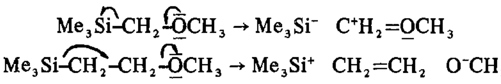
similar intramolecular interactions have been postulated.[1,15,34-38]

$CH_3O(CH_2)_nSi(CH_3)_3$. The $\Delta\nu$ values of pyrrole for the $CH_3O(CH_2)_nSi(CH_3)_3$ (n = 1 to 3) series are also listed in Table II. The relative order of increasing basicity is $n = 0 < n = 1 < n = 2 > n = 3$.

It might be noted that this order is identical with that which has been found for several other $Y(CH_2)_nM(CH_3)_3$ series, for example, the $CH_3O(CH_2)_nC(CH_3)_3$ and $NH_2(CH_2)_nSi(CH_3)_3$ compounds.[7,9,16,39,40] Chvalovský has interpreted the relative base strengths of (ω-aminoalkyl)trimethylsilanes in terms of hyperconjugation,[39,40] and analogous hyperconjugative limiting structures can also be written for the (ω-methoxyalkyl)trimethylsilanes, although the relative importance of these structures is not clear.



In summary, the presence of an intramolecular O → Si interaction is consistent with the basicity trend of trichlorosilyl compounds, but as noted above this interaction is less important in $Si(CH_3)_3$ (and also the $Si(C_6H_5)_3$[41]) compounds than in SiH_3 or $SiCl_3$ species, and an O → Si interaction would not account for the relative order of basicities in the $CH_3O(CH_2)_nSi(CH_3)_3$ (n = 2 and 3) compounds. In both the trimethylcarbon and the trimethylsilicon compounds, the fact that the $n = 2$ homolog is the strongest base is consistent with the examples in which hyperconjugation was postulated to provide the principal correlation.

The above results would seem to be consistent with previous suggestions[27] that no single concept (inductive effects, hyperconjugation, d orbital participation) adequately accounts for the observed behavior of organosilicon compounds, and that a combination of these effects is required to correlate observed results.

Acknowledgment. This work was supported in part by the Center of Materials Research of the University of Maryland.

Registry No. CH_3OSiCl_3, 1825-97-4; $CH_3OCH_2SiCl_3$, 33415-27-9; $CH_3O(CH_2)_2SiCl_3$, 56629-79-9; $CH_3O(CH_2)_3SiCl_3$, 18171-65-8; $CH_3OSi(CH_3)_3$, 1825-61-2; $CH_3OCH_2Si(CH_3)_3$, 14704-14-4; $CH_3O(CH_2)_2Si(CH_3)_3$, 18173-63-2; $CH_3O(CH_2)_3Si(CH_3)_3$, 18387-32-1; Cl_3SiCH_2Cl, 1558-25-4; $ClCH_2OCH_3$, 107-30-2.

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Kinetic Study of the Iodine Cleavage of $(CH_3)_2As\overline{C{=}CAs(CH_3)_2CF_2C}F_2Mn_2(CO)_8$ and Related Complexes

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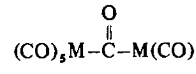
It is well-known that most dinuclear metal carbonyl compounds containing a metal–metal bond are cleaved by halogen to afford the corresponding halogenometal carbonyl derivative.[1] In particular the standard preparation of $M(CO)_5X$ (M = Mn, Tc, Re; X = Cl, Br, I) involves the cleavage of the M–M bonds of $M_2(CO)_{10}$ by halogens.[2,3] Despite numerous reports there have been relatively few mechanistic studies and these have been confined to reactions of the following species with halogen: $Mn_2(CO)_{10}$,[4] $Re_2(CO)_{10}$,[5] $Os_3(CO)_{12}$,[6] $[dienylFe(CO)_2]_2$.[7]

The reaction of iodine with $Mn_2(CO)_{10}$ follows a pseudo-first-order rate law $k_{obsd} = k_a + k_b[I_2]$ where k_a is equal to the rate constant for decomposition in oxygenated solution.[4] The activation enthalpy for the bimolecular path is 31 kcal/mol. A similar rate law is obtained from the reaction of iodine with $Re_2(CO)_{10}$ although the activation enthalpy for the bimolecular path has the lower value of 16.9 kcal/mol.[5] The most recent interpretation of these results[8] would seem to be as in Scheme I. One reaction is iodine independent and governed by k_a and the other bimolecular. In the original publications[4,5] the free-radical intermediate was replaced by the metal-migrated and carbonyl-bridged species

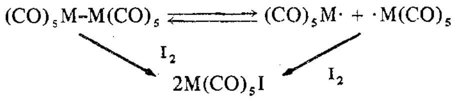


$$(CO)_5M{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}M(CO)_4$$

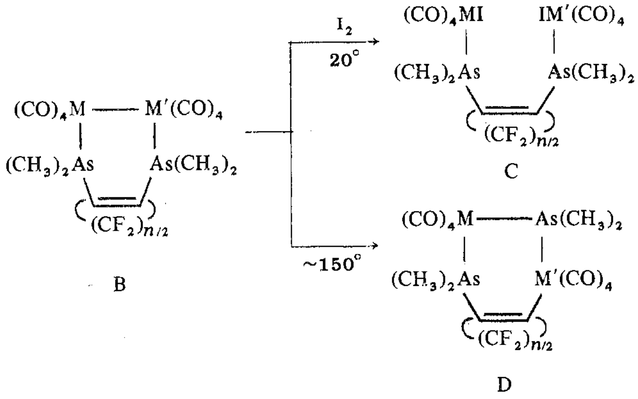
A

Poë and coworkers[4,5] suggested that the difference in activation energies for the bimolecular pathway (M = Mn, Re) indicates a difference in the reaction mechanism but they said little

Scheme I



Scheme II



about possibilities.

We have previously reported[9] that the Mn–Mn bond in f4farsMn$_2$(CO)$_8$,[10] B (Scheme II, $n = 4$) is quantitatively cleaved by iodine to give f4farsMn$_2$(CO)$_8$I$_2$, C, in a reaction which is much more facile than that of Mn$_2$(CO)$_{10}$ with iodine.[9,11]

The thermal "decomposition" of B is also well defined and the product is the isomer D in which an As(CH$_3$)$_2$ moiety has inserted itself between the two manganese atoms of B with concomitant formation of a new Mn–C bond.[9,12]

We have studied the kinetics of both reactions of Scheme II because of the possibility that the iodine cleavage of B might follow the same rate law as found for Mn$_2$(CO)$_{10}$ (Scheme I). The present paper is concerned with the iodine cleavage of B and related complexes. The isomerization reaction is described elsewhere.[13]

Experimental Section

Apart from f6farsRe$_2$(CO)$_8$, whose synthesis is described below, the metal carbonyl complexes (L-L)M$_2$(CO)$_8$ (L-L = f4fars, f6fars; M = Mn, Re) were prepared as described in the literature.[9,13]

Reaction of f6fars with Re$_2$(CO)$_{10}$. f6fars (1.50 g, 3.91 mmol) and Re$_2$(CO)$_{10}$ (1.30 g, 2.00 mmol) were refluxed in *m*-xylene for 6 hr. The solvent was removed and the residue chromatographed on Florisil. Petroleum ether eluted unreacted Re$_2$(CO)$_{10}$. The desired product f6farsRe$_2$(CO)$_8$ was eluted with 9:1 petroleum ether–diethyl ether. It was crystallized from diethyl ether at −78° (0.40 g, 40%). ^{1}H NMR (CCl$_4$ solution): singlet at 2.10 ppm. ^{19}F NMR ((CH$_3$)$_2$CO solution): 101.7 ppm (triplet), 127.0 ppm (quintet), relative area 2:1. ν(CO) (C$_6$H$_{12}$ solution): 2084 (7), 2031 (8), 1986 (10), 1964 (8), 1954 (7), 1940 (sh), 1934 (10) cm^{-1}. Anal. Calcd for C$_{17}$H$_{12}$As$_2$F$_6$O$_8$Re$_2$: C, 20.8; H, 1.2; F, 11.6. Found: C, 20.9; H, 1.2; F, 11.4.

Reaction of f4farsRe$_2$(CO)$_8$ with Bromine. The complex (0.05 g) in cyclohexane (15 ml) was treated dropwise with Br$_2$ (0.009 g) in the same solvent (5 ml). Evaporation of the solvent and drying in vacuo gave f4fars[Re(CO)$_4$Br]$_2$. ^{1}H NMR (CCl$_4$ solution): singlet at 2.35 ppm (external TMS). ν(CO) (C$_6$H$_{12}$ solution): 2112 (4), 2028 (8), 2015 (br), 1955 (br) cm^{-1}. Anal. Calcd for C$_{16}$H$_{12}$As$_2$Br$_2$F$_4$O$_8$Re$_2$: C, 17.6; H, 1.1; Br, 14.7. Found: C, 17.8; H, 1.1; Br, 14.9.

Kinetic Studies. Kinetic measurements were made using a Durrum-Gibson stopped-flow apparatus as supplied except that glass reservoir syringes with Teflon plungers and Viton "O" rings were substituted to enable use of iodine solutions in dichloromethane. Most runs were made under pseudo-first-order conditions.[14] Thus in the presence of excess (L-L)M$_2$(CO)$_8$ the rates were followed by observing the disappearance of the iodine absorption at 510 nm. For reactions using excess iodine the absorption of f4farsRe$_2$(CO)$_8$, f6farsRe$_2$(CO)$_8$, f4farsReMn(CO)$_8$, and f4farsMn$_2$(CO)$_8$ at 330, 327, 330, and 365 nm, respectively, were monitored. The choice of 330 nm for f4farsReMn(CO)$_8$ was made to avoid changing the dispersing element in the instrument. (λ_{max} of the σ–σ^* absorption is at 340 nm.[13])

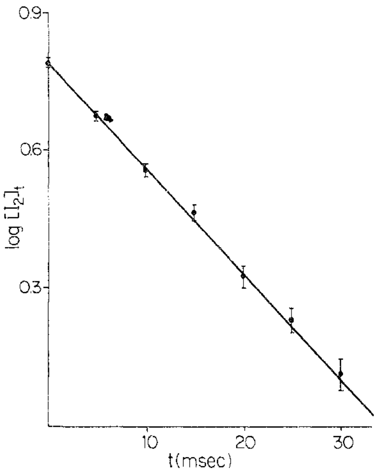


Figure 1. Plot of log [I$_2$] at time *t* against *t* for the reaction of f$_4$farsRe$_2$(CO)$_8$ with iodine under pseudo-first-order conditions.

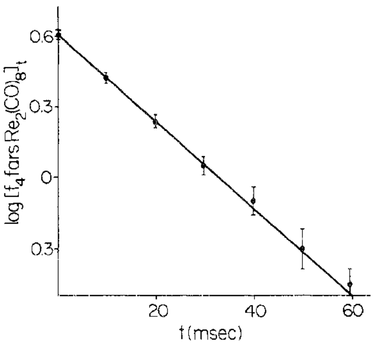


Figure 2. Plot of log [f$_4$farsRe$_2$(CO)$_8$] at time *t* against *t* for the reaction of f$_4$farsRe$_2$(CO)$_8$ with iodine under pseudo-first-order conditions.

In a typical experiment at 25°C, 0.15 ml of 1.18 × 10^{-3} *M* f4farsRe$_2$(CO)$_8$ in dichloromethane was treated with 0.15 ml of 1.10 × 10^{-4} *M* iodine in the same solvent. The I$_2$ disappearance was monitored at 510 nm and a plot of log [I$_2$] at time *t* against *t* is shown in Figure 1. In the same way the reaction between 0.15 ml of 9.18 × 10^{-4} *M* iodine and 0.15 ml of 1.26 × 10^{-4} *M* f4farsRe$_2$(CO)$_8$ was monitored at 330 nm to give the concentration of f4farsRe$_2$(CO)$_8$. A plot of log [complex] at time *t* against *t* is shown in Figure 2.

Results

The plot in Figure 1 is linear indicating that the reaction is first-order in iodine concentration with k_{obsd} = 5.34 × 10 sec^{-1} and $t_{1/2}$ = 13 msec. Furthermore, varying the concentration of iodine had no effect on $t_{1/2}$. The linear plot of Figure 2 indicates the reaction is first order in f4farsRe$_2$(CO)$_8$, and combining the two results we get rate = k[f4farsRe$_2$(CO)$_8$][I$_2$]. The effect of temperature on k was studied over the temperature range 19–35°C. The results are given in Table I together with those from the other kinetic measurements. The experimental enthalpy of activation $\Delta H^\ddagger$ was obtained from the linear plots of log k against $1/T$ via E_a. The reaction of iodine with f4farsMn$_2$(CO)$_8$ was too fast to be monitored with the available apparatus.

Discussion

As mentioned in the introduction the rate law for the reaction of iodine with Mn$_2$(CO)$_{10}$ has the form $k_{obsd} = k_a + k_b$[I$_2$]. At 115° k_a = 1.73 × 10^{-4} sec^{-1} (determined from the reaction of Mn$_2$(CO)$_{10}$ with (C$_6$H$_5$)$_3$P in the absence of CO) and k_b is 9.0 × 10^{-3} M^{-1} sec^{-1}. Thus the complex f4farsMn$_2$(CO)$_8$, B, reacts much more easily with iodine than Mn$_2$(CO)$_{10}$. The same is true when the reactions of Re$_2$(CO)$_{10}$ and f4farsRe$_2$(CO)$_8$ with iodine are compared. For Re$_2$(CO)$_{10}$ at 130° k_a is (0.48 ± 0.49) × 10^{-5} sec^{-1} and k_b is (1.12 ± 0.07) × 10^{-2} M^{-1} sec^{-1}.[5] The bimolecular constant

Table I. Kinetic and Thermodynamic Parameters for the Iodine Cleavage Reactions

Reaction	Temp,[a] K	Rate const,[c] M^{-1} sec^{-1}	$\Delta H^{\ddagger}$,[b] kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
f$_4$farsMn$_2$(CO)$_8$ + I$_2$	295	$>10^4$		
f$_4$farsMnRe(CO)$_8$ + I$_2$	294	3.40×10^2	14.2 ± 0.9	1.4 ± 3.2
	296	4.00×10^2		
	301	5.89×10^2		
	304	7.59×10^2		
f$_4$farsRe$_2$(CO)$_8$ + I$_2$	292	3.40×10^4	6.9 ± 0.3	-13.8 ± 1.0
	298	4.52×10^4		
	303	5.69×10^4		
	308	7.17×10^4		
f$_6$farsRe$_2$(CO)$_8$ + I$_2$	295	2.72×10^3	9.3 ± 0.9	-11.1 ± 3.0
	298	3.18×10^3		
	301	3.75×10^3		
	306	4.88×10^3		

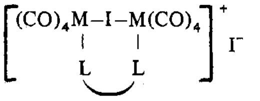
[a] The temperature range is small because of instrumental limitations: D. V. Stynes and B. R. James, *J. Am. Chem. Soc.*, 96, 2733 (1974). [b] Errors are estimated from the Arrhenius plots. [c] Average values from at least two determinations.

for f$_4$farsRe$_2$(CO)$_8$ is 3.40×10^4 M^{-1} sec^{-1}. The rates of isomerization of f$_4$farsMn$_2$(CO)$_8$ and f$_4$farsRe$_2$(CO)$_8$ which could correspond with the values of k_a are 1.78×10^{-4} sec^{-1} (131°) and 1.16×10^{-4} sec^{-1} (193°), respectively. The activation energies for these processes are also high being 36.8 ± 2.0 and 46.8 ± 0.5 kcal mol^{-1}, respectively.[13] Thus the intermediates involved in the isomerization reactions are presumably not involved in the reaction with iodine which takes place at room temperature. These results and the kinetic data indicate that we need consider only a bimolecular pathway for the reaction with iodine and that the mechanism of the reaction is probably the same for each reaction.

The currently popular measure of bond strength in compounds with metal–metal bonds is the σ–σ^* electronic transition[13,15,16] associated with the metal–metal bond. The wavelengths of this transition are as follows: f$_4$farsMn$_2$(CO)$_8$, 365 nm; f$_4$farsRe$_2$(CO)$_8$, 330 nm; f$_6$farsRe$_2$(CO)$_8$, 327 nm; f$_4$farsReMn(CO)$_8$, 340 nm. The order of bond strength so indicated [Mn–Mn < Mn–Re < f$_4$farsRe–Re < f$_6$farsRe–Re] is *not* that which would be expected from the activation enthalpies, Table I, if breaking the metal–metal bond was the most important part of the activation process.[17] (The order Mn–Mn < Mn–Re < Re–Re is the order of $\Delta H^{\ddagger}$ obtained for the first-order isomerization reaction typified by B → D.[13]) However, the σ–σ^* transitions of the derivatives are all at lower energies than those of the parent carbonyls indicating a weaker metal–metal bond. This is also suggested by the bond length of the Mn–Mn bond in f$_4$farsMn$_2$(CO)$_8$, B, which is longer than that in Mn$_2$(CO)$_{10}$.[18] This weakening of the metal–metal bond probably contributed to the ease of the bimolecular reaction with iodine. However the argument cannot be taken too far.

The reactions of Os$_3$(CO)$_{12}$ with Cl$_2$ or Br$_2$, which yield the linear Os$_3$(CO)$_{12}$X$_2$, are qualitatively similar to those studied in the present investigation.[6] The reaction with chlorine is rapid at 25° and has $\Delta H^{\ddagger} = 11.8 \pm 0.7$ kcal mol^{-1} and seems to involve initial formation of a complex between Os$_3$(CO)$_{12}$ and Cl$_2$ which decomposes to products. Although intermediate complex formation was not detected in the case of the Br$_2$ reaction ($\Delta H^{\ddagger} = 12.7 \pm 0.2$ kcal mol^{-1}), the reaction probably goes through such an initial step. The intermediate complex could be of the sort recently proposed[7] to account for the products obtained by halogenating [(π-dienyl)Fe(CO)$_2$]$_2$. Here the proposed mechanism is based on the well-known, but apparently little substantiated, one for electrophilic addition of halogen to alkenes and alkynes.[19-21]

The activation parameters for electrophilic addition of halogen to unsaturated systems seem to be in the region of 10 ± 5 kcal/mol for $\Delta H^{\ddagger}$ and −35 ± 5 eu for $\Delta S^{\ddagger}$.[20,21] Thus the $\Delta H^{\ddagger}$ values listed in Table I are comparable although the $\Delta S^{\ddagger}$ values are more positive. The large negative values of $\Delta S^{\ddagger}$ in the organic reactions do not necessarily indicate a cyclic symmetrical halogenonium intermediate. In fact a whole range of intermediates from α-halocarbonium ions to the symmetrical halogenonium ions seems possible.[20,21] In the present context, if the reaction mechanism does involve electrophilic attack by iodine,[22] intermediates like E and F are conceivable.



E

F

Transition states would be less ordered than for the organic reactions, and hence more positive $\Delta S^{\ddagger}$ values could be expected. The nearly zero $\Delta S^{\ddagger}$ for the Mn–Re complex is difficult to rationalize,[23] and the large $\Delta H^{\ddagger}$ for this reaction is not reconcilable with the apparently lower bond strength as discussed above. Perhaps here also the main effect is due to the polarity of the bond rather than its strength since the values of $\Delta H^{\ddagger}$ for the reaction of $C_2H_5C{\equiv}CC_2H_5$ and $C_6H_5C{\equiv}CH$ with bromine are 8.4 ± 0.2 and 11.7 kcal mol^{-1}, respectively.[20]

The slight decrease in reactivity from f$_4$farsRe$_2$(CO)$_8$ to f$_6$farsRe$_2$(CO)$_8$ may be indicative of electrophilic attack since the CO stretching frequencies of the f$_6$fars complex (2074 (4), 2034 (8), 2007 (7), 1982 (10), 1976 (8), 1960 (6), 1934 (6) cm^{-1}) are generally higher than those of f$_4$farsRe$_2$(CO)$_8$ (2076 (8), 2024 (9), 1985 (10), 1957 (9), 1953 (sh), 1937 (sh), 1932 (10) cm^{-1}). Here, the buildup of electron density on the metals, due to the poor π-acceptor properties of the ligand, which would enhance electrophilic attack relative to the parent carbonyls, seems to be less in the case of the f$_6$fars derivative.[24]

Finally, we report that the reaction of bromine with f$_4$farsRe$_2$(CO)$_8$ is also facile. The pattern of the carbonyl stretching frequencies of the product is similar to those of the diiodides C and hence the same type of structure is proposed.

Acknowledgment. We thank the National Research Council of Canada for financial support, Dr. B. R. James for discussions, and referees for constructive criticism.

Registry No. f$_4$farsMn$_2$(CO)$_8$, 34398-99-7; f$_4$farsMnRe(CO)$_8$, 56700-25-5; f$_4$farsRe$_2$(CO)$_8$, 34399-00-3; f$_6$farsRe$_2$(CO)$_8$, 56700-26-6; I$_2$, 7553-56-2; Br$_2$, 7726-95-6; Re$_2$(CO)$_{10}$, 14285-68-8; f$_4$fars[Re(CO)$_4$Br]$_2$, 56700-27-7; f$_6$fars, 37718-76-6.

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Formation of Fluorosilylamines by the Interaction of Trisilylamine with Phosphorus Pentafluoride. Synthesis of 1,1'-Difluorotrisilylamine

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The selective halogenation of the silicon–hydrogen bond in hydrosilyl derivatives by inorganic halides has been shown to be a particularly good preparative method for obtaining a variety of specific halosilanes that may be difficult to prepare by other methods.[1,2] However at the present time it is by no means clear which hydrosilyl derivatives can be successfully halogenated by this method, particularly when the hydrosilyl derivative contains other reactive bonds. For example, PF_5 can be used to introduce silicon–fluorine bonds into $(SiH_3)_2O$ but not CH_3OSiH_3, $(Si_2H_5)_2O$, $(SiH_3)_2S$, or $(CF_3)_2PSiH_3$.[2,3] Tin(IV) chloride can be used to chlorinate partially the Si–H bonds of $(SiH_3)_3N$ but not $(SiH_3)_2O$.[4] In the present study, we have investigated the synthesis of fluorosilylamines by the interaction of $(SiH_3)_3N$ and $[HSi(CH_3)_2]_2NH$ with PF_5.

Experimental Section

Apparatus. A conventional Pyrex-glass high-vacuum system was used to manipulate all volatile compounds. Mass spectra were obtained at 70 eV on an AEI Model MS-9 mass spectrometer; infrared spectra were obtained on a Perkin-Elmer Model 457 spectrophotometer with the samples contained in a 10-cm gas cell fitted with KBr windows. Proton NMR spectra were obtained on a Hitachi Perkin-Elmer R-20 spectrometer operating at ambient temperature. Sample concentrations were approximately 5–10% by volume in cyclopentane, with a small amount of $(CH_3)_4Si$ added as an internal reference.

Materials. Trisilylamine and $[HSi(CH_3)_2]_2NH$ were prepared by the interaction of SiH_3Br and $HSi(CH_3)_2Cl$, respectively, with ammonia.[5] The purity of $[HSi(CH_3)_2]_2NH$ was checked by its gas-phase molecular weight (found 132.2, calcd 133.3) and infrared spectrum.[6] The purity of $(SiH_3)_3N$ was checked by its infrared[7] and mass spectra. Phosphorus pentafluoride was obtained commercially and purified on the vacuum line by its distillation through a trap at −134° (mol wt found 126.6, calcd 126.0; the infrared spectrum was identical with the published spectrum[8]).

Reactions of PF_5. (a) With Trisilylamine. $(SiH_3)_3N$ (1 mmol) and PF_5 (3 mmol) were condensed into an all-glass break-seal tube and allowed to react for 20 min at 0°. The volatile products were distilled through a trap maintained at −96° into a trap at −196°. An unidentified solid material remained in the reaction tube. The material in the −196° trap was identified as being a mixture of PF_3, SiH_3F, SiH_2F_2, and unreacted PF_5 by an infrared spectroscopic analysis.[8-11] The small amount of material in the −96° trap could not be conclusively identified by infrared spectroscopy, but a mass spectrum of the material clearly indicated the presence of $(SiH_3)_2NSiH_2F$, $SiH_3N(SiH_2F)_2$, and $N(SiH_2F)_3$, the majority of the sample being $SiH_3N(SiH_2F)_2$. Although the intensities of the parent ions of the fluorosilylamines were weak, the (parent − 1) peaks were strong and thus were used for obtaining precise mass measurements (ion, calculated mass, measured mass: Si_3H_7FN, 123.9870, 123.9886; $Si_3H_6F_2N$, 141.9776; 141.9782; $Si_3H_5F_3N$, 159.9682, 159.9674).

We repeated the reaction of $(SiH_3)_3N$ with PF_5 several times at different temperatures (−96 to 0°) and also by using different ratios of starting materials [1:1 and 6:1 mole ratios of PF_5:$(SiH_3)_3N$]. Fluorosilylamines were produced at temperatures between −50 and 0°, and it was observed that even when the mole ratios of starting materials were altered, the chief fluorosilylamine produced in most of the experiments was $SiH_3N(SiH_2F)_2$.

The fluorosilylamines produced in the above experiments could not be separated from one another by standard trap-to-trap vacuum-line fractionation techniques. Gas chromatography, using the equipment and columns available, also failed to purify the compounds. Partial success in separating the amines was achieved by using a low-temperature fractionating column similar to the one described by Jolly.[12] The materials subjected to this distillation were the combined −96° fractions obtained from the studies described above. Although the mass spectral results indicated that some $(SiH_3)_2NSiH_2F$ was present, we were not able to isolate any of this compound from the distillation. The bulk of the original sample was known to be $SiH_3N(SiH_2F)_2$ and we were able to obtain a sample of the pure difluoro derivative in the distillation. The experimental gas-phase molecular weight of the compound was 143.3 (calcd 144.4). A small amount of material believed to be $(FSiH_2)_3N$ from its proton NMR spectrum was also recovered. The yield of fluorosilylamines produced in any one reaction was usually small and did not exceed 5–10% overall.

(b) With 1,1,1',1'-Tetramethyldisilazane. Equimolar amounts (1.2 mmol) of PF_5 and $[HSi(CH_3)_2]NH$ were condensed into a glass reaction tube equipped with a vacuum Teflon stopcock and allowed to react for 45 min at −45°. The products were distilled through a −64° trap into a −196° trap. An infrared and mass spectral analysis revealed that the −64° trap contained unreacted $[HSi(CH_3)_2]_2NH$, while the −196° trap contained a mixture of PF_3, PF_5, $(CH_3)_2SiHF$, and $(CH_3)_2SiF_2$.[13] There was no mass spectral evidence of any fluorosilylamines in the products. The reaction was repeated at −78° for 10 min, after which time the previously cited distillation was repeated. Again, the −64° trap contained unreacted $[HSi(CH_3)_2]_2NH$ and the −196° trap contained the phosphorus and dimethylsilyl fluorides obtained in the initial reaction. We found no evidence of any fluorodimethylsilylamines in the reaction products.

Results and Discussion

At relatively low temperatures, the interaction of $(SiH_3)_3N$ with PF_5 proceeds along two pathways. The predominant reaction involves the cleavage of the silicon–nitrogen bond producing SiH_3F, while the second is an exchange reaction that results in the formation of fluorosilyl derivatives, i.e.

$$>N{-}SiH_3 + PF_5 \rightarrow >N{-}SiH_2F + [HPF_4]$$

The final form of the phosphorus-containing product in the cleavage reaction was not determined, and while we saw no direct evidence of fluorophosphoranes in the exchange reaction, the presence of PF_3 in the reaction products was confirmed and this compound is known to be one of the decomposition products of HPF_4 (or H_2PF_3), particularly in a glass vessel.[14] Precedence for the occurrence of both of these reactions involving PF_5 with silyl derivatives is available; for example both cleavage and hydrogen–fluorine exchange occur in the low-temperature reaction of $(SiH_3)_2O$ with PF_5.[2]

We were primarily interested in studying the fluorination reaction since it potentially offered a convenient synthesis of partially fluorinated silylamines. Mass spectral data unequivocally identified the presence of three fluorosilylamines in the volatile products of the fluorination reactions and this coupled with NMR data led us to identify the compounds as being $(SiH_3)_2NSiH_2F$, $SiH_3N(SiH_2F)_2$, and $(FSiH_2)_3N$. Although all three were detected in the reaction, for practical purposes only the difluoro compound could be conveniently synthesized by this procedure. Reaction conditions were altered to favor the formation of the monofluoro and the trifluoro derivatives by decreasing and increasing, respectively, the amount of PF_5 relative to $(SiH_3)_3N$ used in the reaction.