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Reactions of Difluorosilylene with Amines, Phosphines and Halomethanes The First Evidence of the Insertion of Difluorosilylene into Tetrafluorosilane

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The reactions of SiF_2/SiF_4 with amines, phosphines and various halomethanes were studied. The results show that in the presence of strong Lewis base (Et_3N, $HNEt_2$, PR_3, PR_2Cl), SiF_2 inserts initially into SiF_4 to form Si_2F_6, which was followed by subsequent reactions leading to products containing SiF_3 groups. This is the first report of the insertion of SiF_2 into SiF_4. When the reactants were a weaker base (such as $RPCl_2$, CX_3Br, X=F, Cl), insertion of SiF_2 into P-Cl and C-Br bonds became predominant.

INTRODUCTION

The chemistry of difluorosilylene has been extensively studied.[1] Like all other silylenes (SiX_2), the main chemistry of SiF_2 can be classified as (1) addition onto carbon-carbon double bonds and triple bonds,[2] and (2) insertion into M-H bonds, where M=O, S, and M-X bonds where M=B, and C, X=I.[3]

Unlike other members of the silylene family however, SiF_2 forms at -196 °C dimeric diradical species $\cdot SiF_2SiF_2 \cdot$ (sometimes trimeric diradical), which is responsible for the majority of the chemistry of difluorosilylene in condensation experiments. Also, gaseous SiF_2 has long been known to be inert toward SiF_4 whereas other SiX_2 species insert into Si-X bonds of SiX_4 to form Si_2X_6 readily (X=Cl, Br).[4]

$$SiX_{2(g)} + SiX_{4(g)} \rightarrow Si_2X_{6(g)}$$

$$X=Cl, Br \quad X \neq F$$

In a series of systematic studies we have clarified the dilemma of monomeric SiF_2 vs. dimeric $\cdot SiF_2SiF_2 \cdot$ dispute.[5] In this paper we report our rationalization about the other anomaly of SiF_2.

RESULTS AND DISCUSSION

(a) the insertion of SiF_2 into SiF_4

When the mixture of SiF_2 and SiF_4 passed the on-line IR cell, the spectrum showed typical bands for SiF_4 (1035 and 1029 cm^{-1}) and the broad bands near 860 cm^{-1} for SiF_2.[6] On introducing Lewis base (Et_3N, $HNEt_2$, PR_3, PR_2Cl) into the cell, the absorption of SiF_2 disappeared and the bands characteristic for Si_2F_6 (990, 822 cm^{-1}) grew up immediately (Fig. 1).

$$SiF_{2(g)} + SiF_{4(g)} \xrightarrow{B} Si_2F_{6(g)}$$

$$B=Et_3N, HNEt_2, PR_3, PR_2Cl$$

These results strongly suggest that in the presence of a Lewis base environment, SiF_2 inserts into Si-F bonds of SiF_4 to form Si_2F_6. In order to figure out the detailed function of the Lewis base, a number of organic phosphorus compounds were used as Lewis bases to measure the yield of Si_2F_6. The basicities and the cone angles of the phosphorus compounds and the yields of Si_2F_6 are listed in Table 1.

According to these results, we found that higher basicity causes higher yield of Si_2F_6. However, when phosphins of similar basicity such as PMe_3, PEt_3, P^nPr_3 P^iPr_3 are compared, it was found that a smaller cone angle causes a higher yield of Si_2F_6. When alkylchlorophosphines were used as Lewis bases, only monochlorophosphines showed the capability to help form Si_2F_6. In the cases of dichloro-

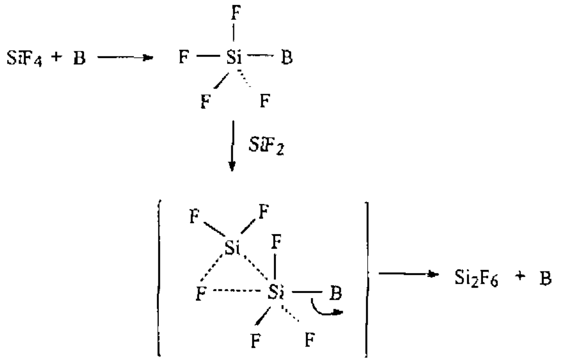
Table 1. The IR Absorption Intensity of Si_2F_6 Generated from the in situ Reaction of SiF_2/SiF_4 with Various Phosphines

Lewis base	$I_{Si_2F_6}$	cone angle, θ	pKa
PMe_3	0.347	118	8.65
PMe_2Ph	0.279	122	6.50
PEt_3	0.272	132	8.69
PEt_2H	0.277		
$P(^nPr)_3$	0.243	132	~8.51
$P(^iPr)_3$	0.200	160	~8.50
PMe_2Cl	0.212		
$PMeCl_2$	Not observed		
PEt_2Cl	0.247		
$PEtCl_2$	Not observed		
PCl_3	Not observed		

$I_{Si_2F_6}$ IR absorption intensity of Si_2F_6 observed at 990 cm^{-1}.

and trichloro-phosphines, where the basicity decreased as the chlorine atoms increased in the phosphines, no Si_2F_6 absorption could be observed in the IR spectra. It is generally known that the basicity and cone angle of a Lewis base are the indicators for the ability of coordination.[7] Those results imply that the yield of Si_2F_6 is related to the coordinating ability of the base. The spectroscopic study and theoretical calculation of the 1:1 adduct of SiF_4 and NH_3 showed that $SiF_4 \cdot NH_3$ had a trigonal bipyramidal arrangement with NH_3 occupying one of the axial positions.[8] The axial and equatorial Si-F bond distances were found to be 1.591 Å and 1.584 Å respectively, significantly longer than that in SiF_4 (1.556 Å).[9]

These data may suggest that the bonds of Si-F in the adduct are considerably weakened and the insertion of SiF_2 into Si-F bonds of the adduct may take place more easily.



(b) the insertion of *SiF_2 into N-H bond*

Ennan and Gavrilova reported the formation of adducts from SiF_4 and amines.[10] In the case of diethylamine, thermal decomposition of the 1:2 adduct, $SiF_4 \cdot 2Et_2H$, yielded diethyltrifluorosilylamine Et_2NSiF_3.[11] Since the difluorosilylene generated in our experimental conditions cannot be separated from the unreacted SiF_4 because it is actually a mixture of approximately 1:1 of SiF_2:SiF_4, the reactions between SiF_4 and the amines under these experimental conditions must be studied first as a "blank" test.

SiF_4 and NEt_3 were mixed in a 1:1 ratio and condensed at -190 °C. On warming the condensate to room temperature, adduct products $SiF_4 \cdot NEt_3$ and $SiF_4 \cdot 2NEt_3$ were obtained. When the reaction was carried out with SiF_4:NEt_3 = 1:2, only the 1:2 adduct was obtained.

Under our experimental conditions, the reaction between SiF_4 and $HNEt_2$ yielded, in addition to $SiF_4 \cdot 2NEt_2H$ and Et_2NSiF_3, a new product $(Et_2N)_2SiF_2$. This compound was considered the product from double dehydrofluorination of $SiF_4 \cdot 2NEt_2H$.

In the cocondensation reaction between SiF_2/SiF_4 and NEt_3 the only products were *$SiF_4 \cdot nNEt_3$ (n = 1,2) and the* $(SiF_2)_x$ polymer. However, an on-line IR experiment showed that the initial reaction product was hexafluorodisilane.

The *cocondensation reaction between* SiF_2/SiF_4 and diethylamine yielded Et_2NSiF_3 **1**, $HSiF_3$ **2** and Et_2NSiF_2H **3** in addition to the adduct product $SiF_4 \cdot 2NEt_2H$. This reac-

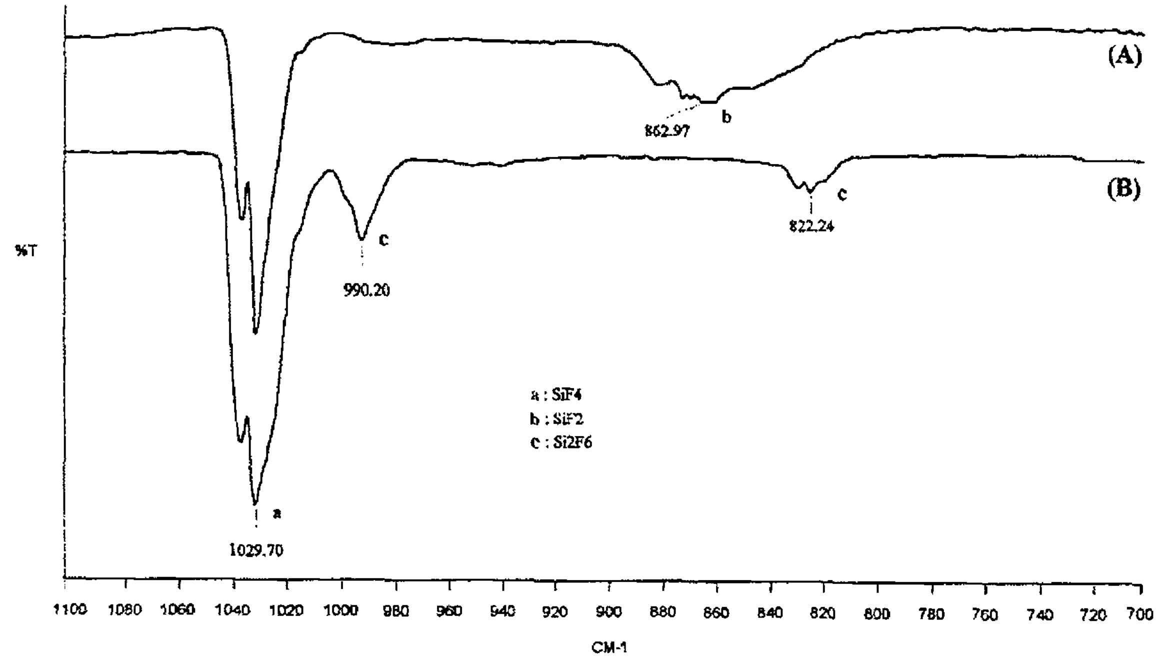


Fig. 1. The in situ IR experiment of SiF_2/SiF_4 and Et_3N: (A) before the introducing of Et_3N. (B) after the introducing of Et_3N.

tion can be best understood by the following studies:

(i) when SiF_2/SiF_4 and $HNEt_2$ were kept in 1:1 ratio, $SiF_4{\cdot}2NEt_2H$, **1**, **2** and **3** were obtained;

(ii) when SiF_2/SiF_4 and $HNEt_2$ were kept in 1:2 ratio, $SiF_4{\cdot}2NEt_2H$, $(NEt_2)_2SiF_2$ **4** and $(NEt_2)_2SiFH$ **5** were obtained;

(iii) when compounds **1**, **2** and **3** from (i) were reacted with excess $HNEt_2$, complete conversion to compounds **4** and **5** was observed in 30 min;

and (iv) the on-line IR experiment showed that mixing SiF_2/SiF_4 and $HNEt_2$ yielded Si_2F_6, and $HSiF_3$ rapidly.

From the above results, it is reasonable to assume that the reaction between SiF_2/SiF_4 and $HNEt_2$ was initiated by the formation of Si_2F_6, which reacted with $HNEt_2$ to form **1** and **2**. Subsequent reactions of **1** and **2** with excess $HNEt_2$ lead to the products **3**, **4** and **5** through dehydrofluorination.

$$SiF_2 + SiF_4 \xrightarrow{HNEt_2} Si_2F_6$$

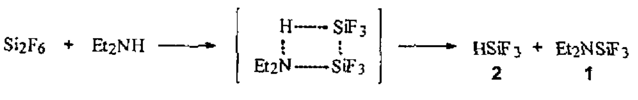
$$Si_2F_6 + HNEt_2 \longrightarrow \underset{\mathbf{1}}{Et_2NSiF_3} + \underset{\mathbf{2}}{HSiF_3}$$

$$\underset{\mathbf{1}}{Et_2NSiF_3} + HNEt_2 \xrightarrow{-HF} \underset{\mathbf{4}}{(Et_2N)_2SiF_2}$$

$$\underset{\mathbf{2}}{HSiF_3} + HNEt_2 \xrightarrow{-HF} \underset{\mathbf{3}}{Et_2NSiF_2H} \xrightarrow[HNEt_2]{-HF} \underset{\mathbf{5}}{(Et_2N)_2SiFH}$$

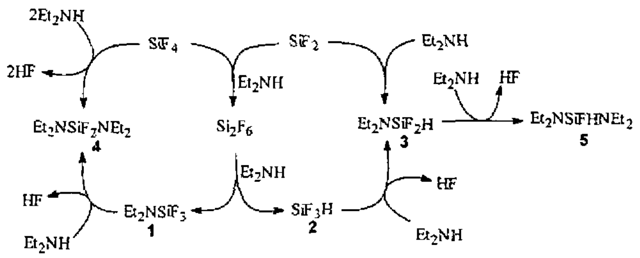
In order to prove the assumption, freshly prepared Si_2F_6 was reacted with $HNEt_2$ under the same experimental conditions. On mixing Si_2F_6 and $HNEt_2$ (in excess) compounds **1**, **2** and SiF_4 were observed immediately from the on-line IR spectrum. The gaseous mixture passing through the IR cell was condensed at -196 °C. On warming to room temperature the nmr showed that the products were **1**, **2**, **3**, **4** and **5**. This mixture of products reacted further with excess $HNEt_2$ and it was found that **1**, **2** and **3** converted to **4** and **5** completely in 24 hr. These results agree entirely with the reaction scheme proposed above. The experimental conditions and reaction products are summarized in Table 2.

The formation of compounds **1** and **2** can be rationalized by a four-centered transition state:



If this were the true mechanism, such a reaction would not be expected between Si_2F_6 and Et_3N. Indeed, no product other than Si_2F_6 was observed in the gaseous reaction between SiF_2/SiF_4 and Et_3N. Similar reaction pathway involving the cleavage of Si-Si bond in Si_2Cl_6 was proposed for the reactions of Si_2Cl_6 with germyl and stannylphosphanes.[12]

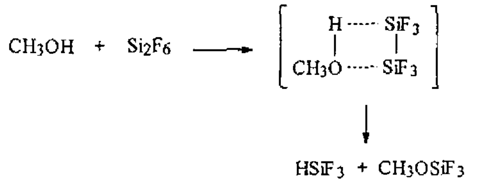
It is interesting to note that two possible pathways may be responsible for the formation of Et_2NSiF_2H **3**: (i) the insertion of SiF_2 into the N-H bond of $HNEt_2$, and (ii) the dehydrofluorination reaction between $HNEt_2$ and $HSiF_3$ **2**. In the reaction of Si_2F_6 with $HNEt_2$, small amount of **3** was obtained. Although the yield was low (<5%), it confirmed the existence of dehydrofluorination pathway because no SiF_2 was involved in this case. In the reaction of SiF_2/SiF_4 with $HNEt_2$, however, the yield of compound **3** was much higher (~20%). It is quite certain that in the latter case the SiF_2 insertion pathway is significant. The overall reaction of SiF_2/SiF_4 and Et_2NH can be illustrated by the following scheme:



In the early literature of SiF_2 chemistry, the reaction of SiF_2 with methanol was considered rather unusual because its major products, $HSiF_3$ and F_3SiOCH_3 were neither insertion products nor addition products. It was interpreted that SiF_4 reacted with CH_3OH in the gas phase to form CH_3OSiF_3 and HF, and SiF_2 inserted into HF to give SiF_3H.[13]

$$CH_3OH + SiF_4 \rightarrow CH_3OSiF_3 + HF$$
$$SiF_2 + HF \rightarrow SiF_3H$$

With our new understanding from this work, it is obvious that the reaction with methanol can also be interpreted by the initial formation of Si_2F_6 (just as in the case of the reaction with $HNEt_2$), which subsequently reacts with CH_3OH to form the observed products through a four-centered transition state.



Indeed, when SiF_2/SiF_4 and CH_3OH were introduced into the on-line IR cell, the spectrum showed clearly the im-

Table 2. Reactions Conditions and Products of the Reaction of SiF_2 with Et_2NH

Reagent (reagent ratio)	Reaction condition	Products (relative ratio of the products)
SiF_4; NEt_3 (1:1)	condense reaction	$SiF_4{\cdot}NEt_3$; $SiF_4{\cdot}2NEt_3$
SiF_4; NEt_3 (1:2)	condense reaction	$SiF_4{\cdot}2NEt_3$
SiF_4; $HNEt_2$	condense reaction	$SiF_4{\cdot}2NEt_2H$; $(Et_2N)_2SiF_2$ **4**
SiF_2/SiF_4; NEt_3	condense reaction	$SiF_4{\cdot}nNEt_3$ (n=1,2); $(SiF_2)_n$ polymer
SiF_2/SiF_4; NEt_3	in situ (gas)	Si_2F_6
SiF_2/SiF_4; $HNEt_2$ (1:1)	condense reaction	Et_2NSiF_3 **1**; $HSiF_3$ **2**; Et_2NSiF_2H **3** (20%)
SiF_2/SiF_4; $HNEt_2$ (1:2)	condense reaction	$SiF_4{\cdot}2NEt_2H$; $(Et_2N)_2SiF_2$ **4**; $(Et_2N)_2SiFH$ **5**
SiF_2/SiF_4; $HNEt_2$	in situ (gas)	Si_2F_6
Si_2F_6; $HNEt_2$	in situ (gas)	Et_2NSiF_3 **1**; $HSiF_3$ **2**; SiF_4
Si_2F_6; $HNEt_2$	condense reaction	Et_2NSiF_3 **1**; $HSiF_3$ **2**; Et_2NSiF_2H **3** (5%); $(Et_2N)_2SiF_2$ **4**; $(Et_2N)_2SiFH$ **5**
Et_2NSiF_3 **1**; Et_2NSiF_2H **3**; $HNEt_2$	room temperature reaction	$(Et_2N)_2SiF_2$ **4**; $(Et_2N)_2SiFH$ **5**
SiF_2/SiF_4; CH_3OH	in situ (gas)	Si_2F_6

mediate disappearance of SiF_2 and the formation of Si_2F_6.

(c) insertion of SiF_2 into C-X bond

The insertion reaction of SiF_2 with C-X bonds has seldomly been addressed in previous literature. Margrave and Sharp reported the reaction of SiF_2 and CF_3I.[14] In addition to a number of mixed halosilanes, compound CF_3SiF_2I was obtained as the insertion product. Here, we report the cocondensation reactions of SiF_2 and alkyl halides.

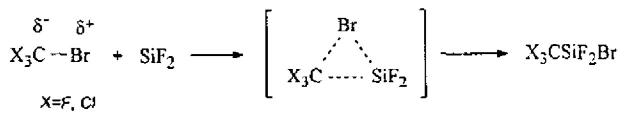
Cocondensation reactions of SiF_2 with proplychloride, propylbromide carbon tetrachloride and carbon tetrabromide failed to form any insertion products. In the reactions with halogen substituted methanes only those possessing considerable dipole moment would react with SiF_2 and formed insertion products.

$$CH_3CH_2CH_2X + SiF_2 \longrightarrow \text{no insertion products}$$

X=Br, Cl

$$CX_4 + SiF_2 \longrightarrow \text{no insertion products}$$

X=Br, Cl



(d) insertion of SiF_2 into P-Cl bond

The reaction pathway between SiF_2 and alkylchlorophosphines can be understood by the following studies:

(1) the reaction between SiF_2 and dimethylchlorophosphine

$$\underset{1}{SiF_2/SiF_4} + \underset{1}{PMe_2Cl} \longrightarrow \underset{9}{(Me_2P)_2} + \underset{10}{Me_2PSiCl_3} + \underset{11}{(Me_2P)_2SiCl_2} + SiF_{4-m}Cl_m \quad m=0\sim4$$

1 : 1

In the reaction between SiF_2 and dimethylchlorophosphine, instead of insertion products with $-PSiF_2Cl$ fragment, $(Me_2P)_2$, Me_2PSiCl_3 and $(Me_2P)_2SiCl_2$ were obtained as the major products. When SiF_2/SiF_4 and dimethylchlorophosphine were introduced into the on-line IR cell, the spectrum showed clearly the disappearance of SiF_2 and the formation of Si_2F_6. From these results, it is reasonable to assume that the reaction between SiF_2/SiF_4 and dimethylchlorophosphine was initiated by the formation of Si_2F_6, which cleaved to SiF_3 radicals in the present of the phosphine compounds.[15] Subsequent radical reactions that led to the products **9**, **10** and **11** can be rationalized as follow:

$$SiF_4 + SiF_2 \xrightarrow{B} Si_2F_6 \qquad B=PMe_2Cl$$

$$Si_2F_6 + PMe_2Cl \longrightarrow {\cdot}SiF_3 + SiF_3Cl + {\cdot}PMe_2$$

$${\cdot}SiF_3 + PMe_2Cl \longrightarrow SiF_3Cl + {\cdot}PMe_2$$

$$2\,{\cdot}PMe_2 \longrightarrow \underset{9}{(Me_2P)_2}$$

$${\cdot}SiF_3 + SiF_3Cl \xrightarrow{\text{halogen exchange}} SiCl_mF_{4-m} + {\cdot}SiCl_nF_{3-n}$$

$${\cdot}SiCl_nF_{3-n} + {\cdot}PMe_2 \longrightarrow Me_2PSiCl_nF_{3-n} \xrightarrow{\text{halogen exchange}} \underset{10}{Me_2PSiCl_3}$$

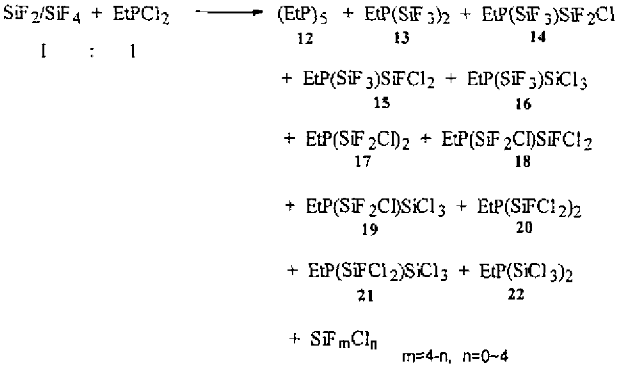
$${\cdot}SiCl_nF_{3-n} + \underset{10}{Me_2PSiCl_3} \longrightarrow SiCl_mF_{4-m} + PMe_2SiCl_2{\cdot}$$

$$PMe_2SiCl_2{\cdot} + {\cdot}PMe_2 \longrightarrow \underset{11}{(Me_2P)_2SiCl_2}$$

m=0~4, n=0~3

In principle, compound **10** could also be formed via insertion of SiF_2 followed by halogen exchange. Based on our experimental evidence, this possibility cannot be ruled out.

(2) the reaction between SiF_2 and ethyldichlorophosphine



$$\underset{1\quad:\quad1}{\mathrm{SiF_2/SiF_4}} + \mathrm{EtPCl_2} \longrightarrow \underset{\mathbf{12}}{\mathrm{(EtP)_5}} + \underset{\mathbf{13}}{\mathrm{EtP(SiF_3)_2}} + \underset{\mathbf{14}}{\mathrm{EtP(SiF_3)SiF_2Cl}}$$
$$+ \underset{\mathbf{15}}{\mathrm{EtP(SiF_3)SiFCl_2}} + \underset{\mathbf{16}}{\mathrm{EtP(SiF_3)SiCl_3}}$$
$$+ \underset{\mathbf{17}}{\mathrm{EtP(SiF_2Cl)_2}} + \underset{\mathbf{18}}{\mathrm{EtP(SiF_2Cl)SiFCl_2}}$$
$$+ \underset{\mathbf{19}}{\mathrm{EtP(SiF_2Cl)SiCl_3}} + \underset{\mathbf{20}}{\mathrm{EtP(SiFCl_2)_2}}$$
$$+ \underset{\mathbf{21}}{\mathrm{EtP(SiFCl_2)SiCl_3}} + \underset{\mathbf{22}}{\mathrm{EtP(SiCl_3)_2}}$$
$$+ \mathrm{SiF_mCl_n} \quad m=4-n,\ n=0\sim4$$

Compound **17**, a typical product from the insertion of SiF_2 into the P-Cl bonds of $EtPCl_2$, was initially obtained as the major product. Compounds **13**, **14**, **15** and **16** were also present as minors. After the reaction mixture had been kept at room temperature for three days, the nmr spectra showed that compounds **13** and **14** disappeared, other compounds reduced in intensities, and compounds **19**, **20**, **21** and **22** became the major products. We propose that this reaction was initiated by the insertion of SiF_2 into P-Cl bonds of ethyldichlorophosphine, then the halogen exchange reaction converted compound **17** to the other compounds. Small amounts of **12** and $SiCl_nF_{4-n}$ were obtained, therefore the radical pathway cannot be entirely ruled out.

CONCLUSION

Difluorosilylene has been considered to be inert toward SiF_4 in the literature.[4a] However, the evidence of the present work shows clearly this is invalid when certain Lewis bases are present in the mixture of SiF_2 and SiF_4. Insertion product Si_2F_6 was obtained immediately after the introduction of Lewis bases.

Therefore, when SiF_2/SiF_4 is reacted with amines and phosphines, two kinds of reaction pathways are possible: (1) an initial formation of Si_2F_6 which was followed by subsequent reactions leading to products containing SiF_3 groups; and (2) the traditional insertion reactions of SiF_2 into N-H or P-Cl bonds. The choice of the reaction pathway depends on the basicity of the amines and the phosphines. In the case of a strong Lewis base (R_3N, R_2NH, PR_3, PR_2Cl), the insertion of SiF_2 into Si-F bond of SiF_4 to form Si_2F_6 is the major initial reaction. In the case of a weaker Lewis base ($PRCl_2$), the insertion of SiF_2 into P-Cl bond followed by the subsequent halogen exchange reactions is the major reaction pathway.

EXPERIMENTAL SECTION

All reactions were carried out in a greaseless vacuum system and difluorosilylene was generated as a mixture of approximate 1:1 SiF_2/SiF_4 by passing SiF_4 through a column of silicon lumps heated at 1150 °C.[16] All reagents were commercial products used without further purification. Liquid reagents were degassed before used. The quantities of reagents used in reactions were controlled by a mass flow control system.

All mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer operating at 12 eV. The NMR spectra were obtained using a Bruker AM 400 spectrometer operating at 400.13, 376.5, 100.0 and 161.977 MHz for ^1H, ^{19}F ^{13}C and ^{31}P spectra, respectively. Chemical shifts of ^1H and ^{13}C spectra were measured as δ values; for the ^{13}C data listed below, the spectral multiplicity following each chemical shift is due to the coupling with heteronuclei, whereas the coupling patterns in $^{13}C\text{-}\{^1H\}_{cw}$ are included in parentheses. The ^{19}F NMR chemical shifts were measured in parts per million upfield from the internal standard CCl_3F. The ^{31}P NMR chemical shifts were measured in parts per million upfield from the standard H_3PO_4. In the $^{29}Si\text{-}\{^1H\}$ NMR data, the spectral multiplicity following each chemical shift is due to the coupling with heteronuclei.

Volatile products were fractionated and collected as various temperatures (-45 °C to 0 °C), but only partial separation was achieved. The attempt of further separating the volatile products was not successful because the boiling points of the products were close.

Reactions between SiF_4 and Amines

SiF_4 and Et_3N in approximate 1:1 ratio were introduced into the vacuum system and condensed at -196 °C. No volatile products were found after the unreacted reagents were pumped out at room temperature; two solid products (one white and one yellow) were obtained. They are $SiF_4{\cdot}2NEt_3$ (white) and $SiF_4{\cdot}NEt_3$ (yellow), respectively, and are the same as those obtained by Ennan and Gavrilova's room temperature reaction.

SiF_4 and Et_3N in approximate 1:2 ratio were introduced into the vacuum system and condensed at -196 °C. After the unreacted reagents were pumped out at room temperature, white solid $SiF_4{\cdot}2NEt_3$ was obtained as the only product. The yield base on the quantity of amine used was about 90%.

SiF_4 and Et_2NH in approximate 1:1 ratio were introduced into the vacuum system and condensed at -196 °C. After unreacted reagents were pumped out, a white solid and a colorless liquid were obtained. The white solid is $SiF_4 \cdot 2Et_2NH$ and the colorless liquid is compound **4**. The total yield of compound **4** and $SiF_4 \cdot 2Et_2NH$ base on the quantity of amine used was about 95%.

Reactions between SiF_2/SiF_4 and Amine

The reaction between SiF_2/SiF_4 and diethylamine was carried out at condensation reaction condition with different SiF_2/SiF_4: amine ratio. SiF_2/SiF_4 and diethylamine were mixed in different ratios and introduced into the vacuum system and condensed at -196 °C. Compounds **1**, **2** and **3** were obtained when the SiF_2/SiF_4: amine ratio was kept at approximately 1:1. When the SiF_2/SiF_4: amine ratio was kept to 0.5, **4**, **5** and $SiF_4 \cdot 2Et_2NH$ were obtained instead.

The reaction between SiF_2/SiF_4 and triethylamine was carried out at condensation reaction conditions. SiF_2/SiF_4 and Et_3N in approximate 1:1 ratio were introduced into the vacuum system and condensed at -196 °C. After unreacted reagents were pumped out, in addition to $SiF_4 \cdot 2NEt_3$ (white) and $SiF_4 \cdot NEt_3$ (yellow), $(SiF_2)_n$ polymer was obtained. No volatile product was found.

Reactions between Si_2F_6 and Diethylamine

Si_2F_6 and Et_2NH in approximate 1:1 ratio were introduced into the vacuum system and condensed at -196 °C. After unreacted reagents were pumped out, compounds **1**, **2**, **3**, **4** and **5** were obtained as colorless liquids. The total yield of those compounds based on the quantity of amine used was about 95%.

Reactions between Et_2NSiF_3 1, Et_2NSiF_2H 3 and Diethylamine

Compounds $(Et_2N)_2SiF_2$ **4** and $(Et_2N)_2SiFH$ **5** were obtained by reacting Et_2NSiF_3 **1**, Et_2NSiF_2H **3** and Et_2NH at room temperature for 24 hr. The reaction was quantitative.

Reactions between SiF_2/SiF_4 and Various Halomethanes

The reaction between SiF_2/SiF_4 and various halomethanes was carried out at condensation reaction conditions with SiF_2/SiF_4 and halomethane in approximate 1:1 ratio. SiF_2/SiF_4 and halomethane were mixed and introduced into the vacuum system and condensed at -196 °C. After unreacted reagents were pumped out, in addition to $(SiF_2)_n$ polymer insertion product **6** was obtained in the reaction of SiF_2/SiF_4 with bromotrichloromethane. In the reaction of SiF_2/SiF_4 with dibromodichloromethane insertion product **7** was obtained. The reaction of SiF_2/SiF_4 with dibromochlorofluoromethane yielded insertion product **8**.

Reaction between SiF_2/SiF_4 and Dimethylchlorophosphine

The reaction between SiF_2/SiF_4 and dimethylchlorophosphine was carried out at condensation experiment conditions with SiF_2/SiF_4 and dimethylchlorophosphine in approximate 1:1 ratio. SiF_2/SiF_4 and dimethylchlorophosphine were mixed in the vacuum system and condensed at -196 °C. After unreacted reagents were removed, compounds **9**, **10**, **11** and various chlorofluorosilanes ($SiCl_4$, $SiCl_3F$, $SiCl_2F_2$, $SiClF_3$) were obtained in addition to $(SiF_2)_n$ polymer.

Reaction between SiF_2/SiF_4 and Ethyldichlorophosphine

The reaction between SiF_2/SiF_4 and ethyldichlorophosphine was carried out at condensation experiment conditions with SiF_2/SiF_4 and ethyldichlorophosphine in approximate 1:1 ratio. The liquid collected at -30 °C containing compounds **13**, **14**, **15**, **16**, **17**, **18**, **20**, **21**, **22** and various chlorofluorosilanes ($SiCl_4$, $SiCl_3F$, $SiCl_2F_2$, $SiClF_3$) was obtained. A solid product $(EtP)_5$ **12** was also obtained.

The in situ IR Experiment

The gaseous reagents were mixed and introduced into the IR gas cell that was connected to the pumping system. The IR spectra were taken as soon as the reagents were mixed. The reactions were initiated by the insertion of SiF_2 into SiF_4 in the presence of Lewis bases such as Et_2NH, CH_3OH, trialkylphosphine, dialkylchlorophosphine, alkyldichlorophosphine. In these reactions, Si_2F_6 was the common initial product. In the in situ IR experiment of Si_2F_6 and Et_2NH compounds Et_2NSiF_3 **1**; $HSiF_3$ **2** and SiF_4 were detected.

The spectral data of the products:

(i) Compound **1** $(C_2H_5)_2NSiF_3$. Mass spectrum: m/e 157 (M^+, $C_4H_{10}F_3NSi^+$), 142 ($C_3H_7F_3NSi^+$), 114 ($CH_3F_3NSi^+$), 95 ($CH_3F_2NSi^+$), 85 (F_3Si^+). IR adsorption: 2978.5, 2943.0, 2884.3, 1389.9, 1223.1, 1174.2, 1107.6, 1053.3, 979.1, 953.9, 853.8, 789.5, 656.7, 502.6 cm^{-1}. ^1H NMR: δ 1.77 t, $\mathrm{-NCH_2C}H_3$, 3.61 qq, $\mathrm{-NC}H_2\mathrm{CH_3}$. ^{19}F NMR: δ -151 s (br), $\mathrm{-NSi}F_3$. ^{13}C NMR: δ 16.01 q, $\mathrm{-NCH_2}CH_3$; 39.90 t, $\mathrm{-N}C\mathrm{H_2CH_3}$. $^{29}Si\{^1H\}$ NMR: δ -87.10 q, $\mathrm{-N}Si\mathrm{F_3}$. $^1J_{Si\text{-}F} = 204$ Hz.

(ii) Compound **3** $(C_2H_5)_2NSiF_2H$. Mass spectrum: m/e 139 (M^+, $C_4H_{11}F_2NSi^+$), 138 ($C_4H_{10}F_2NSi^+$), 124 ($C_3H_8F_2NSi^+$), 110 ($C_2H_6F_2NSi^+$). IR adsorption: 2250, 2166, 1107, 906, 793, 717 cm^{-1}. ^1H NMR: δ 1.7 t, $\mathrm{-NCH_2C}H_3$; 3.6 qt, $\mathrm{-NC}H_2\mathrm{CH_3}$; 5.1 t, $\mathrm{-SiF_2}H$. ^{19}F NMR: δ -130.8 s (dq^n), $\mathrm{-Si}F_2\mathrm{H}$. ^{13}C NMR: δ 16.3 t (qm), $\mathrm{-NCH_2}CH_3$; 39.9 t (tm),

$\mathrm{-N}C\mathrm{H_2CH_3}$. $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR: δ -53.49 s, $\mathrm{-}Si\mathrm{F_2H}$. $^1J_{\mathrm{Si\text{-}F}} = 274$ Hz.

(iii) Compound **4** $[(\mathrm{C_2H_5})_2]_2\mathrm{NSiF_2}$. Mass spectrum: m/e 210 ($\mathrm{M^+}$, $\mathrm{C_8H_{20}F_2N_2Si^+}$), 181 ($\mathrm{C_6H_{15}F_2N_2Si^+}$), 136 ($\mathrm{C_4H_8F_2NSi^+}$), 122 ($\mathrm{C_3H_6F_2NSi^+}$), 86 ($\mathrm{C_3H_8NSi^+}$). ^{1}H NMR: δ 1.75 t, $\mathrm{-NCH_2C}H_3$; 3.58 qt, $\mathrm{-NC}H_2\mathrm{CH_3}$. ^{19}F NMR: δ -144.0 s (br), $\mathrm{-NSi}F_2\mathrm{N-}$. ^{13}C NMR: δ 16.24 q (qt), $\mathrm{-NCH_2}C\mathrm{H_3}$; 40.88 t (qtd), $\mathrm{-N}C\mathrm{H_2CH_3}$. $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR: δ -64.4 t, $\mathrm{-N}Si\mathrm{F_2N-}$. $^1J_{\mathrm{Si\text{-}F}} = 222$ Hz.

(iv) Compound **5** $[(\mathrm{C_2H_5})_2]_2\mathrm{NSiFH}$. ^{1}H NMR: δ 1.8 t, $\mathrm{-NCH_2C}H_3$; 3.6 qd, $\mathrm{-NC}H_2\mathrm{CH_3}$; 5.1 d, $\mathrm{-SiF}H\mathrm{-}$. ^{19}F NMR: δ -138.6 s (dm), $\mathrm{-Si}F\mathrm{H-}$. $^1J_{\mathrm{Si\text{-}F}} = 273$ Hz.

(v) Compound **6** $\mathrm{CCl_3SiF_2Br}$. Mass spectrum: m/e 227 ($\mathrm{M\text{-}Cl^+}$, $\mathrm{CCl_2BrF_2Si^+}$), 183 ($\mathrm{M\text{-}Br^+}$, $\mathrm{CCl_3F_2Si^+}$), 145 ($\mathrm{BrF_2Si^+}$), 82 ($\mathrm{CCl_2^+}$), 47 ($\mathrm{CCl_2^+}$, $\mathrm{FSi^+}$). ^{19}F NMR: δ -124.3 s (s), $\mathrm{-Si}F_2\mathrm{Br}$. ^{13}C NMR: δ 83.5 t (t), $\mathrm{-}C\mathrm{Cl_3}$. $^1J_{\mathrm{Si\text{-}F}} = 320.0$ Hz, $^2J_{\mathrm{C\text{-}F}} = 25.2$ Hz.

(vi) Compound **7** $\mathrm{CCl_2BrSiF_2Br}$. Mass spectrum: m/e 271 ($\mathrm{M\text{-}Cl^+}$, $\mathrm{CClBr_2F_2Si^+}$), 227 ($\mathrm{M\text{-}Br^+}$, $\mathrm{CCl_2BrF_2Si^+}$), 192 ($\mathrm{M\text{-}ClBr^+}$, $\mathrm{CClBrF_2Si^+}$), 145 ($\mathrm{BrF_2Si^+}$), 47 ($\mathrm{CCl_2^+}$, $\mathrm{FSi^+}$). ^{19}F NMR: δ -124.0 s (s), $\mathrm{-Si}F_2\mathrm{Br}$. ^{13}C NMR: δ 64.5 t (t), $\mathrm{-}C\mathrm{BrCl_2}$. $^1J_{\mathrm{Si\text{-}F}} = 320.1$ Hz, $^2J_{\mathrm{C\text{-}F}} = 24.1$ Hz.

(vii) Compound **8** $\mathrm{CClBrFSiF_2Br}$. Mass spectrum: m/e 255 ($\mathrm{M\text{-}Cl^+}$, $\mathrm{CBr_2F_3Si^+}$), 211 ($\mathrm{M\text{-}Br^+}$, $\mathrm{CClBrF_3Si^+}$), 178 ($\mathrm{M\text{-}ClBr^+}$, $\mathrm{CBrF_3Si^+}$), 132 ($\mathrm{ClF_3Si^+}$), 47 ($\mathrm{CCl_2^+}$, $\mathrm{FSi^+}$). ^{19}F NMR: δ -80.05 br (br), $\mathrm{C}F\mathrm{BrCl}$, δ -124.5 AB (AB), $\mathrm{-Si}F_2\mathrm{Br}$. ^{13}C NMR: δ 99.7 dt (dt), $\mathrm{-}C\mathrm{ClBrF}$. $^1J_{\mathrm{Si\text{-}F}} = 323.6$ Hz, $^2J_{\mathrm{Si\text{-}F}} = 49.6$ Hz, $^2J_{\mathrm{C\text{-}F}} = 28.0$ Hz, $^1J_{\mathrm{C\text{-}F}} = 301.0$ Hz, $^2J_{\mathrm{F\text{-}F}} = 55.3$ Hz, $^3J_{\mathrm{F\text{-}F}} = 0.8$ Hz.

(viii) Compound **9** $[(\mathrm{CH_3})_2\mathrm{P}]_2$. Mass spectrum: m/e 122 ($\mathrm{M^+}$, $\mathrm{C_4H_{12}P_2^+}$), 107 ($\mathrm{C_3H_9P_2^+}$), 79 ($\mathrm{CH_5P_2^+}$), 61 ($\mathrm{CH_2P^+}$), 45 ($\mathrm{CH_2P^+}$). ^{1}H NMR: δ 1.11 $\mathrm{A_6XX'A'_6}$, $\mathrm{-P(C}H_3)_2$. ^{13}C NMR: δ 10.68 t (qt). $\mathrm{-P(}C\mathrm{H_3)_2}$ $^1J_{\mathrm{C\text{-}H}} = 128.9$ Hz. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR: δ -58.2 s(m). $\mathrm{-}P\mathrm{(CH_3)_2}$ $^1J_{\mathrm{C\text{-}P}} \doteqdot {}^2J_{\mathrm{C\text{-}P}} \doteqdot 3.9$ Hz, $^2J_{\mathrm{H\text{-}P}} = 2.9$ Hz, $^3J_{\mathrm{H\text{-}P}} = 11.25$ Hz.

(ix) Compound **10** $(\mathrm{CH_3})_2\mathrm{PSiCl_3}$. Mass spectrum: m/e 194 ($\mathrm{M^+}$, $\mathrm{C_2H_6Cl_3PSi^+}$), 133 ($\mathrm{SiCl_3^+}$), 113 ($\mathrm{CH_3SiCl_2^+}$), 96 ($\mathrm{C_2H_6PCl^+}$), 61 ($\mathrm{C_2H_6P^+}$). ^{1}H NMR: δ 1.06 d, $\mathrm{-P(C}H_3)_2$. ^{13}C NMR: δ 8.38 d (qdq). $\mathrm{-P(}C\mathrm{H_3)_2}$. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR: δ -96.5 s(m). $\mathrm{-}P\mathrm{(CH_3)_2}$. $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR: δ -64.4 t, $\mathrm{-P}Si\mathrm{Cl_3}$. $^1J_{\mathrm{C\text{-}P}} = 18.1$ Hz, $^1J_{\mathrm{Si\text{-}P}} = 82.5$ Hz, $^2J_{\mathrm{H\text{-}P}} = 3.9$ Hz.

(x) Compound **11** $[(\mathrm{CH_3})_2\mathrm{P}]_2\mathrm{SiCl_2}$. Mass spectrum: m/e 220 ($\mathrm{M^+}$, $\mathrm{C_4H_{12}Cl_2P_2Si^+}$), 205 ($\mathrm{C_3H_9Cl_2P_2Si^+}$), 160 ($\mathrm{C_2H_7Cl_2PSi^+}$), 113 ($\mathrm{CH_3Cl_2Si^+}$), 61 ($\mathrm{C_2H_6P^+}$). ^{1}H NMR: δ 1.23 $\mathrm{A_6XX'A'_6}$, $\mathrm{-P(C}H_3)_2$. ^{13}C NMR: δ 7.0 AXX' (m). $\mathrm{-P(}C\mathrm{H_3)_2}$ $^1J_{\mathrm{C\text{-}H}} = 128.9$ Hz. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR: δ -109.5 s(m). $\mathrm{-}P\mathrm{(CH_3)_2}$ $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR: δ 45.3 t, $\mathrm{-P}Si\mathrm{Cl_2}$. $^1J_{\mathrm{Si\text{-}P}} = 88.1$ Hz, $^2J_{\mathrm{H\text{-}P}} = 3.1$ Hz.

(xi) Compound **13** $\mathrm{C_2H_5P(SiF_3)_2}$. Mass spectrum: m/e 230 ($\mathrm{M^+}$, $\mathrm{C_2H_5F_6PSi_2^+}$), 202 ($\mathrm{HF_6PSi_2^+}$), 183 ($\mathrm{HF_5PSi_2^+}$), 85 ($\mathrm{SiF_3^+}$), 57 ($\mathrm{C_4H_9^+}$). ^{1}H NMR: δ 1.01 qm, $\mathrm{-PC}H_2\mathrm{CH_3}$, 1.61 tm, $\mathrm{-PCH_2C}H_3$. ^{13}C NMR: δ 5.93 d. $\mathrm{-PCH_2}C\mathrm{H_3}$, 16.14 d. $\mathrm{-P}C\mathrm{H_2CH_3}$. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR: δ -220.3 m(m). $\mathrm{-}P\mathrm{CH_2CH_3}$. $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR: δ -117.45, d, $\mathrm{-PSi}F_3$. $^1J_{\mathrm{Si\text{-}F}} = 328.1$ Hz, $^2J_{\mathrm{P\text{-}F}} = 10.77$ Hz, $^1J_{\mathrm{C\text{-}P}} = 12.5$ Hz, $^2J_{\mathrm{C\text{-}P}} = 9.2$ Hz.

(xii) Compound **14** $\mathrm{C_2H_5P(SiF_3)(SiClF_2)}$. Mass spectrum: m/e 246 ($\mathrm{M^+}$, $\mathrm{C_2H_5ClF_5PSi_2^+}$), 218 ($\mathrm{HClF_5PSi_2^+}$), 183 ($\mathrm{HF_5PSi_2^+}$), 85 ($\mathrm{SiF_3^+}$), 57 ($\mathrm{C_4H_9^+}$). ^{1}H NMR: δ 1.06 qm, $\mathrm{-PC}H_2\mathrm{CH_3}$, 1.63 tm, $\mathrm{-PCH_2C}H_3$. ^{13}C NMR: δ 7.21 d. $\mathrm{-PCH_2}C\mathrm{H_3}$, 16.01 d. $\mathrm{-P}C\mathrm{H_2CH_3}$. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR: δ -196.9 qt (qtm). $\mathrm{-}P\mathrm{CH_2CH_3}$. $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR: δ -117.66, dt, $\mathrm{-PSi}F_3$, -104.3, AB, $\mathrm{-PSi}F_2\mathrm{Cl}$. $^1J_{\mathrm{Si\text{-}F}} = 328.6$ Hz, $^2J_{\mathrm{F\text{-}F}} = 58.0$ Hz, $^1J_{\mathrm{C\text{-}P}} = 13.1$ Hz, $^2J_{\mathrm{C\text{-}P}} = 10.3$ Hz, $^2J_{\mathrm{F\text{-}P}} = 9.87$ Hz, $^3J_{\mathrm{H\text{-}H}} = 7.65$ Hz.

(xiii) Compound **15** $\mathrm{C_2H_5P(SiF_3)(SiFCl_2)}$. Mass spectrum: m/e 262 ($\mathrm{M^+}$, $\mathrm{C_2H_5Cl_2F_4PSi_2^+}$), 234 ($\mathrm{HCl_2F_4PSi_2^+}$), 215 ($\mathrm{HF_3PSi_2^+}$), 199 ($\mathrm{HClF_4PSi_2^+}$), 117 ($\mathrm{SiFCl_2^+}$). ^{1}H NMR: δ 1.12 qm, $\mathrm{-PC}H_2\mathrm{CH_3}$, 1.74 tm, $\mathrm{-PCH_2C}H_3$. ^{13}C NMR: δ 8.52 d. $\mathrm{-PCH_2}C\mathrm{H_3}$, 15.68 d. $\mathrm{-P}C\mathrm{H_2CH_3}$. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR: δ -175.1 dq (dqm). $\mathrm{-}P\mathrm{CH_2CH_3}$. $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR: δ -117.87, dd, $\mathrm{-PSi}F_3$, -95.5, dq, $\mathrm{-PSi}F\mathrm{Cl_2}$. $^1J_{\mathrm{Si\text{-}F}} = 329.7$ Hz, $^1J_{\mathrm{Si\text{-}F}} = 375.5$ Hz, $^4J_{\mathrm{F\text{-}F}} = 2.90$ Hz, $^1J_{\mathrm{C\text{-}P}} = 13.9$ Hz, $^2J_{\mathrm{C\text{-}P}} = 11.3$ Hz, $^2J_{\mathrm{F\text{-}P}} = 8.98$ Hz, $^3J_{\mathrm{H\text{-}H}} = 7.71$ Hz.

(xiv) Compound **16** $\mathrm{C_2H_5P(SiF_3)(SiCl_3)}$. Mass spectrum: m/e 278 ($\mathrm{M^+}$, $\mathrm{C_2H_5Cl_3F_3PSi_2^+}$), 250 ($\mathrm{HCl_3F_3PSi_2^+}$), 215 ($\mathrm{HCl_2F_3PSi_2^+}$), 133 ($\mathrm{Cl_3Si^+}$), 98 ($\mathrm{SiCl_2^+}$). ^{1}H NMR: δ 1.18 qm, $\mathrm{-PC}H_2\mathrm{CH_3}$, 1.72 tm, $\mathrm{-PCH_2C}H_3$. ^{13}C NMR: δ 9.71 d. $\mathrm{-PCH_2}C\mathrm{H_3}$, 15.30 d. $\mathrm{-P}C\mathrm{H_2CH_3}$. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR: δ -155.9 q (qm). $\mathrm{-}P\mathrm{CH_2CH_3}$. $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR: δ -118.22, d, $\mathrm{-PSi}F_3$. $^1J_{\mathrm{Si\text{-}F}} = 330.8$ Hz, $^1J_{\mathrm{Si\text{-}P}} = 57.5$ Hz, $^1J_{\mathrm{C\text{-}P}} = 14.3$ Hz, $^2J_{\mathrm{C\text{-}P}} = 12.6$ Hz, $^2J_{\mathrm{F\text{-}P}} = 8.53$ Hz, $^3J_{\mathrm{H\text{-}H}} = 7.67$ Hz.

(xv) Compound **17** $\mathrm{C_2H_5P(SiClF_2)_2}$. Mass spectrum: m/e 262 ($\mathrm{M^+}$, $\mathrm{C_2H_5Cl_2F_4PSi_2^+}$), 234 ($\mathrm{HCl_2F_4PSi_2^+}$), 215 ($\mathrm{HF_3PSi_2^+}$), 199 ($\mathrm{HClF_4PSi_2^+}$), 117 ($\mathrm{SiFCl_2^+}$). ^{1}H NMR: δ 1.12 qm, $\mathrm{-PC}H_2\mathrm{CH_3}$, 1.65 tm, $\mathrm{-PCH_2C}H_3$. ^{13}C NMR: δ 8.52 d. $\mathrm{-PCH_2}C\mathrm{H_3}$, 15.68 d. $\mathrm{-P}C\mathrm{H_2CH_3}$. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR: δ -175.1 m (m). $\mathrm{-}P\mathrm{CH_2CH_3}$. $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR: δ -104.5, AB, $\mathrm{-PSi}F_2\mathrm{Cl}$. $^2J_{\mathrm{F\text{-}F}} = 59.0$ Hz, $^1J_{\mathrm{C\text{-}P}} = 13.5$ Hz, $^2J_{\mathrm{C\text{-}P}} = 11.3$ Hz, $^2J_{\mathrm{F\text{-}P}} = 7.8$ Hz, $^2J_{\mathrm{F\text{-}P}} = 2.8$ Hz, $^3J_{\mathrm{H\text{-}H}} = 7.71$ Hz.

(xvi) Compound **18** $\mathrm{C_2H_5P(SiFCl_2)(SiClF_2)}$. Mass spectrum: m/e 278 ($\mathrm{M^+}$, $\mathrm{C_2H_5Cl_3F_3PSi_2^+}$), 250 ($\mathrm{HCl_3F_3PSi_2^+}$), 215 ($\mathrm{HCl_2F_3PSi_2^+}$), 133 ($\mathrm{Cl_3Si^+}$), 98 ($\mathrm{SiCl_2^+}$). ^{1}H NMR: δ 1.18 qm, $\mathrm{-PC}H_2\mathrm{CH_3}$, 1.72 tm, $\mathrm{-PCH_2C}H_3$. ^{13}C NMR: δ 9.73 d. $\mathrm{-PCH_2}C\mathrm{H_3}$, 15.18 d. $\mathrm{-P}C\mathrm{H_2CH_3}$. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR: δ -155.1 ddd (dddm). $\mathrm{-}P\mathrm{CH_2CH_3}$. $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR: δ -95.8, dt, $\mathrm{-PSi}F\mathrm{Cl_2}$, -104.0, AB, $\mathrm{-PSi}F_2\mathrm{Cl}$. $^1J_{\mathrm{Si\text{-}F}} = 376.6$ Hz, $^1J_{\mathrm{C\text{-}P}} = 14.3$ Hz, $^2J_{\mathrm{C\text{-}P}} = 12.9$ Hz, $^2J_{\mathrm{F\text{-}P}} = 7.9$ Hz, $^2J_{\mathrm{F\text{-}P}} = 13$ Hz, $^2J_{\mathrm{F\text{-}P}} = 3.7$ Hz, $^3J_{\mathrm{H\text{-}H}} = 7.67$ Hz.

(xvii) Compound **19** $\mathrm{C_2H_5P(SiCl_3)(SiClF_2)}$. Mass spectrum: m/e 294 ($\mathrm{M^+}$, $\mathrm{C_2H_5Cl_4F_2PSi_2^+}$), 266 ($\mathrm{HCl_4F_2PSi_2^+}$), 231 ($\mathrm{HCl_3F_2PSi_2^+}$), 142 ($\mathrm{C_2H_5PSiFCl^+}$), 114 ($\mathrm{HPSiFCl^+}$). ^{1}H

NMR: δ 1.22 qm, -PCH_2CH$_3$, 1.79 tm, -PCH$_2$CH_3. ^{13}C NMR: δ 10.82 d. -PCH$_2C$H$_3$, 14.85 d. -PCH$_2$CH$_3$. ^{31}P{^{1}H} NMR: δ -137.4 dd (m). -PCH$_2$CH$_3$. ^{19}F{^{1}H} NMR: δ -104.0, AB, -PSiF_2Cl. $^1J_{\text{Si-P}}$ = 45.3 Hz, $^1J_{\text{C-P}}$ = 15.1 Hz, $^2J_{\text{C-P}}$ = 13.9 Hz, $^2J_{\text{F-P}}$ = 9.7 Hz, $^2J_{\text{F-P}}$ = 4.7 Hz, $^3J_{\text{H-H}}$ = 7.65 Hz, $^2J_{\text{F-F}}$ = 57 Hz.

(xviii) Compound **20** $C_2H_5P(SiFCl_2)_2$. Mass spectrum: m/e 294 (M$^+$, $C_2H_5Cl_4F_2PSi_2^+$), 266 ($HCl_4F_2PSi_2^+$), 231 ($HCl_3F_2PSi_2^+$), 142 ($C_2H_5PSiFCl^+$), 114 ($HPSiFCl^+$). ^{1}H NMR: δ 1.22 qm, -PCH_2CH$_3$, 1.79 tm, -PCH$_2$CH_3. ^{13}C NMR: δ 10.85 d. -PCH$_2$CH$_3$, 14.80 d. -PCH$_2$CH$_3$. ^{31}P{^{1}H} NMR: δ -136.8 dd (m). -PCH$_2$CH$_3$. ^{19}F{^{1}H} NMR: δ -96.1, d (dm), -PSiFCl$_2$. $^1J_{\text{Si-F}}$ = 378.2 Hz, $^1J_{\text{Si-P}}$ = 44.5 Hz, $^1J_{\text{C-P}}$ = 15.1 Hz, $^2J_{\text{C-P}}$ = 13.8 Hz, $^2J_{\text{F-P}}$ = 12.1 Hz, $^2J_{\text{F-P}}$ = 4.7 Hz, $^3J_{\text{H-H}}$ = 7.65 Hz.

(xix) Compound **21** $C_2H_5P(SiCl_3)(SiFCl_2)$. Mass spectrum: m/e 310 (M$^+$, $C_2H_5Cl_5FPSi_2^+$), 295 ($CH_2Cl_5FPSi_2^+$), 231 ($HCl_5FPSi_2^+$), 142 ($C_2H_5PSiFCl^+$), 114 ($HPSiFCl^+$). ^{1}H NMR: δ 1.28 qm, -PCH_2CH$_3$, 1.84 tm, -PCH$_2$CH_3. ^{13}C NMR: δ 11.9 d. -PCH$_2C$H$_3$, 14.60 d. -PCH$_2$CH$_3$. ^{31}P{^{1}H} NMR: δ -121.1 d (dm). -PCH$_2$CH$_3$. ^{19}F{^{1}H} NMR: δ -96.5, d(dm), -PSiFCl$_2$. $^1J_{\text{Si-F}}$ = 379.3 Hz, $^1J_{\text{C-P}}$ = 15.9 Hz, $^2J_{\text{C-P}}$ = 14.8 Hz, $^2J_{\text{F-P}}$ = 11.7 Hz, $^3J_{\text{H-H}}$ = 7.72 Hz.

(xx) Compound **22** $C_2H_5P(SiCl_3)_2$. Mass spectrum: m/e 326 (M$^+$, $C_2H_5Cl_6PSi_2^+$), 298 ($HCl_6PSi_2^+$), 263 ($HCl_5PSi_2^+$), 130 (HCl_2PSi^+), 63 ($SiCl^+$). ^{1}H NMR: δ 1.33 qm, -PCH_2CH$_3$, 1.89 tm, -PCH$_2$CH_3. ^{13}C NMR: δ 12.96 d. -PCH$_2C$H$_3$, 14.41 d. -PCH$_2$CH$_3$. ^{31}P{^{1}H} NMR: δ -106.4 s (m). -PCH$_2$CH$_3$. ^{19}F{^{1}H} NMR: δ -96.5, d(dm), -PSiFCl$_2$. $^1J_{\text{Si-P}}$ = 66.3 Hz, $^1J_{\text{C-P}}$ = 16.8 Hz, $^2J_{\text{C-P}}$ = 15.6 Hz, $^3J_{\text{H-H}}$ = 7.9 Hz.

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Key Words

Difluorosilylene; Amine; Phospine; Insertion.

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