parameter since the $^4A_{2g} \rightarrow (^2E_g, ^2T_{1g})$ transition could not be detected in our work. The value of β_{55} is close to that of β_{35}. This demonstrates that the π^*-antibonding delocalization is more or less of equal importance as σ^*-antibonding delocalization, presumably because the orbitals of the lower triplet have the correct symmetry to overlap with the empty π^*-antibonding orbitals of the cyanide ligands. This results in a further depression of the triplet with respect to the upper doublet, which accounts for the relatively higher value of $10Dq$, and also argues against applying to cyano complexes the simple "electrostatic crystal field" approach in which π-bonding is ignored.

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CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
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The Preparation and Properties of Some New Nitrogen and Fluorine Derivatives of Disilane[1a]

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Disilanyl bromide, H_3SiSiH_2Br, has been found to react with $(CH_3)_2NH$ to yield the new compounds $H_3SiSiH_2N(CH_3)_2$ and $H_3SiSiH[N(CH_3)_2]_2$. Boron trifluoride underwent reaction with $(H_3SiSiH_2)_3N$ at low temperatures to give the addition compound $(H_3SiSiH_2)_3N \cdot BF_3$, which then decomposed to yield the new species, H_3SiSiH_2F. A number of physical properties of the above new compounds have been examined and the significance of certain properties of analogous silyl, disilanyl, methyl, and ethyl compounds are discussed.

As a continuation of a study of the Si–Si bond as reflected in the properties of compounds containing this linkage,[2–5] it was considered desirable to investigate further the properties of disilanylamines since only one nitrogen derivative of disilane, $(H_3SiSiH_2)_3N$, had previously been described.[3] Although the silylamines $(H_3Si)_3N$, $(H_3Si)_2NCH_3$, and $H_3SiN(CH_3)_2$ have all been isolated,[6–8] $H_3SiN(CH_3)_2$ is reported to be unstable thermally and it decomposes at a measurable rate at 3–4°.[8] It was therefore of interest to attempt to prepare $H_3SiSiH_2N(CH_3)_2$ to see what effect the substitution of an Si–H bond in $H_3SiN(CH_3)_2$ by a SiH_3 group would have on the stability of the amine. A second purpose of the investigation was to ascertain whether BF_3 would cleave the Si–N bond in $(H_3SiSiH_2)_3N$ to give H_3SiSiH_2F in an analogous reaction to that between BF_3 and $(H_3Si)_3N$,[9,10] *viz.*

$$(H_3Si)_3N + BF_3 \longrightarrow H_3SiF + (H_3Si)_2NBF_2 \qquad (1)$$

or whether cleavage would occur preferentially at the Si–Si bond.

Results and Discussion

Disilanyl bromide, H_3SiSiH_2Br, and $(CH_3)_2NH$ were found to undergo reaction at low temperatures to yield the new compound N-disilanyldimethylamine, $H_3SiSiH_2N(CH_3)_2$.

$$H_3SiSiH_2Br + 2(CH_3)_2NH \longrightarrow H_3SiSiH_2N(CH_3)_2 + (CH_3)_2NH{\cdot}HBr \qquad (2)$$

The presence of the H_3SiSiH_2 group in the compound appeared, if anything, to make the material more stable thermally than the silyl analog, $H_3SiN(CH_3)_2$, since 80% of a sample of $H_3SiSiH_2N(CH_3)_2$ could be recovered unchanged after standing for 47 hr. at 0°.

Also formed in the above reaction was the new compound, 1,1-bis-(dimethylamino)-disilane, $H_3SiSiH[N(CH_3)_2]_2$. It appears that this may have been formed by the decomposition of some of the $H_3SiSiH_2N(CH_3)_2$ before it could be isolated and purified since a considerable quantity of Si_2H_6 also was found among the reaction products, *viz.*

$$2H_3SiSiH_2N(CH_3)_2 \longrightarrow H_3SiSiH[N(CH_3)_2]_2 + Si_2H_6 \qquad (3)$$

The fact that CH_3NH_2, $(CH_3)_3N$, and NH_3 catalyze the decomposition of $(H_3Si)_3N$,[11] *viz.*

$$3(H_3Si)_3N \longrightarrow (SiH_2NSiH_3)_3 + 3SiH_4 \qquad (4)$$

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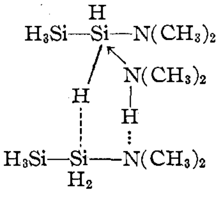
strongly suggests that a slight excess (5%) of $(CH_3)_2NH$ which was used in the reaction may have promoted the decomposition of the $H_3SiSiH_2N(CH_3)_2$.

The formation of the unsymmetrical bis-(dimethylamino)-disilane could arise as follows. The $(CH_3)_2NH$ could attack the α-silicon as shown below to give the adduct $H_3SiSiH_2N(CH_3)_2 \cdot NH(CH_3)_2$. This adduct then could interact with another molecule of $H_3SiSiH_2N(CH_3)_2$ through hydrogen bonding of the hydrogen attached to nitrogen. Transfer of the N–H and a Si–H hydrogen atom then could yield the species $H_3SiSiH_3 \cdot NH(CH_3)_2$, which would instantly decompose to Si_2H_6 and $(CH_3)_2NH$.



That the first intermediate species, $H_3SiSiH_2N(CH_3)_2 \cdot NH(CH_3)_2$, is likely to be formed is suggested by the fact that a compound of approximate composition $SiH_3I \cdot 2[(CH_3)_3N]$ has been isolated from the reaction of SiH_3I with $(CH_3)_3N$.[12] It is to be expected that the α-silicon rather than the β-silicon would be attacked since the acidic character of a silicon atom must be increased by the presence of an attached electronegative atom in order for adduct formation with amines to occur. Thus, SiH_3Cl, but not SiH_4, forms an adduct with $(CH_3)_3N$.[13] This also would explain the instant decomposition of the postulated intermediary, $Si_2H_6 \cdot NH(CH_3)_2$.

1,1-Bis-(dimethylamino)-disilane is more stable thermally than $H_3SiSiH_2N(CH_3)_2$ and it can be held at room temperature for 2–3 days without appreciable decomposition occurring. This material is of particular interest since it is the first isomerically pure unsymmetrically disubstituted derivative of disilane to be characterized and because of the presence of the reactive Si–N bonds it should serve as a useful starting material for the preparation of many derivatives containing the $H_3SiSiH{=}$ group.

Boron trifluoride and $(H_3SiSiH_2)_3N$ formed the solid addition compound $(H_3SiSiH_2)_3N \cdot BF_3$ at −134°, which appeared to dissociate at low temperatures (eq. 5) but to decompose at higher temperatures to give the

$$(H_3SiSiH_2)_3N \cdot BF_3 \rightleftharpoons (H_3SiSiH_2)_3N + BF_3 \qquad (5)$$

new compound, disilanyl fluoride, H_3SiSiH_2F, and a substance which was presumed to be $(H_3SiSiH_2)_2NBF_2$ by analogy with the products of the similar reaction between BF_3 and $(H_3Si)_3N$[9,10] (eq. 1). The over-all reaction can be represented by eq. 6 but it appears likely that rearrangement of the adduct in the solid state (eq. 7) may have taken place prior to liberation of H_3SiSiH_2F. No evidence of any cleavage of the Si–Si bond was observed.

$$(H_3SiSiH_2)_3N + BF_3 \longrightarrow H_3SiSiH_2F + (H_3SiSiH_2)_2NBF_2 \qquad (6)$$

$$(H_3SiSiH_2)_3N \cdot BF_3(s) \longrightarrow (H_3SiSiH_2)_2NBF_2 \cdot H_3SiSiH_2F(s) \qquad (7)$$

Disilanyl fluoride showed no sign of decomposition when held for a day at 0°. This is of interest since there are conflicting reports concerning the thermal stability of SiH_3F, SiH_2F_2, and $HSiF_3$.[9,14–17] It appears most probable that if either the silyl or disilanyl fluorides are completely free from traces of impurities they will be thermally stable. This also is true for most disilanyl compounds so far studied.[2–5] The slow decomposition of H_3SiSiH_2I at 0° is now believed to be caused by traces of aluminum iodide impurity which is difficult to remove from the relatively high-boiling disilanyl compound.

It is of interest to note that all the silyl halides, although heavier molecules than their methyl analogs, boil at lower or approximately the same temperatures as the methyl compounds.[18] This would appear to be caused, at least in part, by the presence of p_π–d_π bonding between the halogen and silicon which acts to reduce the polarity of the silyl halide molecules and helps to compensate for their higher molecular weights. That p_π–d_π bonding can greatly modify the polarity of a silyl halide molecule is illustrated, for example, by the fact that although silicon has a smaller electronegativity than carbon, SiH_3Cl has a smaller, rather than larger, dipole moment than CH_3Cl.[19] However, in the case of the disilanyl halides, it is found that they all boil at considerably higher temperatures than their ethyl analogs.[2,4,5] Here there is only one silicon–halogen bond for every two silicon atoms in the molecule and the decrease in polarity due to p_π–d_π bonding is not sufficient to compensate for the increased mass of the second silicon atom.

It has been shown previously that a linear relationship exists between the boiling points of analogous silyl and methyl compounds.[18] This may be represented by the equation: b.p. SiH_3 derivative = 1.110[b. p. CH_3 derivative] − 2.10. A similar relationship is also found for analogous disilanyl and ethyl compounds: b. p. Si_2H_5 derivative = 1.079[b. p. C_2H_5 derivative] + 26.10. The experimental and calculated values are given in Table I. Since the Trouton's constants of all the

TABLE I
EXPERIMENTAL AND CALCULATED BOILING POINTS OF SILYL AND DISILANYL HALIDES

H_3SiX, X =	Exptl.[9,13] b.p.	Calcd. b.p.	Si_2H_5X, X =	Exptl. b.p.	Calcd. b.p.
F	−88.1	−89.1	F	−10.0	−8.4
Cl	−30.4	−28.7	Cl	40.1[5]	39.4
Br	1.9	1.8	Br	69.5[4]	67.5
I	45.4	45.0	I	102.8[2]	104.2

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compounds concerned are normal, a linear relationship therefore exists between the molar heats of vaporization of analogous silyl and methyl halides and disilanyl and ethyl halides, respectively.

It has been shown previously that for comparable structures, the degree of intermolecular attraction is less in certain silicon compounds than in their carbon analogs since the change in boiling point per molecular weight unit, Δb.p./Δmol. wt., between analogous methyl and ethyl compounds on the one hand, and analogous silyl and disilanyl compounds on the other, is greater in the former case than in the latter.[3] In other words, the insertion of a CH_2 group in a methyl compound causes a greater increase in boiling point per unit increase in mass than the insertion of a SiH_2 group in a silyl compound. This property also is exemplified in the halides listed in Table II.

TABLE II

BOILING POINT AND MOLECULAR WEIGHT DIFFERENCE RATIOS BETWEEN SILYL AND DISILANYL COMPOUNDS AND THEIR CARBON ANALOGS

	Δb.p./ Δmol. wt.		Δb.p./ Δmol. wt.
C_2H_5F - CH_3F	3.31	Si_2H_5F - SiH_3F	2.60
C_2H_5Cl - CH_3Cl	2.59	Si_2H_5Cl - SiH_3Cl	2.34
C_2H_5Br - CH_3Br	2.49	Si_2H_5Br - SiH_3Br	2.25
C_2H_5I - CH_3I	2.14	Si_2H_5I - SiH_3I	1.91

Experimental

Apparatus.—All work was carried out in a Pyrex glass vacuum system. All apparatus, instruments, and techniques used were identical with those previously described.[2-5] Mass spectra were measured by means of a Consolidated Electrodynamics Corporation Model 21-130 mass spectrometer. The proton magnetic resonance spectrum was recorded by means of an HR 60 Varian Associates spectrometer, Model 4300D with flux stabilizer, operated at 60 Mc./sec. at room temperature.

Materials.—Anhydrous commercial $(CH_3)_2NH$ was dried with sodium metal and its purity was confirmed by measuring its vapor pressure at −40.6° (found, 61.5 mm., calcd.,[20] 58.8 mm.). Disilanyl bromide and iodide were prepared by the reaction of Si_2H_6 with HBr[21] and HI,[2] respectively. Vapor pressures were measured at 0° (Si_2H_5Br, found, 44.5 mm., lit.[4] 45.0 mm.; Si_2H_5I, found, 11.0 mm., lit.[2] 9.5 mm.). Trisdisilanylamine was obtained by the reaction of Si_2H_5I with NH_3.[3] Its infrared spectrum was identical with that given for the pure material[3]; melting point, found, −98.9°, lit.[3] −97.1°. After distillation, the purity of a sample of commercial BF_3 was confirmed by its molecular weight (found, 66.9, calcd., 67.82; vapor pressure at −111.5°, found, 307 mm., calcd.,[22] 314 mm.) and by its infrared spectrum, which was identical with that of the pure material.[23]

Reaction of Si_2H_5Br with $(CH_3)_2NH$.—Disilanyl bromide (1.0535 g.; 7.466 mmoles) and $(CH_3)_2NH$ (0.7060 g.; 15.66 mmoles) were transferred to a tube attached to the bottom of a 2-l. bulb. The tube then was warmed from liquid nitrogen temperature by surrounding it with a −78° bath. Reaction appeared to commence immediately, and after 30 min. it was placed in a −46° bath for 10 min., after which it was allowed to stand at room temperature for 15 min. The interior of the flask was coated with a white solid. The reaction apparatus was shaken occasionally while at the lower temperatures. The volatile products of the reaction were separated by distillation through a low temperature fractionating column held at −64°.

The first major fraction was found to consist chiefly of Si_2H_6 (1.82 mmoles; mol. wt., found 61.6, calcd. 62.16, confirmed by infrared spectrum[24]). This represented 24.4% of the silicon present in the Si_2H_5Br used. Dimethylamine (1.58 mmoles; mol. wt., found 47.9, calcd. 45.09), the infrared spectrum of which[25] showed the presence of some Si_2H_6,[24] also was obtained in addition to $H_3SiSiH_2N(CH_3)_2$ (0.61 mmole; mol. wt., found 104.5, calcd. 105.23).

The second major fraction collected from the fractionating column was found to consist of very slightly impure $H_3SiSiH_2N(CH_3)_2$ (1.87 mmoles). It was further purified by passage through traps immersed in −46, −78, and −196° baths. The material condensing in the −78° bath was found to be pure $H_3SiSiH_2N(CH_3)_2$ (mol. wt., found 105.4, calcd. 105.23; vapor pressure at −24.2°, 7.70 mm.). This, together with the pure $H_3SiSiH_2N(CH_3)_2$ obtained above, represented 33.2% of the silicon present in the Si_2H_5Br used.

A further fraction distilled from the column at temperatures between −20 and −14° and was found to consist of impure $H_3SiSiH[N(CH_3)_2]_2$. It was further purified by distillation through traps immersed in −23 and −196° baths. The material which collected in the −23° trap appeared to be homogeneous, but traces of non-volatile white deposits remained each time it was distilled in the vacuum system. The whole sample therefore was sealed in a glass tube which was allowed to stand at room temperature for 72 hr. Upon distillation, pure $H_3SiSiH[N(CH_3)_2]_2$ (as indicated by the elemental analysis described below), which no longer left a deposit on evaporation, was found to condense in a −23° trap.

In another experiment in which 14.37 mmoles of Si_2H_5Br and 30.12 mmoles of $(CH_3)_2NH$ were used, approximately 2 mmoles of slightly impure $H_3SiSiH[N(CH_3)_2]_2$ was obtained from which 0.424 mmole of the pure compound was isolated. This had infrared and mass spectra identical with those of the sample previously prepared. The slightly impure $H_3SiSiH[N(CH_3)_2]_2$ represented 13.9% of the silicon present in the Si_2H_5Br used.

Assuming similar yields of products in the two experiments, 71.5% of the silicon present in the Si_2H_5Br used was recovered as $H_3SiSiH_2N(CH_3)_2$, $H_3SiSiH[N(CH_3)_2]_2$, and Si_2H_6.

Because of the low volatility of the compound, it was necessary to determine its molecular weight by measuring the pressure exerted by a known weight of material when present in a given volume at a temperature of 71.2°; mol. wt., found 149.4, calcd. 148.30.

The proton magnetic resonance spectrum of the compound showed that it was the pure, unsymmetrical, bis-(dimethylamino) isomer. The spectrum was run on an approximately 15% solution in benzene. The chemical shifts observed, relative to tetramethylsilane, were CH_3 (7.43 τ), SiH_3 (6.60 τ), and SiH (4.88 τ). Their ratios were $CH_3:SiH_3:SiH = 12:3:1$. The Si–H chemical shifts in a number of derivatives of monosilane have been observed[26] in the range 5.39–5.66 τ.

The mass spectrum of $H_3SiSiH[N(CH_3)_2]_2$ showed a somewhat weak parent ion peak at mass number 148. Possible assignments for the major fragments (in decreasing order of abundance) are: $H_3SiSiHN^+$, $[(CH_3)_2N]_2SiH^+$, $(CH_3)_2NSi^+$, $(CH_3)_2N^+$, and $(CH_3)_2NH^+$. A somewhat weak SiH_3^+ peak also was observed. The $(CH_3)_2NH^+$ species is apparently a rearrangement fragment. Its presence is not surprising since rearrangement fragments are often found in the mass spectra of both organic amines and silicon amines.[27]

Analysis.—$H_3SiSiH_2N(CH_3)_2$ (0.1037 g.; mol. wt., found

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105.4, calcd. 105.23; vapor pressure 7.50 mm. at −24.2°) upon hydrolysis in a 35% aqueous solution of sodium hydroxide (15 ml.) containing alcohol (2 ml.) and piperidine (2 ml.) after warming to approximately 50° upon two occasions, yielded 131.7 ml. of hydrogen at S.T.P. (calcd., 132.4 ml.). The alkaline hydrolysate was transferred to a large platinum basin from which most of the liquid was evaporated on the steam bath. Silicon was determined as SiO_2.[28] *Anal.* Calcd. for $C_2H_{11}NSi_2$: Si, 53.33. Found: Si, 53.6. Nitrogen and carbon analyses were performed[29] on a separate sample from a second preparation (mol. wt., found 104.3, calcd. 105.23; vapor pressure 7.70 mm. at −24.2°). *Anal.* Calcd. for $C_2H_{11}NSi_2$: C, 22.83; N, 13.31. Found: C, 22.96; N, 13.07.

A sample of pure $H_3SiSiH[N(CH_3)_2]_2$ analyzed as follows: *Anal.* Calcd. for $C_4H_{16}N_2Si_2$: C, 32.39; H, 10.87; N, 18.89; Si, 37.84. Found[29]: C, 32.77; H, 10.58; N, 18.31; Si, 37.48.

Both $H_3SiSiH_2N(CH_3)_2$ and $H_3SiSiH[N(CH_3)_2]_2$ melted below −134°.

Vapor Pressure and Thermal Stability of $H_3SiSiH_2N(CH_3)_2$.—An all-glass tensimeter and connecting mercury manometer were pretreated at 0° for 15 hr. with $H_3SiSiH_2N(CH_3)_2$. A freshly distilled sample (mol. wt., found 105.3, calcd. 105.23; vapor pressure at −23.1°, 8.15 mm.) of the compound then was placed in the manometer. Vapor pressures at various temperatures are given in Table III.

TABLE III

VAPOR PRESSURES OF $H_3SiSiH_2N(CH_3)_2$[a,b]

Temp., °C.	P, mm. obsd.	P, mm. calcd.	Temp., °C.	P, mm. obsd.	P, mm. calcd.
−66.4	0.40	0.24	− 8.6	22.10	22.10
−45.1	1.95	1.68	0.0	36.70	36.75
−34.5	3.85	3.85	0.0	43.10[c,d]	36.75
−30.2	5.30	5.28	−45.2	4.45[c]	1.67
−23.2	8.65	8.64	−196	0.65[c]	0.00
−18.5	11.80	11.83			

[a] Duration of experiment 11 hr. [b] The molecular weight of the whole sample at the conclusion of the experiment was 104.4 (calcd., 105.23). [c] Pressure observed on decreasing the temperature. [d] Sample was raised to 27.5° before this vapor pressure was recorded.

Vapor pressures in the range −66.4 to 0° are represented by the equation

$$\log P_{\text{mm}} = -\frac{1851.04}{t + 273.16} + 8.34160$$

Additional values to those given in Table III were used to derive the above relationship. The extrapolated boiling point is 65.8°, the heat of vaporization is 8.47 kcal. mole^{-1}, and Trouton's constant is 25.0 cal. deg.$^{-1}$ mole^{-1}.

The irreversibility of the vapor pressure curve on decreasing the temperature indicated that some thermal decomposition had occurred during the vapor pressure determinations; however, the fact that the molecular weight of the entire sample at the conclusion of the experiment had changed by less than 1% suggested that decomposition was not extensive. The sample (1.02 mmoles) therefore was held in the tensimeter at 0° for 47 hr., during which time the vapor pressure rose from 44.3 to 93.6 mm. After this time, only 0.8 mm. of non-condensable gas (presumably hydrogen) had been evolved. Upon distillation the sample yielded pure $H_3SiSiH_2N(CH_3)_2$ (0.81 mmole; mol. wt., found 105.6, calcd. 105.23; vapor pressure at −23.4°, found 8.0 mm., calcd. 8.52 mm.) and Si_2H_6 (0.15 mmole; vapor pressure at −78.4°, found 23.35 mm., calcd.[30] 23.08 mm.; infrared spectrum identical with that of pure compound[24]). A small quantity of less volatile material, possibly $H_3SiSiH[N(CH_3)_2]_2$, also was obtained.

Vapor Pressure and Thermal Stability of $H_3SiSiH[N(CH_3)_2]_2$.—An all-glass immersible tensimeter was employed in conjunction with compensating manometers at room temperature in order to avoid the necessity of making corrections due to the change in the density of mercury with the increase in temperature. The constant temperature bath was controlled to ±0.05° by a Sargent (Model S) Thermonitor. Vapor pressures at various temperatures are given in Table IV.

TABLE IV

VAPOR PRESSURES OF $H_3SiSiH[N(CH_3)_2]_2$[a]

Temp., °C.[b]	P, mm. obsd.	P, mm. calcd.	Temp., °C.[b]	P, mm. obsd.	P, mm. calcd.
37.95	23.10	24.07	81.05	152.91	153.11
43.55	31.49	31.49	92.33	227.27	231.23
51.90	46.19	46.22	100.04	293.18	302.11
55.93	55.38	55.24	92.13	238.52[c]	229.59
64.37	79.27	79.13	43.35	42.34[c]	31.20
67.29	90.41	89.24	−196	0.0[c]	0.0
76.16	127.48	127.01			

[a] Duration of experiment 9 hr. [b] Second decimal place estimated. [c] Pressure observed on decreasing the temperature.

Vapor pressures in the range 37.95 to 81.05° are given by the equation

$$\log P_{\text{mm}} = -\frac{2054.63}{t + 273.16} + 7.98561$$

Additional values to those given in Table IV were used to derive the above relationship. The extrapolated boiling point is 129.3°, the heat of vaporization is 9.40 kcal. mole^{-1}, and Trouton's constant is 23.4 cal. deg.$^{-1}$ mole^{-1}. The irreversibility of the vapor pressure curve on decreasing the temperature indicates that some thermal decomposition had occurred during the above determinations. However, the material is relatively stable for long periods of time at room temperature as indicated by the fact that it was held at room temperature for 72 hr. during its purification.

Reaction of $(H_3SiSiH_2)_3N$ with BF_3.—Trisdisilanylamine (0.3399 mmole) and BF_3 (0.5195 mmole) were condensed together at −196° in an approximately 10-ml. tube. The reaction mixture was warmed to room temperature and then immediately cooled to −46°. A white solid coated the walls of the tube. This procedure was repeated on four occasions to ensure complete reaction. The mixture then was cooled to −134° and material volatile at this temperature was removed completely by a 3-min. distillation. The condensate was found to consist of BF_3 (0.1873 mmole; identified by infrared spectrum[23]). The presence of a very weak Si–H absorption peak in the infrared spectrum indicated the presence of only a minute quantity of impurity. The quantity of $(H_3SiSiH_2)_3N$ and BF_3 which had undergone reaction indicated the formation of an addition compound containing $(H_3SiSiH_2)_3N$ and BF_3 in the ratio of 1.02/1.00.

The adduct exhibited zero pressure at −134° and 6.1 mm. at −112°. Infrared analysis of the vapor indicated that it consisted essentially of pure BF_3. This suggests that the equilibrium system given by eq. 5 exists at low temperatures. On warming to −95.9°, the pressure fell to 5.0 mm., and the gas in equilibrium with the solid adduct again consisted of BF_3. It seems possible that the decrease in pressure is caused by a rearrangement of the adduct in the solid state as indicated by eq. 7 to give a solid solution of $(H_3SiSiH_2)_3N \cdot BF_3$ in $(H_3SiSiH_2)_2NBF_2 \cdot H_3SiSiH_2F$. A similar explanation has been offered to explain the decrease in pressure observed in the $(CH_3)_3SiCN$–BF_3 system.[31] At −63.9° the equilibrium vapor pressure was 11.5 mm. and infrared analysis of the vapor phase showed that it consisted

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[28] A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis, Theory and Practice," 2nd Ed., Longmans, Green and Co., London, 1951, p. 503.

[29] Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y. Sample was transported in liquid nitrogen.

[30] K. Stokland, *Kgl. Norske Videnskab. Selskabs Skrifter*, **No. 3**, **1**, 47 (1950).

[31] E. C. Evers, W. O. Freitag, W. A. Kriner, A. G. MacDiarmid, and S. Sujishi, *J. Inorg. Nucl. Chem.*, **13**, 239 (1960).

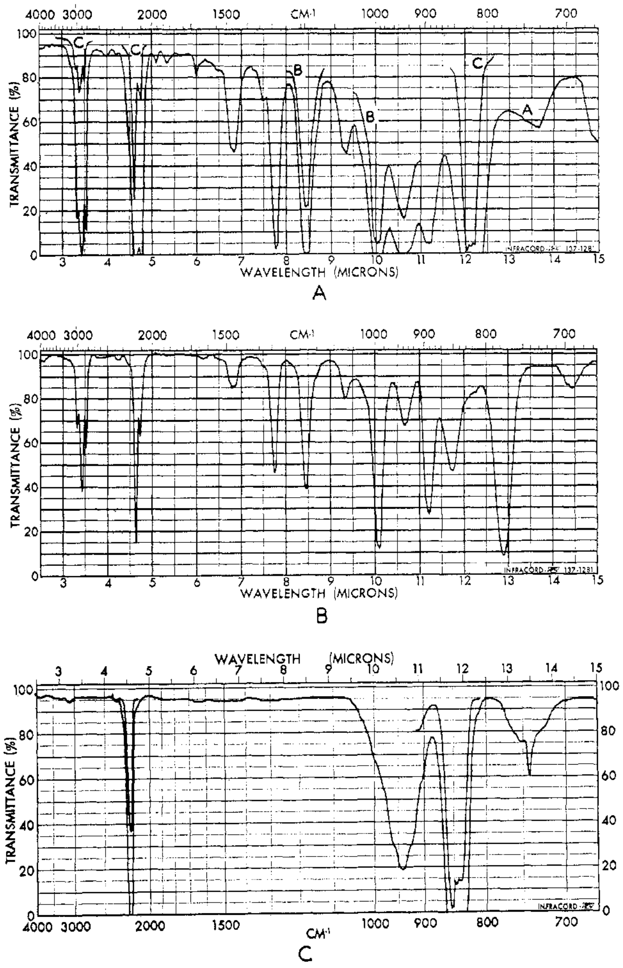

Fig. 1.—Infrared spectra of (A) $H_3SiSiH_2N(CH_3)_2$; (B) $H_3SiSiH[N(CH_3)_2]_2$; (C) H_3SiSiH_2F.

entirely of H_3SiSiH_2F. No non-condensable gas was formed during the above measurements.

Preparation of H_3SiSiH_2F.—$(H_3SiSiH_2)_3N$ (1.52 mmoles) and BF_3 (0.76 mmole) were condensed together at −196° and then warmed to room temperature. The reaction tube was shaken gently to promote mixing of the reactants and then immediately cooled to −78°, where they solidified to a white slush. Materials volatile at −78° were continuously distilled from the reaction tube during a period of 27 hr., during which time the tube occasionally was warmed briefly to room temperature. The volatile material consisted of a mixture of BF_3 and H_3SiSiH_2F. The unreacted BF_3 was returned to the reaction tube together with an additional 0.76 mmole of BF_3 and distillation at −78° was continued as above for a further 21 hr. The volatile material again consisted of BF_3 and H_3SiSiH_2F. This mixture was not returned to the reaction tube. An additional 0.76 mmole of BF_3 then was transferred to the reaction tube and distillation was continued for another 8 hr. at −78°. The residue in the reaction tube was assumed to consist chiefly of $(H_3SiSiH_2)_2NBF_2$ and was not examined further. The crude H_3SiSiH_2F fractions obtained then were combined and freed from BF_3 by distillation through a −126° trap in which H_3SiSiH_2F but not BF_3 condensed. Last traces of BF_3 were removed by distilling the compound from a trap held at −112°. The first portion to distil, which was most likely to contain BF_3, was rejected. The pure H_3SiSiH_2F obtained (1.18 mmoles; mol. wt., found 79.7, calcd. 80.16; vapor pressure at −64.1°, 34.05 mm.) represented a 77.6% yield based on the reaction given by eq. 6.

The melting points of three different samples of H_3SiSiH_2F were −100.7°, −100.3°, and −100.4°.

Table V

Vapor Pressures of $H_3SiSiH_2F^{a,b}$

Temp., °C.	*P*, mm. obsd.	*P*, mm. calcd.	Temp., °C.	*P*, mm. obsd.	P, mm. calcd.
−95.1	2.45	2.41	−58.8	49.55	49.10
−91.5	3.20	3.43	−53.0	72.30	72.39
−87.1	4.85	5.18	−45.9	114.15	113.63
−81.1	8.80	8.83	−64.0	34.30[c]	34.00
−76.1	13.40	13.42	−95.0	2.40[c]	2.44
−70.1	21.45	21.57	−196	0.0[c]	0.0
−64.1	34.00	33.76			

[a] Duration of experiment 11 hr. [b] The molecular weight of the whole sample at the conclusion of the experiment was 79.7 (calcd., 80.16). [c] Pressure observed on decreasing the temperature.

Table VI

Absorption Maxima of $H_3SiSiH_2N(CH_3)_2$, $H_3SiSiH[N(CH_3)_2]_2$, and H_3SiSiH_2F (cm.$^{-1}$)

H_3SiSiH_2F	H_3SiSiH_2N-$(CH_3)_2$	H_3SiSiH-$[N(CH_3)_2]_2$	Interpretation	Ref.
	3022 m	3020 w	C–H stretch	32, 33, 34, 35, 36
	2945 s	2930 s		
	2850 m	2834 w		
2198 vs	2178 vs	2160 vs	Si–H stretch	37
	2112 s	2122 w		
	1960 vw		Unassigned	
	1870 vw			
	1660 vw			
	1467 w	1471 vw	CH_3 deform.	35, 38
	1332 vw		Unassigned	
	1283 s	1290 m	CH_3 deform.	32
	1185 s	1183 s	CH_3 rock	34
	1073 w	1072 vw	N–C stretch	34
	998 s	990 vs	Si–N stretch	3, 32, 39, 40
853 vs			Si–F stretch	32, 41, 42
	897 s	890 s	CH_3 rock	32
942 s	940 s	937 w	SiH_3 and/or SiH_2 deform.	37, 32, 3 43
846 dvs	830 vs	852 m		
836 dvs	823 vs	777 vs		
743 m	819 vs	692 vw		
	731 vw			

Major fragments observed in the mass spectrum of H_3SiSiH_2F were, in decreasing order of abundance, SiF^+, $H_3Si_2F^+$, $H_5Si_2F^+$, $H_4Si_2F^+$, H_2SiF^+, HSi^+, H_2Si^+, H_3Si^+, and $HSiF^+$.

Freshly distilled disilanyl fluoride (0.02789 g., vapor pressure at −64.0°, found 34.25 mm., calcd. 34.00 mm.; mol. wt., found 80.6, calcd. 80.16) upon hydrolysis in a 35% aqueous solution of sodium hydroxide containing alcohol (2 ml.) and piperidine (2 ml.) after warming to approximatey 50° upon four occasions yielded 46.8 ml. of hydrogen (calcd. 46.76 ml.). A method similar to that described by Booth and Stillwell[15] was employed to determine fluorine. The determination was carried

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(37) H. R. Linton and E. R. Nixon, *Spectrochim. Acta*, **12**, 41 (1958).

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(39) E. A. V. Ebsworth, J. R. Hall, M. J. Mackillop, D. C. McKean, N. Sheppard, and L. A. Woodward, *ibid.*, **13**, 202 (1958).

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(41) G. J. Janz and Y. Mikawa, *Bull. Chem. Soc. Japan*, **34**, 1495 (1961).

(42) J. V. Urenovitch and A. G. MacDiarmid, *J. Chem. Soc.*, 1091 (1963).

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out using a sample of similar purity to that used above. *Anal.* Calcd. for Si_2H_5F: F, 23.70. Found: F, 23.7.

Vapor Pressure and Thermal Stability of H_3SiSiH_2F.—The vapor pressure of freshly distilled H_3SiSiH_2F was measured in an all-glass tensimeter connected to a mercury manometer which previously had been pretreated with H_3SiSiH_2F for 15 hr. Vapor pressures are given in Table V. Vapor pressures in the range -95.1 to $-45.9°$ are represented by the equation

$$\log P_{\mathrm{mm}} = -\frac{1376.015}{t + 273.16} + 8.110310$$

Additional values to those given in Table V were used to derive the above relationship. The extrapolated boiling point is $-10.0°$, the heat of vaporization is 6.30 kcal. mole.$^{-1}$, and Trouton's constant is 23.9 cal. deg.$^{-1}$ mole^{-1}. The fact that the vapor pressure curve is reversible on decreasing the temperature indicates that little, if any, thermal decomposition of the compound had occurred during the experiment.

In order to test the thermal stability further, a sample of freshly distilled H_3SiSiH_2F (vapor pressure at $-63.7°$, found 35.25 mm., calcd. 34.75 mm.) was held at 0° for 25 hr. in a 10-ml. all-glass break-seal tube which previously had been pretreated with a sample of H_3SiSiH_2F at room temperature for 15 hr. All the compound was in the vapor phase. At the conclusion of the experiment, no non-condensable gas had been formed and the vapor pressure was unchanged (vapor pressure at $-63.7°$, found 35.30 mm., calcd. 34.75 mm.). The infrared spectrum of the sample at the conclusion of the experiment was identical with that of the pure material.

Infrared Spectra of $H_3SiSiH_2N(CH_3)_2$, $H_3SiSiH[N(CH_3)_2]_2$, and H_3SiSiH_2F.—All measurements were made with a Perkin-Elmer 137B Infracord spectrophotometer on the gaseous phase at 25° with the sample confined in a 10-cm. cell fitted with 6-mm. potassium bromide windows cemented with glyptal resin. The spectrum of $H_3SiSiH_2N(CH_3)_2$ was observed at pressures of 33.5 mm. (A), 15.0 mm. (B), and 3.5 mm. (C), while that of $H_3SiSiH[N(CH_3)_2]_2$ was observed at 12.0 mm. The spectrum of H_3SiSiH_2F was recorded at pressures of 10.5 and 3.0 mm. The absorption maxima are listed in Table VI and the spectra are given in Fig. 1.

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Stereochemistry of Phosphorus(V) Fluorides

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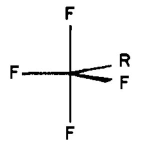
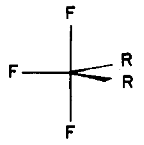
F^{19} n.m.r. spectral data for a number of mono-, di-, and trisubstituted phosphorus(V) fluorides are presented and discussed in terms of stereochemistry, configurational exchange, and general correlation of spin–spin coupling and chemical shift data. All dialkyl, diaryl, and alkyl–aryl derivatives have the R groups in equatorial positions of a trigonal bipyramid. In the cyclic compound $(CH_2)_4PF_3$, a rapid intramolecular, positional exchange of equatorial and apical fluorine atoms occurs; the barrier to this exchange is about 7 kcal.

Recent synthetic advances have made available a number of substituted phosphorus(V) fluorides,[1] and since little is known about stereochemistry in the trigonal bipyramidal or the tetragonal pyramidal structures, we were prompted to undertake a structural analysis of this class of compounds. Our major stereochemical probe has been nuclear magnetic resonance.

Sterically, the most stable isomers in a trigonal bipyramid for the three classes of alkyl or aryl derivatives of PF_5 would appear to be I, II, and III. These assignments are based on the assumptions that the only significant steric interactions are those between groups at 90° angles and that the magnitude of the ligand repulsions increases in the order F–F < F–R < R–R.



I



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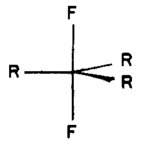
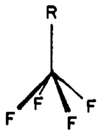


III

Similar considerations for the tetragonal pyramid yield the following favored structures.



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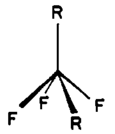
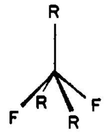


V



VI

As one possible approximation of the bonding in a trigonal bipyramid, phosphorus hybrid orbitals in the equatorial plane may be constructed from a combination of the 3s and two 3p orbitals and those on the apical axis from a 3p3d combination. The difference in energy levels between these two should reflect the s electron promotion energy. It is assumed that the energy difference will be smallest where the ligands are strongly electronegative, *e.g.*, PF_5, and will increase with increasing substitution with electropositive groups. On this basis, it is not unreasonable to presume that hydrogen or an alkyl group would achieve best overlap with a phosphorus sp^2 hybrid orbital in the equatorial plane.[2] Alternatively it may be assumed that better

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[1] (a) L. M. Yagupolskii and Zh. M. Ivanova, *Zh. Obshch. Khim.*, **29**, 3766 (1959); (b) W. C. Smith, *J. Am. Chem. Soc.*, **82**, 6176 (1960); (c) I. P. Komkov, S. Z. Ivin, K. W. Karawanov, and L. Je. Smirnov, *Zh. Obshch. Khim.*, **32**, 301 (1962); (d) R. Schmutzler, *Chem. Ind.* (London), 1868 (1962); (e) R. Schmutzler, to be published.

[2] It is perhaps significant that in $:SF_4$ and $:\ddot{C}lF_3$ the non-bonding electron pairs which should favor orbitals of maximum s character go to equatorial sites. However, since a non-bonding electron pair is a sterically large entity, the same stereochemical conclusions for $:SF_4$ and $:\ddot{C}lF_3$ should be drawn.