 and −196 °C. CF_4, CF_3H, CF_2H_2, CH_3F, $CF_2{=}CFH$, and SiF_4 were found present in the −196 °C trap by infrared and mass spectrometry data. In addition, five partially fluorinated silyl fluorides were isolated from the −131 °C trap by using the gas chromatographic program specified in Table III. The individual silyl fluorides were readily characterized by their simple proton and fluorine magnetic resonance spectra. The value of magnetic resonance in the structural elucidation of these compounds is illustrated in Figures 2–6. Infrared and mass spectra of these compounds are compiled in Tables IV and V, respectively.

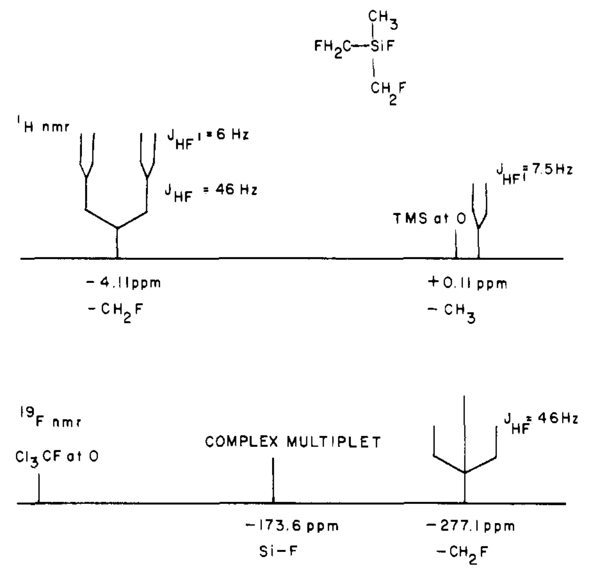

Figure 2.

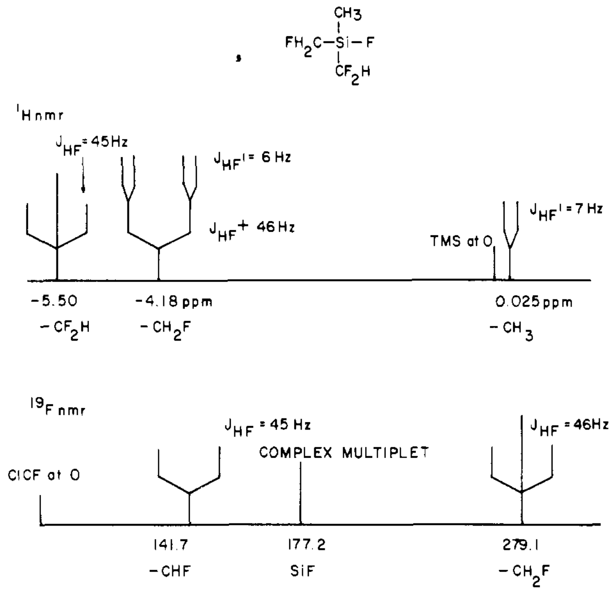

Figure 3.

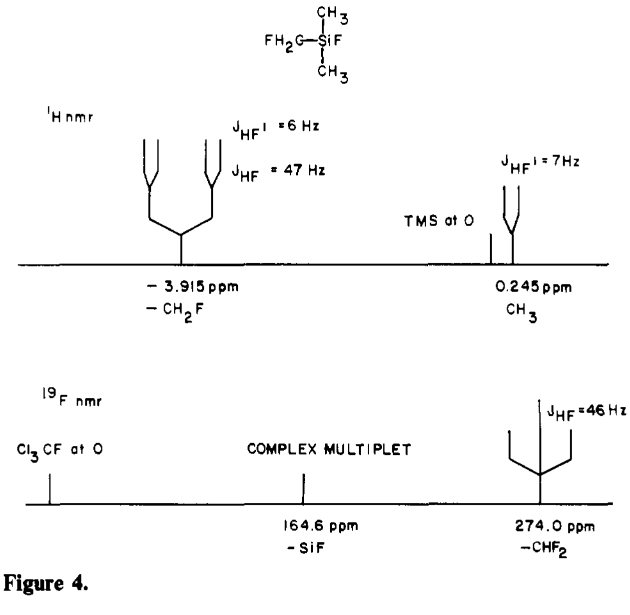

Figure 4.

Results and Discussion

Several attempts to vary reaction conditions in an effort to maintain the metal–metal bonds in the compounds were unsuccessful. In both cases milder fluorination conditions resulted in incomplete replacement of hydrogen by fluorine. In the

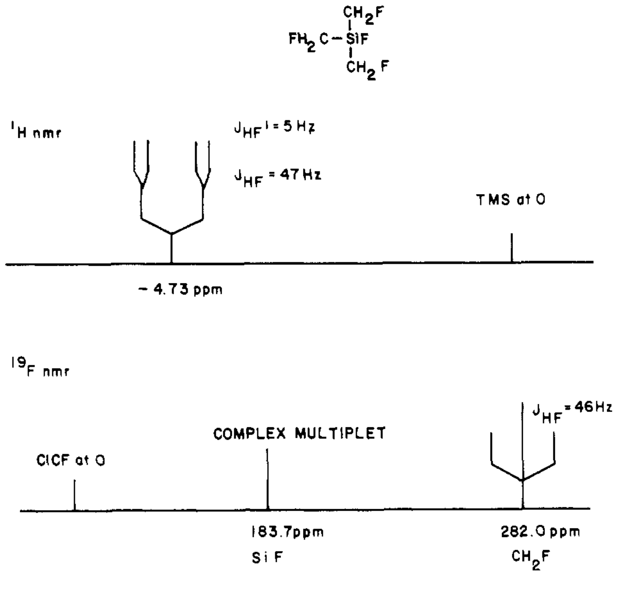

Figure 5.

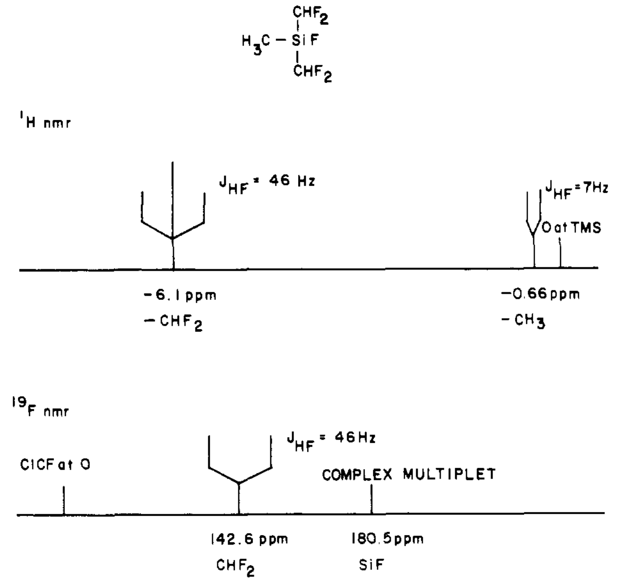

Figure 6.

Table V. Mass Spectra of Partially Fluorinated Methylsilyl Fluorides

	m/e (relative intensity)
$Si(CH_3)(CH_2F)_2F^+$	95 (35), 85 (30), 81 (100), 77 (50), 76 (25), 67 (99), 47 (70), 28 (50)
$Si(CH_3)(CH_2F)(CF_2H)F^+$	95 (30), 85 (80), 81 (100), 76 (27), 67 (80), 51 (85), 47 (70), 28 (90)
$Si(CH_3)_2(CH_2F)F^+$	81 (30), 77 (100), 67 (28), 63 (20), 49 (28), 48 (30)
$Si(CH_2F)_3F^+$	85 (80), 5 (28), 47 (60), 39 (50), 22 (80), 28 (60), 27 (100), 15 (35)
$Si(CH_2F)_2(CH_3)F^+$	93 (30), 85 (100), 81 (90), 51 (45), 47 (45), 28 (35)

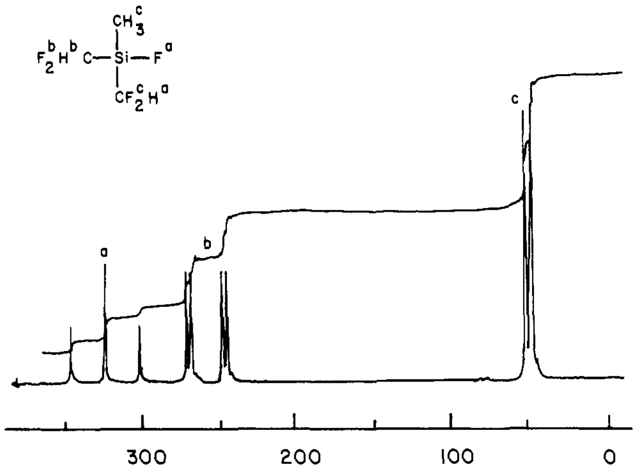

Figure 7. ^1H NMR spectra: (a) CF_2H; (b) CH_2F; (c) CH_3.

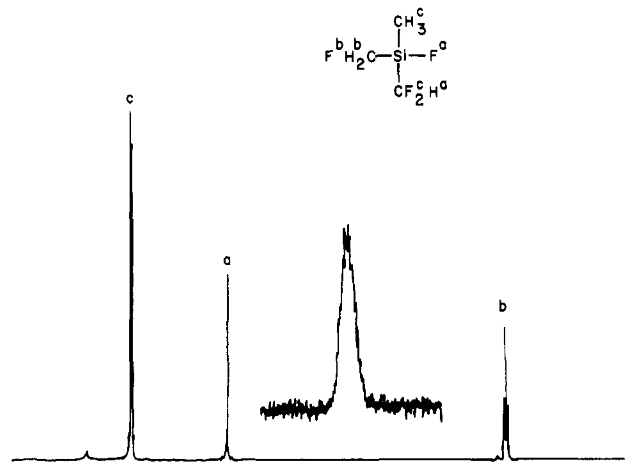

Figure 8. ^{19}F NMR spectra: (a) SiF; (b) CH_2F; (c) CF_2H. Inset: SiF complex coupling.

germanium case, more rapid reactions and/or higher temperatures gave tris(trifluoromethyl)germanium fluoride. However, the metal–metal bond was always broken and converted to the fluoride. In the silicon case, more vigorous reaction with fluorine only led to additional formation of low molecular weight partially fluorinated hydrocarbons and silicon tetrafluoride. Tris(trifluoromethyl)silicon fluoride was not found under any conditions. This result in the silicon case was consistent with earlier findings in the fluorination of tetramethylsilane.[7]

The straightforward NMR spectra of the partially fluorinated silyl fluorides reflected the long and short range coupling of hydrogen to fluorine. The silicon bound to fluorine was seen as a complex multiplet with the satellite doublet attributed to coupling with silicon-29 (4.7% natural abundance). Figure 7 illustrates the recorded spectra of $Si(CH_3)(CH_2F)(CF_2H)F$, showing long range ^1H coupling to ^{19}F in the ^1H NMR. The ^{29}Si isotope pattern and complex multiplicity of the Si–F in the ^{19}F NMR spectrum are evident in Figure 8. The chemical shifts and coupling constants for the methylsilyl fluorides were in good agreement with those reported previously for similar compounds.[7] It was, of course, rather amazing that ~30–40 kcal/mol germanium–carbon and silicon–carbon bonds are preserved during fluorination at low temperatures in the course of the exothermic reaction (104 kcal/mol is released per mol of hydrogen atoms replaced by fluorine). This method provides a very facile and specific route to tris(fluoromethyl) group 4 fluorides.

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Registry No. $Ge_2(CH_3)_6$, 993-52-2; $Si_2(CH_3)_6$, 1450-14-2; $Ge(CF_3)_3F$, 66348-16-1; $Si(CH_3)(CH_2F)_2F$, 65954-64-5; $Si(CH_3)(CH_2F)(CF_2H)F$, 65864-69-9; $Si(CH_3)_2(CH_2F)F$, 54417-69-5; $Si(CH_2F)_3F$, 79792-69-1; $Si(CH_2F)_2(CH_3)F$, 65954-64-5.