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INORGANIC SILYLENES. CHEMISTRY OF SILYLENE, DICHLOROSILYLENE, AND DIFLUOROSILYLENE

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I. Introduction

To a certain extent, silicon chemistry developed in the shadow of organic chemistry. The development may be divided into three stages: (1) period of mimicking, when investigators of silicon chemistry relied on tenuous analogies to organic chemistry and on speculation that a framework reminiscent of organic chemistry could be developed; (2) period of realization of the close similarities and gross differences between the two chemistries; and (3) period of utilization of these differences in various applications. The latter is evidenced by the rapid growth in studies using organosilicon compounds for special organic syntheses. As a result, it is perhaps reasonable to state that silicon chemistry will soon become divided into two areas of almost equal importance: conventional organosilicon chemistry and silaorganic chemistry. Similarly, silylene chemistry seems to have developed in the shadow of carbene chemistry. This is particularly obvious, as one often finds the silylenes referred to in the literature as "carbene analogues."

During the past 10 years, because of discoveries of better reaction conditions and better means to generate silylenes, the chemistry of various silylenes has been studied thoroughly and has reached the stage where general and unique behaviors of each silylene can be described systematically.

Partly because of the direct impact on organosilicon chemistry and partly because of the interests in searching for other related reactive intermediates such as silenes and disilenes, the development of the chemistry of organic silylenes has received much more attention than that of inorganic silylenes. The rapid and exciting development in organic silylene chemistry is apparent from the number of excellent review articles that have appeared (*5, 19, 36, 37, 39, 48, 57, 60, 75*). However, as far as the fundamental reaction mechanism is concerned, studies on inorganic silylenes should perhaps provide more basic information because of the simplicity in both structures and reaction pathways of the inorganic silylenes. In addition, systematic studies on the reaction mechanisms of silylene, dichlorosilylene, and difluorosilylene (most significantly, sometimes quantitative data are becoming available) have clarified a number of basic points that had long confused investigators. For example, the reaction mechanism of difluorosilylene has so far been described in a very confused manner in the review literature (*113*). We will therefore reexamine these results and present an updated summary for these basic silylene species.

No attempt is made to include every known reaction of the three silylenes; rather, we hope to describe in this chapter, in a systematic and critical manner, our understanding of how inorganic silylenes participate in reactions of fundamental interest.

II. Chemistry of Silylene

In view of the fact that silylene, SiH_2, is the simplest divalent silicon species, the variety of reactions that have been studied is surprisingly small. Effort has so far been concentrated on the study of its reaction mechanisms.

Although the existence of SiH_2 was first postulated in pyrolysis studies on silane and higher silanes long ago (*50*), the evidence for the formation of silylene has been controversial (*50, 81, 84*). A balanced view on this matter is that while the possibility of a primary process leading to the formation of silyl radicals cannot be ruled out (*84*), the involvement of SiH_2 in these pyrolysis reactions is generally accepted (*50, 81*).

$$Si_nH_{2n+2} \xrightarrow{\Delta} SiH_2 + Si_{n-1}H_{2n}, \qquad n = 1, 2, 3 \tag{1}$$

The controversy of silylene vs. silyl radical exists in almost every experimental preparation of silylene. For example, in the fast-neutron bombardment experiment, $^{31}\mathrm{P}(n,p)^{31}\mathrm{Si}$ in phosphine–silane mixtures, another useful method for studying silylene chemistry, the formation of disilane has been explained by mechanisms involving either silylene or silyl radicals (*43, 74, 76, 85, 115, 116*):

$$\begin{aligned} \mathrm{PH_3} + n &\longrightarrow {}^{31}\mathrm{Si} + 3\mathrm{H} + p \\ {}^{31}\mathrm{Si} &\xrightarrow{\circ} {}^{31}\mathrm{SiH_2} \\ {}^{31}\mathrm{SiH_2} + \mathrm{SiH_4} &\longrightarrow {}^{31}\mathrm{SiH_3SiH_3} \qquad (2) \end{aligned}$$

or

$$\begin{aligned} {}^{31}\mathrm{Si} &\xrightarrow{\circ} {}^{31}\mathrm{SiH_3} \\ {}^{31}\mathrm{SiH_3} + \mathrm{SiH_3} &\longrightarrow {}^{31}\mathrm{SiH_3SiH_3} \end{aligned}$$

The most studied reaction of silylene is the insertion reaction into silicon–hydrogen bonds. It was first postulated on the basis that higher silanes were generally formed in pyrolysis of silane, disilane, and trisilane (*74, 81, 98*). If silylene is the major intermediate, the higher silanes are formed by insertion reactions of the type

$$\mathrm{SiH_2} + \mathrm{H{-}Si}\leqq \longrightarrow \mathrm{H{-}SiH_2{-}Si}\leqq \qquad (3)$$

When alkylsilanes are copyrolyzed together with $\mathrm{Si_2H_6}$, the reactions are best interpreted by $\mathrm{SiH_2}$ insertion (*14*). For example,

$$\mathrm{Si_2H_6} \longrightarrow \mathrm{SiH_2} + \mathrm{SiH_4} \qquad (4)$$

$$\mathrm{SiH_2} + \mathrm{CH_3SiH_3} \longrightarrow \mathrm{CH_3SiH_2SiH_3} \qquad (5)$$

When $\mathrm{Si_2D_6}$ was used in the same reaction, the fact that $\mathrm{CH_3SiH_2SiHD_2}$ and $\mathrm{SiD_4}$ were obtained instead of $\mathrm{CH_3SiH_2SiD_3}$ and $\mathrm{SiD_3H}$ was considered evidence of silylene intermediacy over silyl radicals.

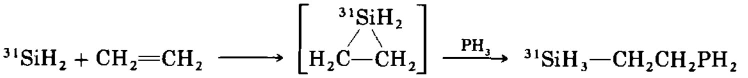
In recoil-atom experiments, disilane has been found to be five times more reactive than silane (*42*). Statistically, a reactivity ratio of 3:2 would be expected. Also, trisilane has been found to produce *n*-tetrasilane and *i*-tetrasilane in the ratio 4.4–5.2:1, much higher than the value expected on the basis of statistical considerations (*14*). These results seem to suggest the competing insertion of silylene into the Si—Si bonds in these reactions. However, the fact that Si—H bond strengths in different silanes vary would also result in a statistically unexpected ratio (*51*).

Measurements of the relative rates of insertion of $\mathrm{SiH_2}$ into M—H bonds (M = Si, Ge, P) have shown the reactivity to decrease in the following order (*89*):

$$\text{H—Si(CH}_3)_3 > \text{H—SiH}_2\text{SiH}_3 > \text{H—SiH(CH}_3)_2 > \text{H—SiH}_2\text{CH}_3 > \text{H—SiH}_3 > \text{H—GeH}_2\text{CH}_2\text{CH}_3$$

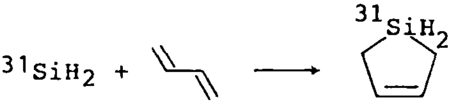
The sequence can be rationalized in terms of the partial negative charge on the target hydrogen atom. In view of this, it is not surprising that SiH_2 does not insert into P—H bonds (*89, 90*). The reluctance of SiH_2 to insert into C—H bonds is probably a related matter (*46, 47*).

The recoil-atom reaction with phosphine–ethylene mixture (*38*) produced a product identified as $^{31}SiH_3CH_2CH_2PH_2$. This finding was rationalized by a mechanism involving addition of silylene to the π-bond of ethylene:



$$^{31}\text{SiH}_2 + \text{CH}_2{=}\text{CH}_2 \longrightarrow \left[\begin{array}{c} ^{31}\text{SiH}_2 \\ \text{H}_2\text{C—CH}_2 \end{array}\right] \xrightarrow{\text{PH}_3} {}^{31}\text{SiH}_3\text{—CH}_2\text{CH}_2\text{PH}_2 \qquad (6)$$

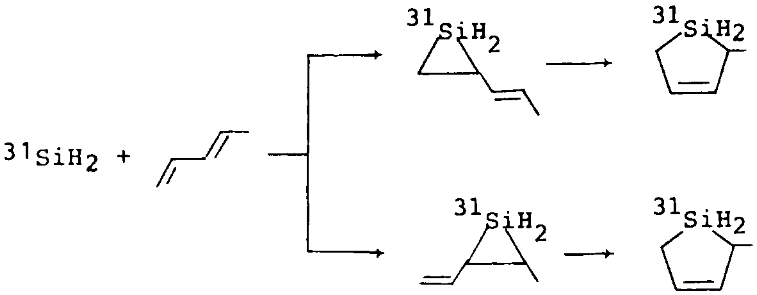
The best studied addition reactions of silylene have been those with conjugated dienes. Earlier studies using the nuclear recoil system have shown that $^{31}SiH_2$ added to 1,3-butadiene to give silacyclopent-3-ene (*44, 99, 100*).



(7)

Studies using NO as scavenger suggested that the reacting silylene was present as 80% triplet and 20% singlet (*118*). In the reactions with conjugated pentadienes the evaluated singlet to triplet ratio was 1:6 (*95*). This result contrasts very much with the result of the reaction of thermally generated silylene, which has a singlet spin state (*35, 79*).

The singlet silylene was proposed to add to the diene system via 1,2-addition, followed by rearrangement involving cleavage of a C—Si bond, by either a concerted or a diradical mechanism (*40*).



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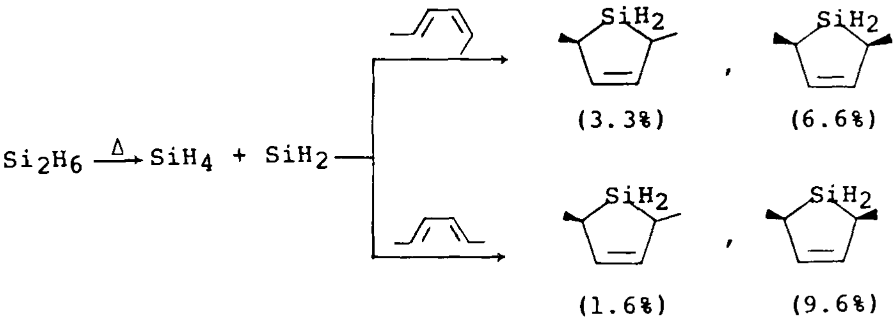
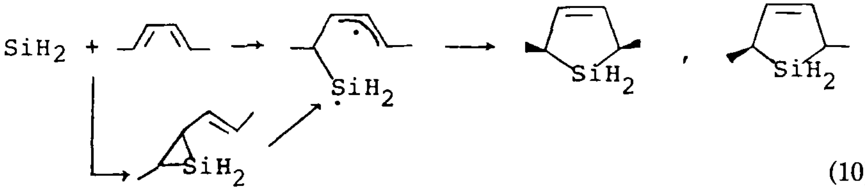
The reactions of SiH_2 with *cis,trans*- and *trans,trans*-2,4-hexadiene were studied in order to differentiate the mechanisms (*37, 40*).



(9)

The nonstereospecific addition was explained by a diradical process, for example, the reaction with *trans,trans*-2,4-hexadiene:



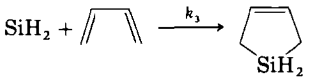
(10)

More recently, competition experiments have been undertaken with substrate mixture (*79*). Two systems have been chosen for studies of relative reactivities:

$$SiH_2 + SiH_3CH_3 \xrightarrow{k_1} SiH_3SiH_2CH_3$$
$$SiH_2 + SiH_4 \xrightarrow{k_2} SiH_3SiH_3$$

and

$$SiH_2 + SiH_4 \xrightarrow{k_2} SiH_3SiH_3$$



Both thermally generated and hot-atom generated silylene were employed in these studies. The results showed that within the temperature range 385–460°C, thermally generated SiH_2 gave a more or less constant k_1/k_2 ratio (~1.35–1.40), in good agreement with the reactivity ratio of 1.32 found in the recoil experiment (*41*). The value of k_2/k_3 for thermally generated SiH_2 was found to be 13 ± 4 at room temperature, which was also similar to the reactivity ratio 9 ± 1 obtained in the recoil experiment (*41*).

Thus quantitative agreement has been found between the relative reactivity of the intermediate from the high-energy silicon atoms in mixtures containing labile hydrogen and ground state singlet silylene. The earlier suggestion based on studies using radical scavengers that silylene reacts principally in a triplet electronic state must be considered a misinterpretation (*118*). The effect of scavengers could be on a species, initiated by silicon atoms, that appeared earlier in the reaction sequence, rather than on the formation of silylene intermediates.

III. Chemistry of Dichlorosilylene

The chemistry of dichlorosilylene can be studied by either gas-phase or cocondensation reactions (*17, 62, 103, 104*). In most cases, dichlorosilylene generated by pyrolysis of perchloropolysilanes was used in the gas-phase reactions whereas thermal reduction was used for cocondensation experiments.

As in the case of SiH_2 chemistry, dichlorosilylene has been found to undergo mainly two types of reactions, namely, insertions and additions according to the types of reaction products formed.

Dichlorosilylene inserts into a great number of compounds involving B—X (*101, 102*), C—H (*9, 10, 16, 18, 21, 22, 24, 32*), C—X (*10, 24, 26–28, 33, 34, 87*), Si—H (*119*), Si—X (*88*), and P—X (*101, 102*) and O—H (*10, 25*) bonds (X = halogen). For example,

$$SiCl_2 + BCl_3 \xrightarrow{-196°C} Cl_3SiBCl_2 \tag{11}$$

$$SiCl_2 + ArCH_3 \xrightarrow{450°-500°C} ArCH_2SiHCl_2 \tag{12}$$

where Ar = phenyl, *o*- and *p*-tolyl, *p*-biphenylyl, α- and β-naphthyl, 2- and 3-thienyl, etc.

$$SiCl_2 + CH_3Cl \longrightarrow CH_3SiCl_3 \tag{13}$$

$$SiCl_2 + SiCl_4 \longrightarrow Si_nCl_{2n+2} \qquad n = 2\text{–}6 \tag{14}$$

$$SiCl_2 + PCl_3 \xrightarrow{-196°C} Cl_3SiPCl_2 \tag{15}$$

Dichlorosilylene also inserts into halogens, hydrogen chloride, and the hydrogen molecule:

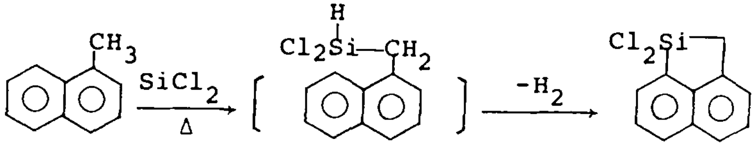
$$SiCl_2 + X_2 \xrightarrow{\Delta} X_2SiCl_2 \tag{16}$$

where X = Cl (*111*), Br, and I (*87*).

$$SiCl_2 + HCl \longrightarrow HSiCl_3 \quad (17)$$

$$SiCl_2 + H_2 \longrightarrow H_2SiCl_2 \quad (18)$$

It is particularly interesting to note that at elevated temperatures some of the products from $SiCl_2$ insertion into C—H and Si—H bonds would undergo hydrogen elimination on cyclization (*10, 24, 119*), for example, Eqs. (19) and (20).



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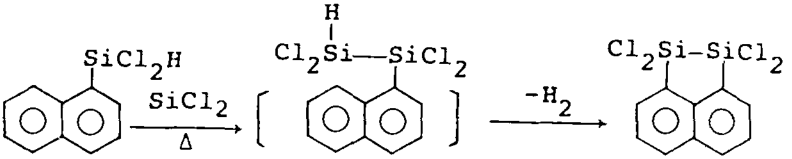
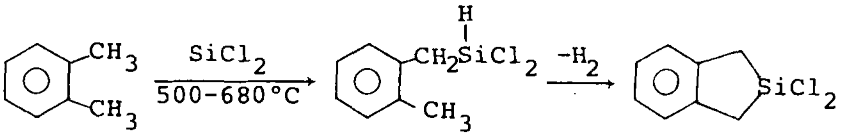


(20)

In cases where the cyclization process mentioned above produced strained rings, further $SiCl_2$ insertion into the rings was observed. This is best illustrated by comparing the two reactions shown [Eq. (21) vs. Eq. (22)] (*9, 18, 21, 22*):



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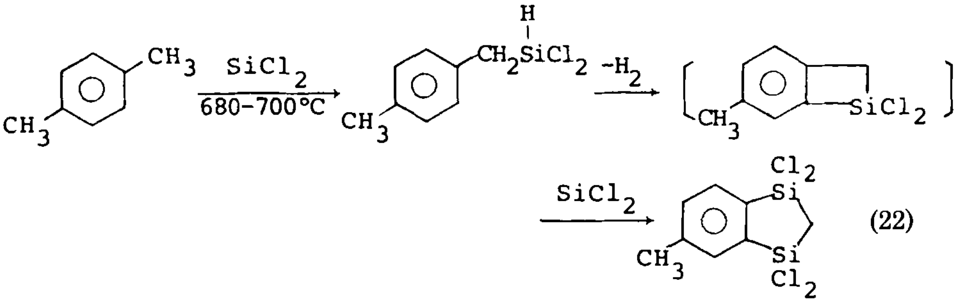
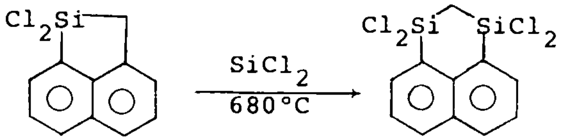


(22)

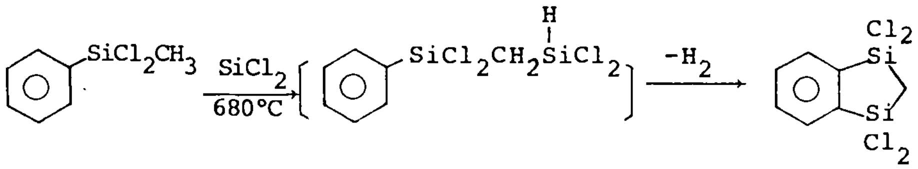
Further $SiCl_2$ insertion occurred in Eq. (22), but not in Eq. (21), presumably because the silacyclobutene intermediate is much more strained than silacyclopentene.

This is confirmed experimentally by the reaction in Eq. (23) (*9, 32*).



(23)

Gas-phase reactions have also shown that the α-C—H bond involving the α-carbon atom attached to the silicon atom is prone to $SiCl_2$ insertion reactions (*9, 22*) [e.g., Eqs. (24) and (25)].



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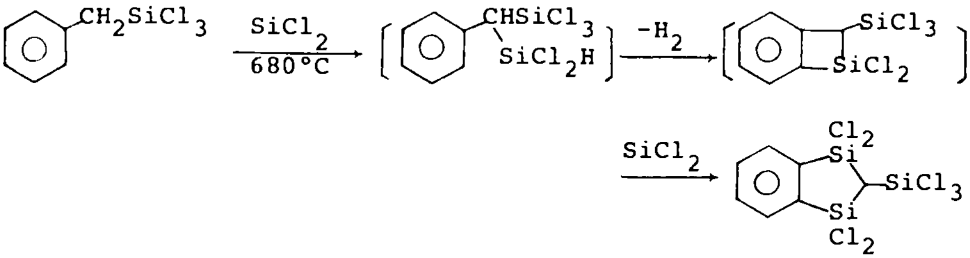
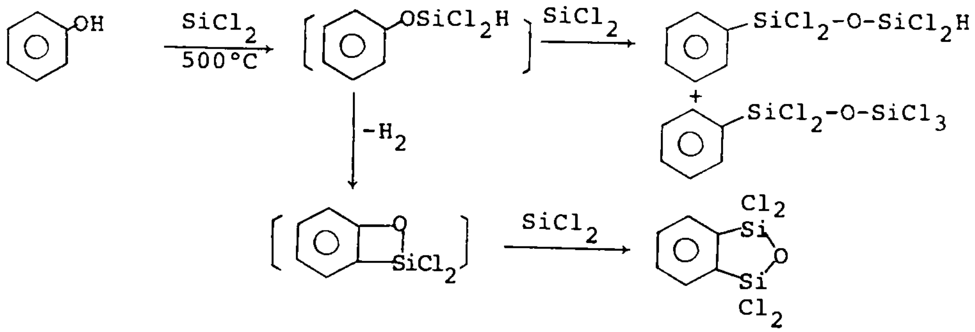


(25)

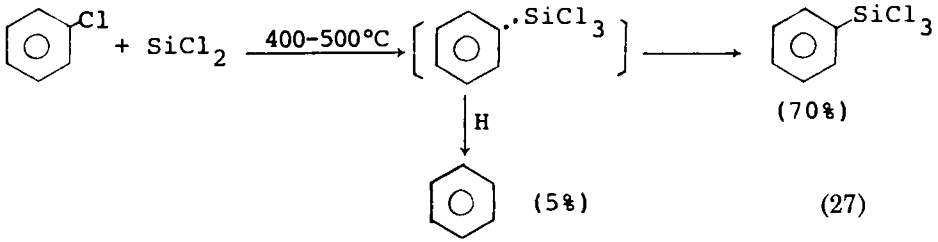
In the reaction with phenol [Eq. (26)], $SiCl_2$ insertions into both O—H and O—C bonds were observed. This is probably due to the unusually strong affinity of silylenes to the oxygen atom (*10, 25*).

Since data for the mechanistic details, such as the spin states and initial attacking site of the insertion of dichlorosilylene is lacking, inferences about the nature of the insertion reactions are at best a straightforward assumption based on the molecular structure of the final products. However, the insertion reactions of $SiCl_2$ into C—X bonds, which proceed through elimination–recombination steps, do resemble the chemistry of singlet carbenes (*59*). It seems reasonably safe



(26)

to state that $SiCl_2$ first extracts the halogen atom from the reactant to form a radical pair, which may either recombine to form the "insertion" product or separate to cause halogen elimination (*10, 24, 26–28*) [Eqs. (27)–(29)].



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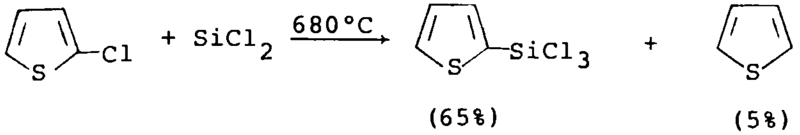


(28)

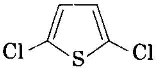
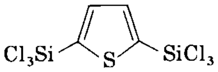
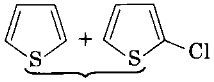
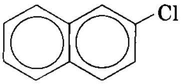
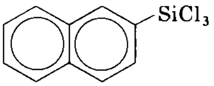
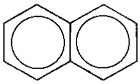
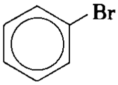
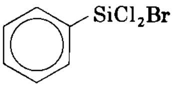
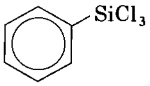
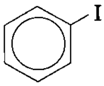
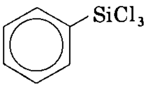
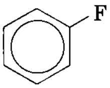
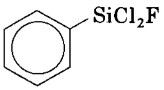
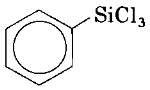
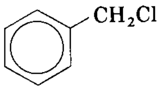
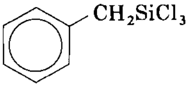
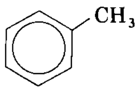
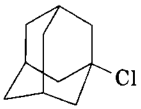
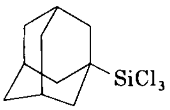
$$ClCH_2SiCl_3 + SiCl_2 \xrightarrow{580\,°C} \underset{(55\%)}{Cl_3SiCH_2SiCl_3} + \underset{(5\%)}{CH_3SiCl_3}$$

(29)

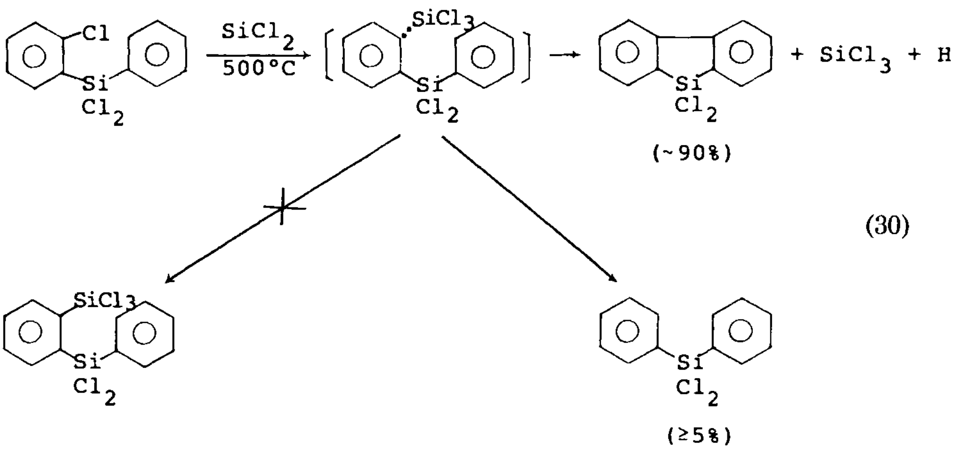
Other reactions with apparently similar mechanisms are summarized in Table I. In almost all cases, the observation of about 5% product from X-elimination/H-abstraction, though small in quantity, is a mechanistically important support to the proposal of radical pair intermediacy.

TABLE I

SOME INSERTION REACTIONS OF DICHLOROSILYLENE INTO C—X BONDS

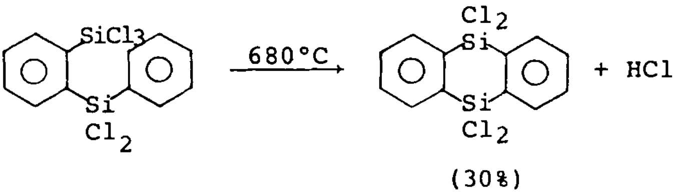
Reactant	Product	
		 (5%)
	 (55%)	 (5%)
	 (22%)	 (44%)
	 (40%)	
	 (15%)	 (20%)
	 (35%)	 (5%)
	 (60%)	

When the chlorine elimination pathway prevails, one observes mainly products from intramolecular cyclization (*10, 33, 34*). Although no inserted $SiCl_2$ group is involved in the products, the reaction mechanism [Eq. (30)] is related to the "insertion reactions" described above.



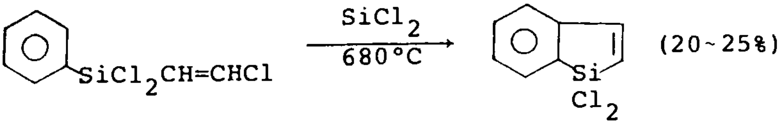
(30)

That the phenyldichlorosilylphenyl radical did not recombine with trichlorosilyl radical to form the insertion product was confirmed by the thermal decomposition reaction of *o*-trichlorosilylphenylphenyldichlorosilane, obtained by means of another preparation, which yielded a product via a different cyclization route [Eq. (31)].

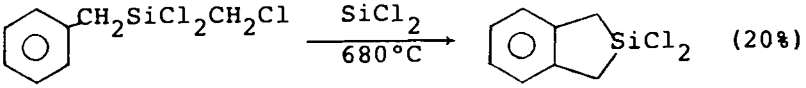


(31)

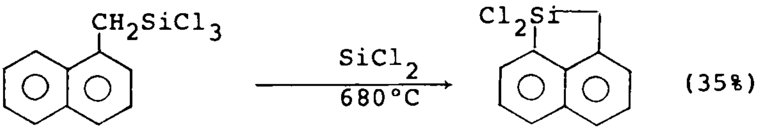
Other reactions of this type were observed with compounds involving C_{aryl}—Cl, $C_{alkenyl}$—Cl, C_{alk}—Cl, and Si—Cl bonds (*10, 24, 26–28, 33, 34, 87*):



(32)



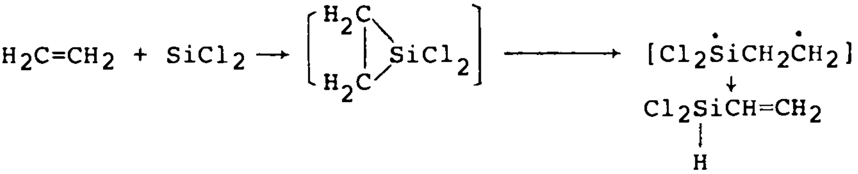
(33)



(34)

The addition reaction with an unsaturated compound is one of the most characteristic reactions of all silylenes. Alkenes and alkynes are the most popular trapping agents. As in the case of SiH_2, it has been generally believed that the primary step is the addition of dichlorosilylene to the double bond of the alkene or to the triple bond of the alkyne to form the silirane or silirene, respectively. The success in synthesizing derivatives of dimethylsilirane and dimethylsilirene has not only confirmed the initial step but made it possible to investigate the subsequent mechanistic details by studying the chemistry of such strained silacycles (*112*).

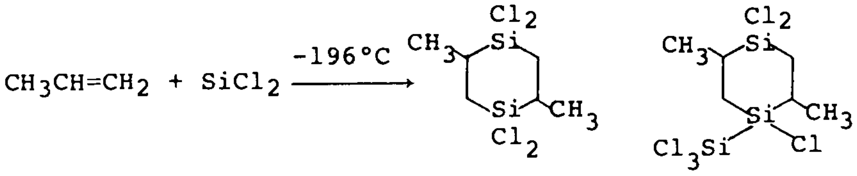
No stable dichlorosilirane has been prepared. The gas-phase reaction of $SiCl_2$ with ethylene is best explained by formation of dichlorosilirane, which opens up and rearranges to dichlorovinylsilane (*9, 30*).



(35)

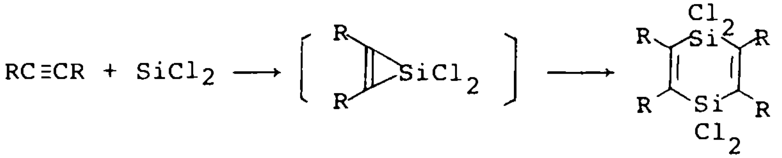
Other products of the reaction [including $Cl_3SiCH{=}CH_2$, $Cl_3SiC_2H_5$, $(H_2C{=}CH)Cl_2SiC_2H_5$, and $(C_2H_5)_2SiCl_2$] are believed to be the results of secondary reactions of the intermediates.

Under cocondensation conditions, propene was reported to react with dichlorosilylene to form tetrachloro-1,4-disilacyclohexane derivatives (*96, 103*).



(36)

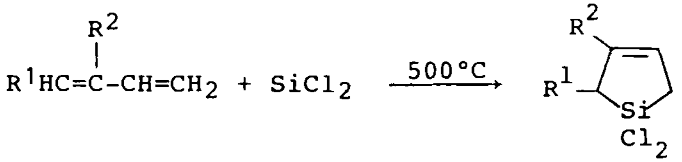
The gas-phase reactions of $SiCl_2$ with alkynes resulted in the formation of 1,4-disilacyclohex-2,5-dienes (*9, 16, 18, 23*) [Eq. (37)].


(37)

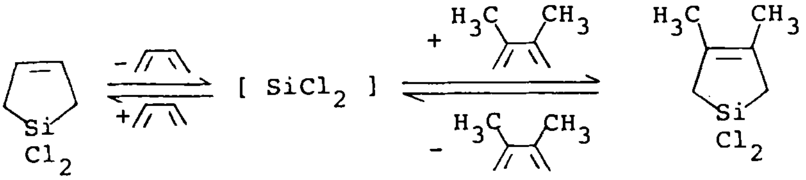
The reaction mechanism for dimerization of the silirene intermediate has been a controversial subject for many years (*3, 4, 7, 45, 49, 58, 86*). It is now generally accepted that in the case of dialkylsilylene, σ-dimerization is probably the true mechanism. Dichlorosilylene is expected to behave similarly.

The reaction of dichlorosilylene with acetylene carried out by a co-condensation experiment also yielded 1,4-disilacyclohexa-2,5-diene, but the result was regarded as unreliable (*103, 104*).

Studies on the gas-phase reactions of dichlorosilylene with conjugated dienes provided more systematic information about the addition reactions of dichlorosilylene (*1, 10, 15, 16, 20, 30, 91*):

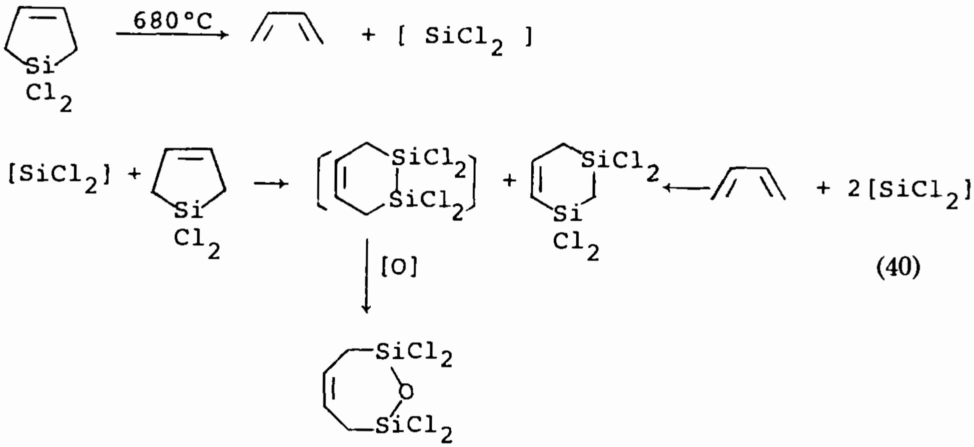

(38)

where R^1=H, CH_3; R^2=H, CH_3, Cl, C_6H_5. The reaction was found to be reversible, as the following reactions [Eq. (39)] were established experimentally:


(39)

The decomposition of dichlorosilacyclopent-3-ene has been proved to be unimolecular by the study of inert dilution. The mass spectral study suggested that the decomposition was concerted, and, in the opinion of the investigators, it corresponded formally to the retro Diels–Alder reaction (*13, 29*). Thus the reaction in Eq. (38) was believed to proceed via a concerted 1,4-cycloaddition.

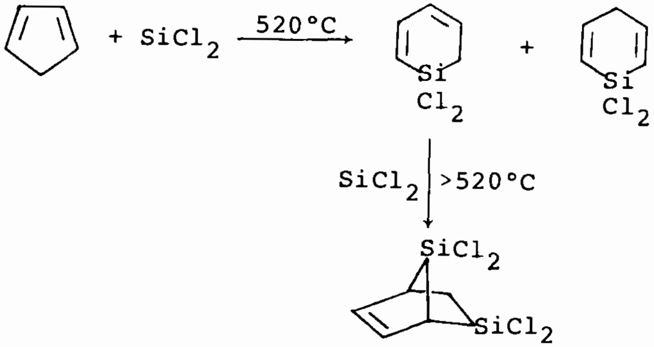
Above 500°C dichlorosilacyclopent-3-ene can be converted to disilacycles in the absence of trapping agent. The dichlorosilylene, formed by the retro-diene decomposition, was presumed to react with either the initial silacyclopentene or the intermediate diene (*29*) [Eq. (40)].



(40)

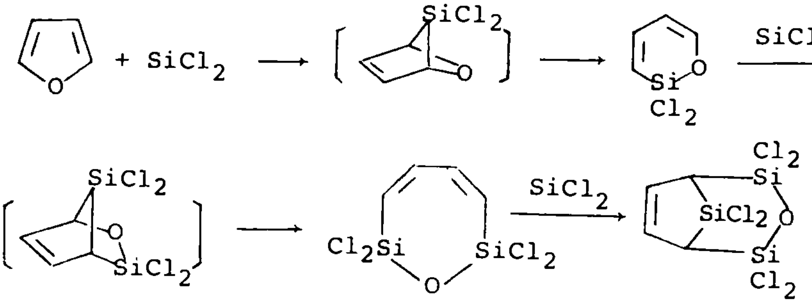
In view of the well-established silirane diradical mechanism in reactions of silylene [Eq. (10)] and dimethylsilylene (*40, 62*), and the involvement of difluorosilirane in the gas-phase reaction of difluorosilylene [Eq. (61), Section IV], it is somewhat surprising to find that dichlorosilylene alone should take a concerted 1,4-addition route toward butadiene. Further studies are needed to settle this argument.

The gas-phase reaction of dichlorosilylene with cyclopentadiene yielded silacyclohexadienes as the major products, one of which underwent further $SiCl_2$ insertion to form a bicyclic product (*31*).



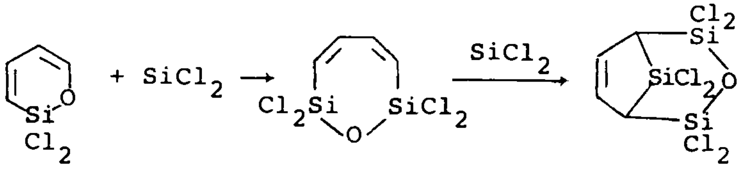
(41)

The reaction with furane apparently proceeded via a similar route (*9, 16, 20*). Here, because of the strong affinity of silicon for oxygen, consecutive 1,4-cycloaddition was proposed which was subjected to a subsequent ring expansion process:



(42)

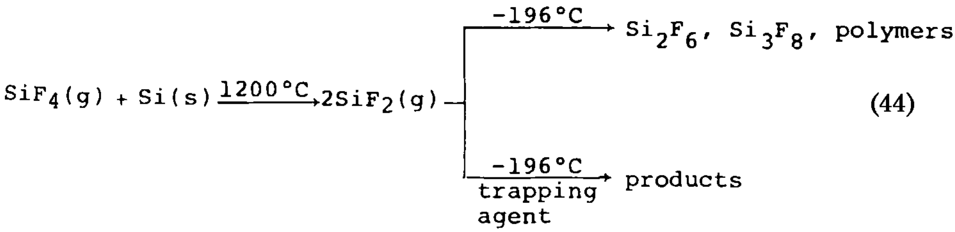
The instability of the two bicyclic intermediates involving oxa-heterocycle can be rationalized by the energetic advantage of Si—O—(Si) bond formation. The reaction mechanism is supported by the observation of the following reactions:



(43)

IV. Chemistry of Difluorosilylene

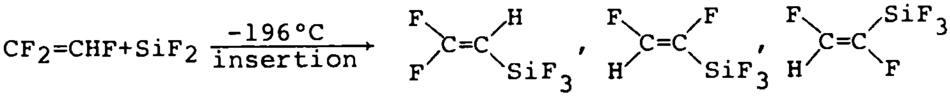
Difluorosilylene has always been considered the exceptional case of the silylene family. Unlike other silylenes, difluorosilylene had been believed to be quite inactive chemically in the gas phase (*73*). As a result, most studies of its chemistry were carried out under cocondensation conditions (*73, 103, 104, 106, 108*). At −196°C, difluorosilylene forms a pale yellowish condensate, which polymerizes and forms small quantities of volatile perfluoropolysilanes (10% of the total yield) when the reaction trap is warmed to room temperature.



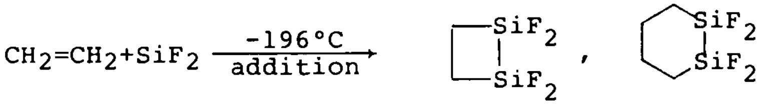
(44)

Earlier studies on the chemistry of difluorosilylene were focused on the reactions with nonmetal halides (*8, 72, 77, 105, 106, 109*) and unsaturated organic compounds (*65–69, 77*). [e.g., Eqs. (45)–(48)].

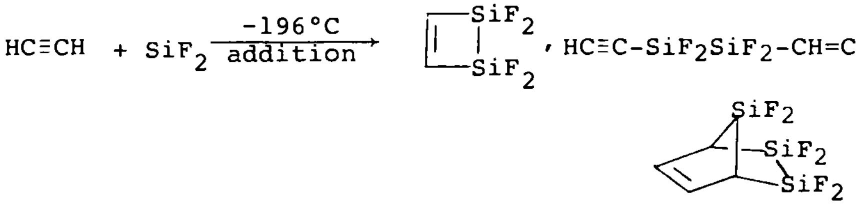
$$BF_3 + SiF_2 \xrightarrow[\text{insertion}]{-196\,°C} BF_2(SiF_2)_nF \qquad n = 1 \sim 3 \tag{45}$$



(46)

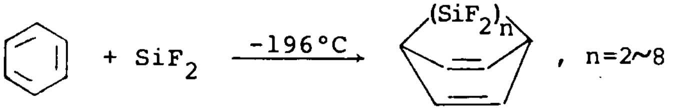


(47)

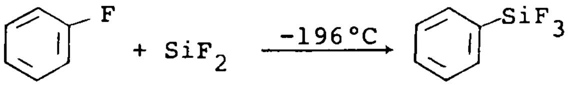


(48)

The reactions of difluorosilylene with olefins and fluoroolefins [e.g., Eqs. (46) and (47)] appear to proceed by quite different pathways. Similarly, the reaction with benzene resulted in addition products (*71, 107*) [Eq. (49)], whereas reaction with fluorobenzene led to insertion products (*107*) [Eq. (50)].



(49)



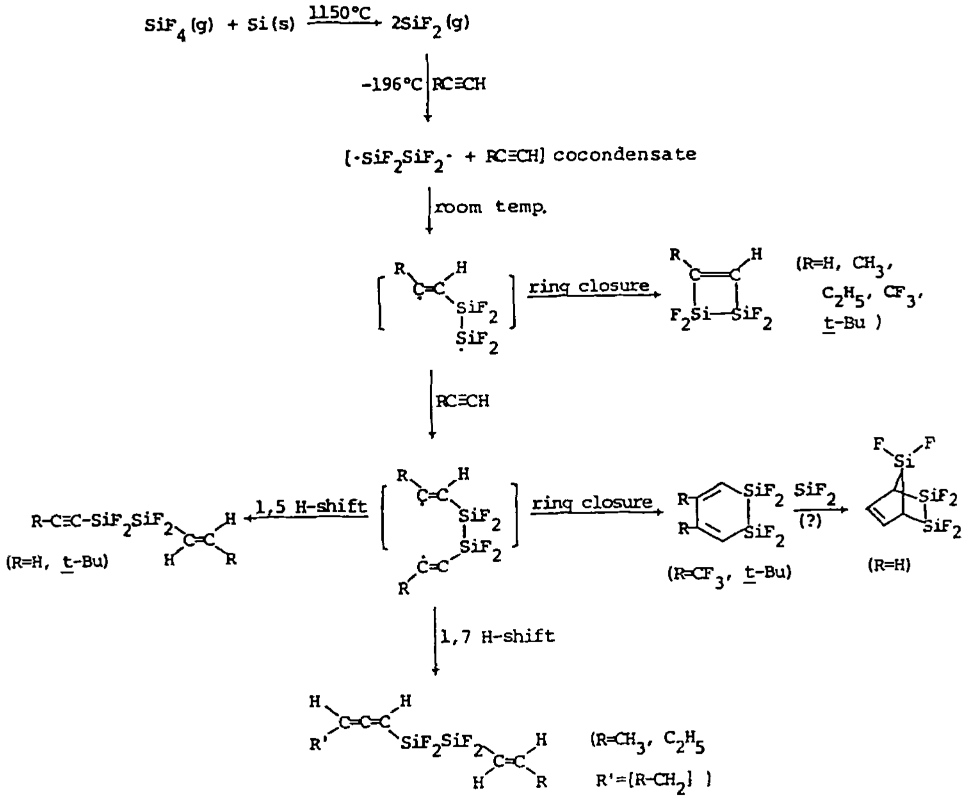
(50)

According to these earlier studies, a reaction mechanism involving diradical intermediates of the type $(SiF_2)_n$ (where $n = 1, 2, 3$, etc.) was established (*70, 73, 80*). This idea is particularly attractive if one considers the facts that in co-condensation reactions polymers are the major products obtained, and that volatile products of co-condensation reactions often contain $(SiF_2)_n$ units with $n > 1$. The earlier ESR study also supported this idea (*52*).

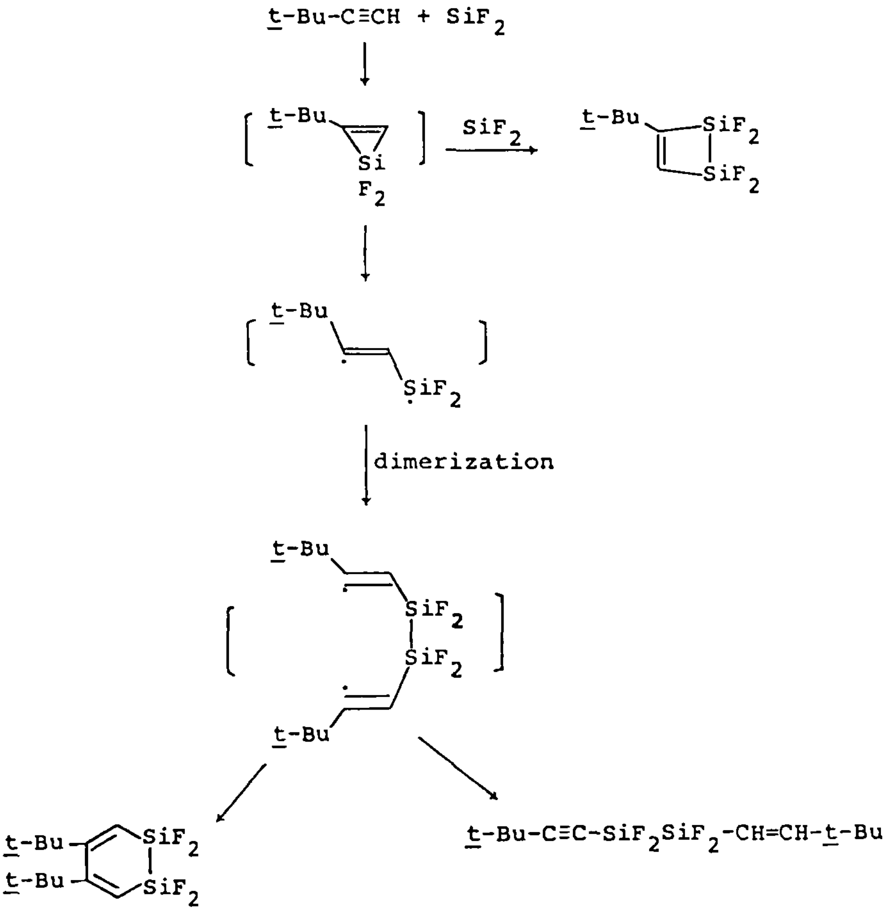
For addition reactions with unsaturated organic compounds, all the reaction products contained the —SiF_2SiF_2— moiety, which led to the conclusion that the most reactive species in these co-condensation reactions must be the $\cdot SiF_2SiF_2\cdot$ diradical (*65, 66*). The reaction mechanism for alkyne system is illustrated in Scheme 1.

When such an $(SiF_2)_n$ polymer (or oligomer) mechanism was cited in the literature, one could not but wonder whether difluorosilylene behaved as a "carbene analogue" at all. With considerable foresight, Gaspar and Herold stated more than a decade ago (*39*), "in view of the poor Si—Si π interaction and the relative weakness of Si—Si single bond, it is very likely that characteristic reactions of difluorosilylene other than polymerization will be found in the near future."

More recently, the synthesis and chemistry of 2,2,3,3-tetramethyl-1,1-difluoro-1-silirane, a long sought possible intermediate species of monomeric SiF_2 chemistry, suggested an alternative reaction mechanism for the addition reactions of SiF_2 with both alkenes and alkynes



SCHEME 1



Scheme 2

(*91*).[1] For example, the reaction with *t*-Bu—C≡CH is illustrated in Scheme 2.

It has been reported that the ^{29}Si NMR spectrum of the soluble part of the polymer, which accounted for 70% of the total products in the cocondensation reaction of SiF_2 and propene, was consistent with the structure $[{>}C(CH_3){-}CH_2SiF_2{-}]_n$. This is strong evidence supporting the silirane mechanism (*110*).

Both schemes explain the results of the "addition" reactions of SiF_2 with alkynes and alkenes well. However, neither of these two mecha-

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[1] Tetramethyl-1,1-difluoro-1-silirane is the only difluorosilirane ever prepared. Statements about the reactions of nonsubstituted difluorosilirane appear in refs. *48* and *113*.

nisms satisfactorily accounts for the details of the "insertion" reactions between SiF_2 and fluoroalkenes.

Three questions closely related to the reaction mechanism must be answered before any conclusion can be reached:

1. Why does SiF_2 "add" to alkenes but "insert" into the C—F bond of fluoroalkenes?
2. In the insertion reactions does SiF_2 attack the C—F bond directly, or does it attack the C=C double bond and then rearrange to the insertion products?
3. For both addition and insertion reactions, which one, the monomeric difluorosilylene or the diradicals $\cdot(SiF_2)_n\cdot$, is the true reaction intermediate?

Questions (1) and (2) above are actually the problem of addition vs. insertion. When the reactions of SiF_2 with *trans*- and *cis*-CHF=CHF were carried out under co-condensation conditions *(64)*, all products were found to be insertion products, with no silacyclopropanes or disilacyclobutanes being observed [Eqs. (51) and (52)]. The most interesting result is the fact that both reactions appear to be nonstereospecific. The relative abundances of the various isomers of the insertion products are shown in Table II.

TABLE II

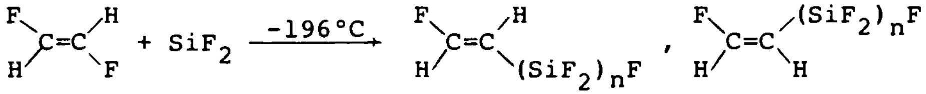
RELATIVE YIELDS OF THE VOLATILE PRODUCTS OF THE REACTIONS WITH *trans*- AND *cis*-CHF=CHF IN VARIOUS CONDITIONS

	Relative yield[a] (%)					
	Cocondensation		Alternate layer		Gas phase	
Reaction product	cis[b]	trans[c]	cis[b]	trans[c]	cis[b]	trans[c]
trans-CHF=CHSiF_3	5	16	6	18	64	64
	(77)	(62)	(78)	(64)		
cis-CHF=CHSiF_3	17	10	21	10	36	36
trans-CHF=CHSiF_2SiF_3	6	57	8	43		
	(88)	(85)	(86)	(77)		
cis-CHF=CHSiF_2SiF_3	44	10	51	13		
trans-CHF=CH$SiF_2SiF_2SiF_3$	2	6	2	13		
	(93)	(86)	(86)	(81)		
cis-CHF=CH$SiF_2SiF_2SiF_3$	26	1	12	3		

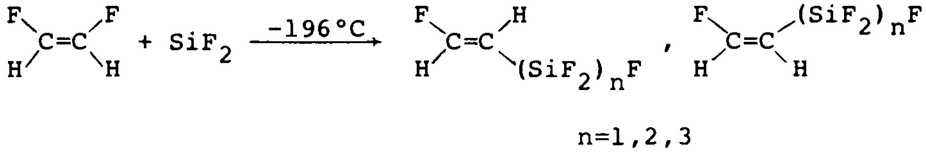
[a] Numbers in parentheses are the percentage of configuration retention.

[b] cis, Reaction with *cis*-CHF=CHF.

[c] trans, Reaction with *trans*-CHF=CHF.



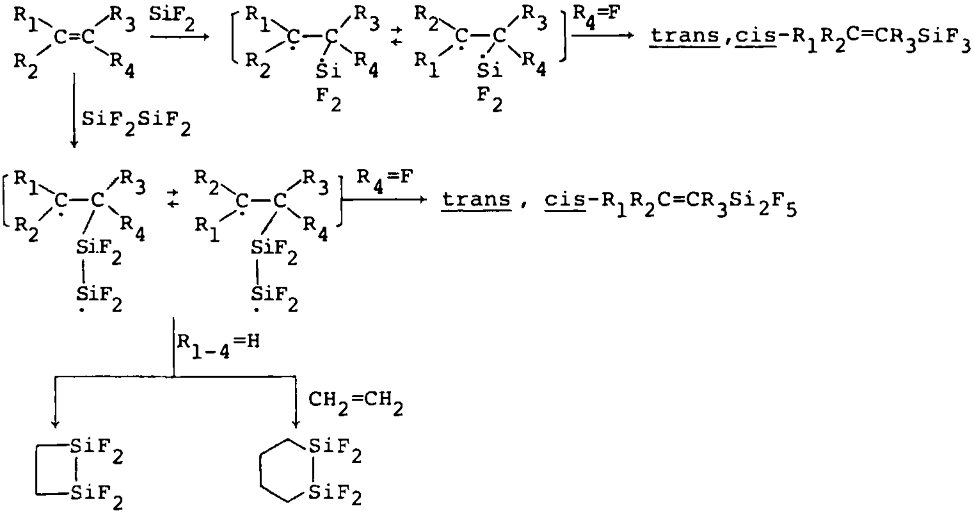
(51)



(52)

Since no trans–cis isomerization of the starting materials was observed, the only reasonable reaction path which leads to both trans and cis isomers of the product of each reaction is an initial attack of $(SiF_2)_n$ on the carbon–carbon double bond, followed by rearrangement. The higher ratio of configuration retention for the reaction of *cis*-difluoroethylene agrees with the known fact that *cis*-CHF=CHF is more stable than its trans isomer (*12*).

This type of reaction pattern can be extended to $(SiF_2)_3$ or even higher units. In fact, both addition and insertion products involving trimeric SiF_2 units are known (*77, 105, 107, 109*). In this reaction scheme (Scheme 3) both insertion and addition reactions can be rationalized



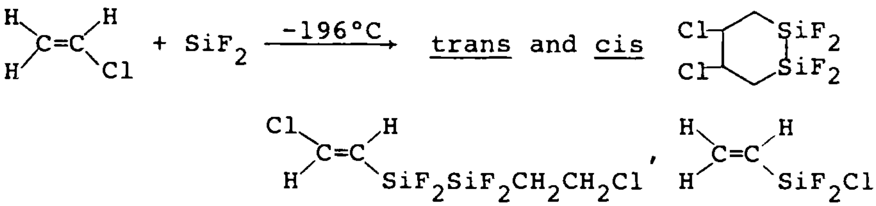
Scheme 3

with the same initial attack of $(SiF_2)_n$ on the double bond, monomeric SiF_2 being no exception. Fluorine atoms cause the different preferences in reaction paths after the initial attack.

The bond energies decrease in the order Si—F > C—F > C—H > Si—H (Table III). The formation of an exceedingly strong Si—F bond in the insertion reactions must have contributed to the driving force of insertion whenever a fluorine is attached to an olefinic carbon.

Since the difference in bond energies between Si—X and C—X decreases with increasing halogen atomic weight (Table III), somewhere along the line one should expect to observe both insertion and addition products from the same reaction, which would reflect the competitive preference of insertion vs. addition after the initial attack of the oligomeric difluorosilylene.

The co-condensation reaction of SiF_2 with vinyl chloride produced, in addition to the addition products, a small quantity of insertion product. However, here the results mainly reflect the very large difference in the preference of initial radical attack on the two sides of the double bond (*63*).



(53)

The true competitive preference of insertion vs. addition is shown in the cocondensation reactions of SiF_2 with *cis*- and *trans*-CHCl═CHCl.

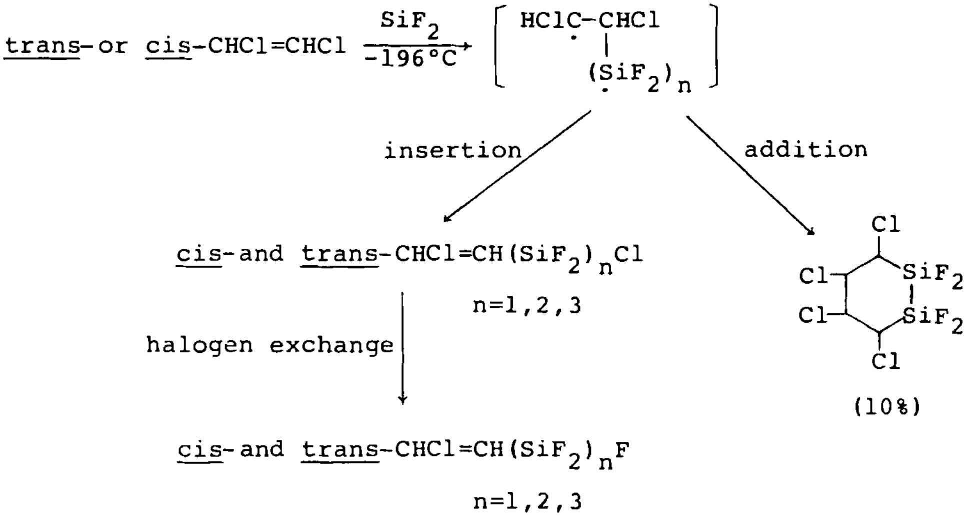
TABLE III

BOND ENERGIES[a] OF Si—X AND C—X

X	Si—X(kcal/mol)	C—X(kcal/mol)	Δ(kcal/mol)[b]
F	135	116	19
Cl	91	78.2	12.8
Br	74	68	6
I	56	51	5
H	76	98.3	−22.3

[a] Data taken from ref. *54*.

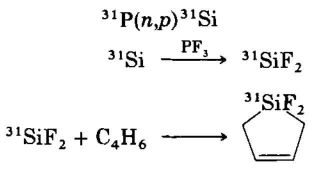
[b] $\Delta = (\text{Bond energy})_{Si—X} - (\text{bond energy})_{C—X}$



SCHEME 4

Indeed both insertion and addition products were obtained (*56b*). The reactions are best interpreted by the mechanism shown in Scheme 4.

Although a number of cocondensation reactions (SiF_2/H_2O, SiF_2/H_2S, SiF_2/C_6F_6, etc.) (*73, 103*) yielded products containing only one SiF_2 unit, monomeric SiF_2 in the gas phase has for many years been considered not reactive. One exception is the study of the reaction of ethylene and conjugated dienes with $^{31}SiF_2$ formed in nuclear recoil systems (*95, 117*). The $^{31}SiF_2$ molecules generated in such system may possess different properties from those generated thermally, and the reaction conditions are very different; nevertheless, the work does show that monomeric $^{31}SiF_2$ in the gas phase is reactive toward unsaturated organic compounds.

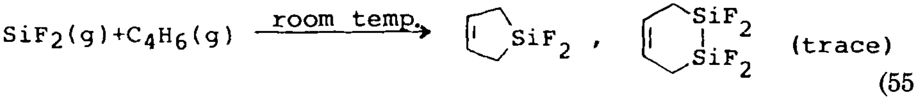


(54)

The singlet to triplet $^{31}SiF_2$ ratios evaluated from these diene systems are all around 1:3. It was proposed that triplet $^{31}SiF_2$ formed $^{31}SiF_2$-donor complexes with paramagnetic molecules such as NO, NO_2, or O_2 before reacting with dienes.

Since a study on the competitive reactions of $^{31}SiH_2$ with silane, methylsilane, and butadiene has rejected the possibility of triplet involvement (*41*), the role of triplet $^{31}SiF_2$ in the present case will have to be subjected to further confirmation.

More recently, it has been found that under proper conditions thermally generated SiF_2 also reacted in reasonably good yield with 1,3-butadiene, *cis*- and *trans*-difluoroethylenes, vinyl chloride, vinyl fluoride, and propene in the gas phase [Eqs. (55)–(59)].



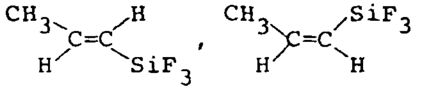
(55)

$$SiF_2(g) + \underline{cis} \text{ or } \underline{trans}\ CHF{=}CHF(g) \xrightarrow{\text{room temp.}} \underline{cis}\text{- and } \underline{trans}\text{-}CHF{=}CHSiF_3 \qquad (56)$$

$$SiF_2(g) + CH_2{=}CHCl(g) \xrightarrow{\text{room temp.}} CH_2{=}CHSiF_3,\ CH_2{=}CHSiF_2Cl,\ CH_2{=}CHSiFCl_2 \qquad (57)$$

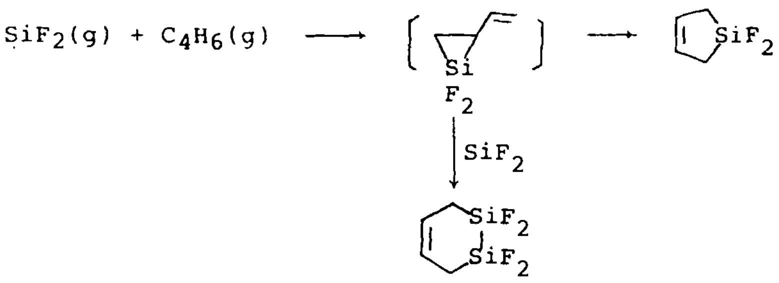
$$SiF_2(g) + CH_2{=}CHF(g) \xrightarrow{\text{room temp.}} CH_2{=}CHSiF_3 \qquad (58)$$

$$SiF_2(g) + CH_3\text{-}CH{=}CH_2(g) \xrightarrow{\text{room temp.}} CH_2{=}CHCH_2SiF_3,\ (CH_3)_2CHSiF_3,$$



(59)

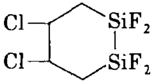
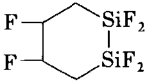
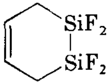
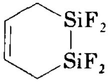
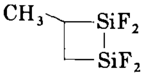
Except the trace amount of 1,2-disilacyclohex-4-ene obtained in the reaction of butadiene, all products in the gas phase consist of only one SiF_2 unit. The formation of 1,2-disilacyclohex-4-ene could be the result of further reaction of the silirane intermediate with SiF_2 (*55*) (Scheme 5).

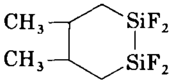
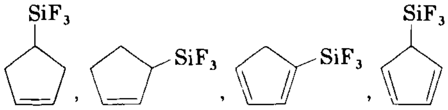
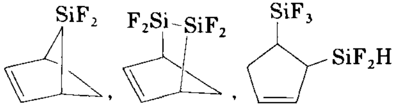
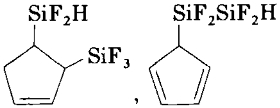
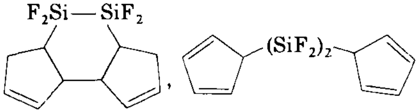
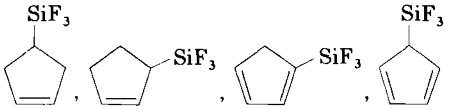
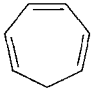
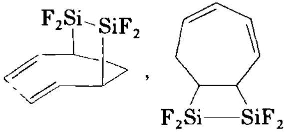
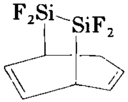
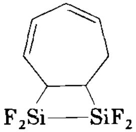


SCHEME 5

TABLE IV

PRODUCTS FROM THE DIFLUOROSILYLENE REACTIONS UNDER VARIOUS EXPERIMENTAL CONDITIONS

Reaction	Experimental conditions Cocontensation	 Gas phase
trans-CHF=CHF	*trans*- and *cis*-$CHF{=}CHSiF_3$ *trans*- and *cis*-$CHF{=}CHSiF_2SiF_3$ *trans*- and *cis*-$CHF{=}CHSiF_2SiF_2SiF_3$	*trans*- and *cis*-$CHF{=}CHSiF_3$
$CH_2{=}CHCl$	$CH_2{=}CHSiClF_2$ (trace) $CHCl{=}CHSiF_2SiF_2CH_2CH_2Cl$ *trans*- and *cis*- 	$CH_2{=}CHSiClF_2$ $CH_2{=}CHSiCl_2F$ $CH_2{=}CHSiF_3$
$CH_2{=}CHF$	$CH_2{=}CHSiF_3$ $CH_2{=}CHSiF_2SiF_3$ *trans*- and *cis*-  $(CH_2{=}CH)_2SiF_2$	$CH_2{=}CHSiF_3$
$CH_2{=}CH{-}CH{=}CH_2$	 $CH_2{=}CHCH{=}CHSiF_2SiF_2CH_2CH_2CH{=}CH_2$  (trace)	  (trace)
$CH_3CH{=}CH_2$		$(CH_3)_2CHSiF_3$ $CH_2{=}CHCH_2SiF_3$

	trans- and cis-  $CH_2{=}CHCH_2SiF_2SiF_2CH_2CH_2CH_3$ $CH_2{=}CHCH_2SiF_3$ $CH_3CH_2CH_2SiF_3$	*trans*- and *cis*-$CH_3CH{=}CHSiF_3$
	   	
	  (trace)	

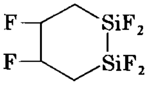
A comparison of the products from cocondensation and gas-phase experiments of each reaction is shown in Table IV. It is interesting to note that the ratio of relative yield of *trans*-$CHF{=}CHSiF_3$ to *cis*-$CHF{=}CHSiF_3$ is constant (64:36) in both reactions of *trans*- and *cis*-$CHF{=}CHF$ carried out in the gas phase, which is in sharp contrast to the results of co-condensation reactions (Table II). This is rationalized by the fact that under the experimental conditions of the gas-phase reactions the reaction product $CHF{=}CHSiF_3$, when initially formed in the gas phase, would carry approximately 95 kcal/mol of energy, which is much more than the activation energy of cis/trans isomerization of various substituted ethylenes (50–60 kcal/mol) (*11*); therefore the constant ratio of trans/cis products actually reflects the thermodynamic distribution according to the energies of the products, namely *trans*- and *cis*-$CHF{=}CHSiF_3$.

When the cocondensation reactions are carried out at −196°C, the kinetic competition of the radical species among various reaction pathways becomes a controlling factor. It is therefore quite reasonable to observe the various relative yields of trans and cis products in these cocondensation reactions (Table II).

The reaction of difluorosilylene with vinyl fluoride in the gas phase gives apparently only one product in good yield, $CH_2{=}CHSiF_3$ (*56a*). The reaction under cocondensation conditions produced $CH_2{=}CHSiF_3$, $CH_2{=}CHSiF_2SiF_3$, 4,5-difluoro-1,1,2,2-tetrafluoro-1,2-disilacyclohexane (**1**) and divinyldifluorosilane (**2**). The relative yields of $CH_2{=}CHSiF_3$, $CH_2{=}CHSiF_2SiF_3$, (**2**), and (**1**) are 18:23:35:24 (Table V).

TABLE V

RELATIVE YIELDS OF VOLATILE PRODUCTS OF THE REACTION OF DIFLUOROSILYLENE WITH VINYL FLUORIDE IN VARIOUS CONDITIONS

	Reactive yield (%)				
	Cocondensation		Alternate layer		
Reaction product	*a*	*b*	*a*	*b*	Gas phase
$CH_2{=}CHSiF_3$	18	57	20	55	100
$CH_2{=}CHSiF_2SiF_3$	23	5	25	6	
$(CH_2{=}CH)_2SiF_2$	35	28	36	30	
	24	10	19	9	

[a] Volatile products from reactions under various conditions.

[b] Products from pyrolysis (at 100°C) of the polymers obtained under various reaction conditions.

One may suspect that vinyltrifluorosilane, which was the major product in the gas-phase reaction (Table IV), might have come from the gas-phase reaction prior to condensation. To clarify this point, the co-condensation experiment was carried out in an "alternate layer" manner so that no gas mixing was allowed. The results are summarized in Table II and Table V.

The products of the alternate layer reactions between $\mathrm{SiF_2}$ and *trans*-$\mathrm{CHF{=}CHF}$, $\mathrm{CH_2{=}CHCl}$, $\mathrm{CH_2{=}CHF}$, and $\mathrm{C_4H_6}$ are found to be the same as those in the corresponding cocondensation experiments; only the absolute yields are substantially reduced due to poor mixing of the reagents in such alternate layer experiments. The most important observation is that the relative yields of the products do not differ significantly from those of the cocondensation experiments. For example, a carefully controlled "alternate layer" reaction was studied quantitatively for the reaction of $\mathrm{CH_2{=}CHF}$. The relative yields of $\mathrm{CH_2{=}CHSiF_3}$, $\mathrm{CH_2{=}CHSiF_2SiF_3}$, (**2**), and (**1**) were found to be 20:25:36:19, very close to those in the co-condensation experiment. These results indicate that the formation of $\mathrm{CH_2{=}CHSiF_3}$ in the gas phase prior to condensation contributes negligibly to the yield of $\mathrm{CH_2{=}CHSiF_3}$ in the co-condensation experiment, and the reaction taking place at -196°C did involve monomeric $\mathrm{SiF_2}$.

The polymer formed in the reaction of $\mathrm{CH_2{=}CHF}$ decomposes under mild conditions. When the yellowish polymer was pyrolyzed, the products include $\mathrm{SiF_4}$, $\mathrm{Si_2F_6}$, $\mathrm{Si_3F_8}$, $\mathrm{CH_2{=}CHSiF_3}$, $\mathrm{CH_2{=}CHSiF_2SiF_3}$, $\mathrm{(CH_2{=}CH)_2SiF_2}$, and (**1**). The relative yield of the last four compounds was found to be 57:5:28:10 (Table V).

For comparison, the polymer obtained in the alternate layer condensation experiment was also subjected to pyrolysis. The same products were obtained in much poorer total yield, but the ratio of relative yield of $\mathrm{CH_2{=}CHSiF_3}$, $\mathrm{CH_2{=}CHSiF_2SiF_3}$, $\mathrm{(CH_2{=}CH)_2SiF_2}$, and (**1**) was found to be 55:6:30:9, almost the same as that of the co-condensation experiment (Table V).

The observation of $\mathrm{CH_2{=}CHSiF_2SiF_3}$ from pyrolysis of the polymer, though in relatively small quantity, strongly suggests that $\mathrm{({-}CH_2{-}CHF{-}SiF_2SiF_2{-})}$ units are involved in the polymer.

There remains an ambiguity about the formation of $\mathrm{CH_2{=}CHSiF_2SiF_3}$ [and also $\mathrm{CHF{=}CH(SiF_2)_{\mathit{n}}F}$, $n = 2, 3$, in the reactions of *trans*- and *cis*-$\mathrm{CHF{=}CHF}$]. Two possible reaction pathways could be considered:

$$\text{(i)}\quad \mathrm{CH_2{=}CHF} \xrightarrow{\mathrm{SiF_2}} \mathrm{CH_2{=}CHSiF_3} \xrightarrow{\mathrm{SiF_2}} \mathrm{CH_2{=}CHSiF_2SiF_3}$$

$$\text{(ii)}\quad \mathrm{CH_2{=}CHF} \xrightarrow{\mathrm{SiF_2}} [\dot{\mathrm{C}}\mathrm{H_2{-}CHF{-}}\dot{\mathrm{S}}\mathrm{iF_2}] \xrightarrow{\mathrm{SiF_2}} [\dot{\mathrm{C}}\mathrm{H_2{-}CHF{-}SiF_2}\dot{\mathrm{S}}\mathrm{iF_2}]$$

$$\longrightarrow \mathrm{CH_2{=}CHSiF_2SiF_3}$$

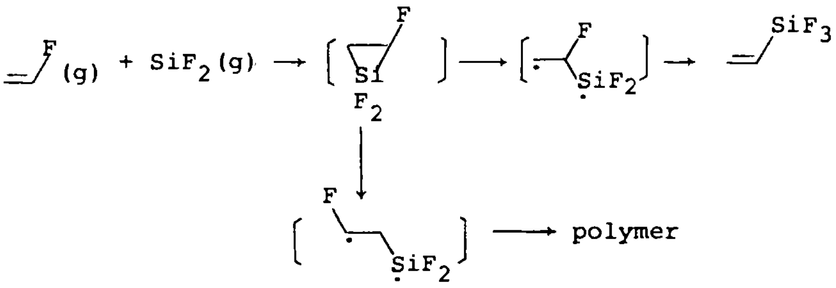
Path (i) is ruled out because in both gas-phase and co-condensation experiments no further insertion of SiF_2 was observed when pure $CH_2{=}CHSiF_3$ and SiF_2 were mixed. Path (ii) was not favored because the ratio of configurational retention of the products $CHF{=}CH(SiF_2)_nF$ in the reactions of *trans*- and *cis*-$CHF{=}CHF$ increases with n, the number of SiF_2 units involved in the products; for example, in the reaction of *trans*-$CHF{=}CHF$, 62% for $n = 1$, 85% for $n = 2$, and 86% for $n = 3$ (Table II). If reactions occurred according to (ii), one would expect the order of the retention ratio to be reversed.

On the other hand, if the products $CHF{=}CH(SiF_2)_nF$ are formed through direct attack at the carbon–carbon double bond by $\cdot(SiF_2)_n\cdot$ diradicals, the intermediates $\dot{C}HF{-}CH(\dot{S}iF_2)_nF$ find a facile path for F migration via either a four-centered (for $n = 2$) or five-centered (for $n = 3$) transition state.

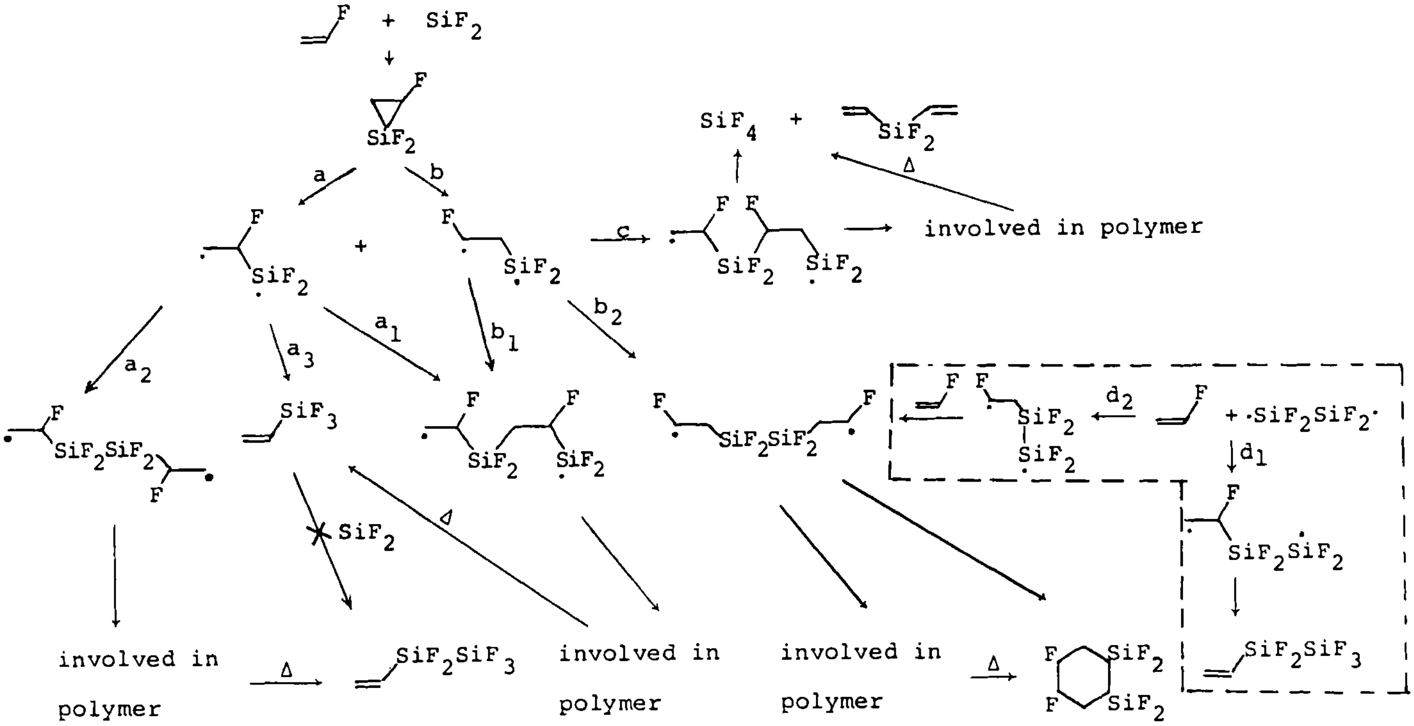
$$\begin{aligned} SiF_2 + CHF{=}CHF &\xrightarrow{-196^\circ C} [\cdot(SiF_2)_n\cdot + CHF{=}CHF] \\ &\longrightarrow CHF{=}CH(SiF_2)_nF \qquad n = 2, 3 \end{aligned} \tag{60}$$

Having clarified the points mentioned above, it seems possible now to draw some conclusions about the reaction mechanism. The reactions of SiF_2 in the gas phase seem rather simple. Difluorosilylene behaves quite similarly to the chemistry of other silylenes. The initial attack of SiF_2 at the carbon–carbon double bond is followed by rearrangement whenever possible. Otherwise it may lead to polymerization. For example, $CH_2{=}CHF$ reacts according to the mechanisms in Scheme 6.

The reactions in cocondensation conditions are much more complicated. If silirane does exist as an intermediate, for example, in the case of $CH_2{=}CHF$, the pathway shown in Scheme 7 can be proposed. Paths a and b (Scheme 7) are the two ways of cleavage of the silirane. Path a_3 results in the product $CH_2{=}CHSiF_3$. Paths a_1, a_2 and b_1, b_2 lead to all possible dimerizations of the diradicals from ring opening,



SCHEME 6

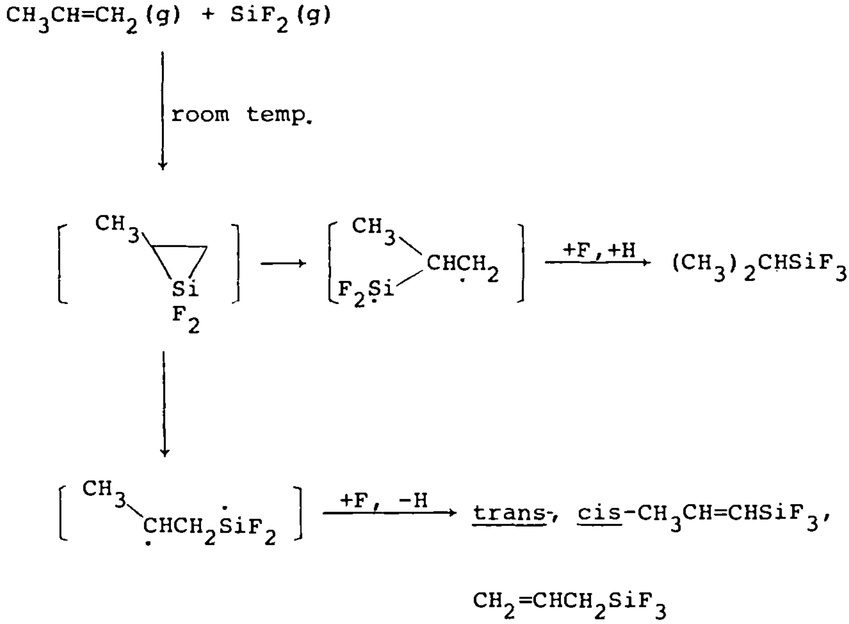


F
+ SiF2
SiF2
a
b
c
Δ
SiF4
+
involved in polymer
a1
a2
a3
b1
b2
d1
d2
SiF3
SiF2SiF2
SiF2SiF3
+ ·SiF2SiF2·
involved in polymer
involved in polymer
involved in polymer
involved in polymer

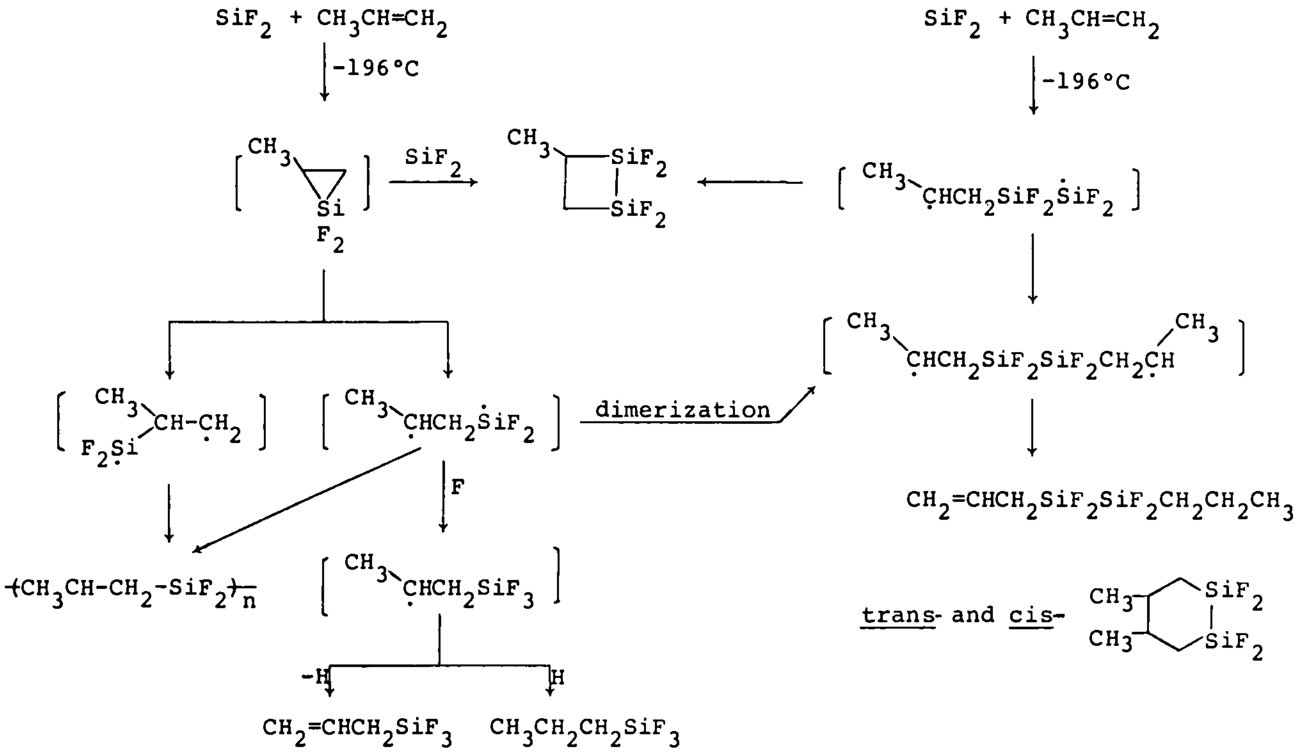
Scheme 7

respectively, which are in turn involved in polymerization. In the case of b_2, ring closure may lead to the product disilacyclohexane. All other products from pyrolysis of the polymers are verified experimentally. Path c represents the other possible pathway, the link of the two different radicals from ring opening of the silirane. This path leads to the formation of $(CH_2{=}CH)_2SiF_2$. Although it seems conceivable to obtain $CH_2{=}CHSiF_2SiF_3$ from the polymer pyrolysis, the observation of this compound in the cocondensation reaction cannot be explained without raising more skeptical assumptions in this reaction scheme based solely on the silirane intermediate. On the other hand, if the $\cdot SiF_2SiF_2\cdot$ diradical is involved, the formation of $CH_2{=}CHSiF_2SiF_3$ becomes straightforward. While the extent each mechanism contributes may vary from reaction to reaction, one tends to conclude that both are generally involved in the cocondensation experiments.

This is true not only for halogen-substituted ethylenes. The reactions of alkyl-substituted ethylenes (*82, 83, 93*) seem to follow the same reaction mechanisms. The products from the reaction of propene under various reaction conditions are summarized in Table IV. The overall picture of the reaction is illustrated in Schemes 8 and 9 (*93*). These reaction mechanisms seem to be generally applicable. Studies on the reactions with cyclic olefins could serve as a further evidence (*61, 78*).



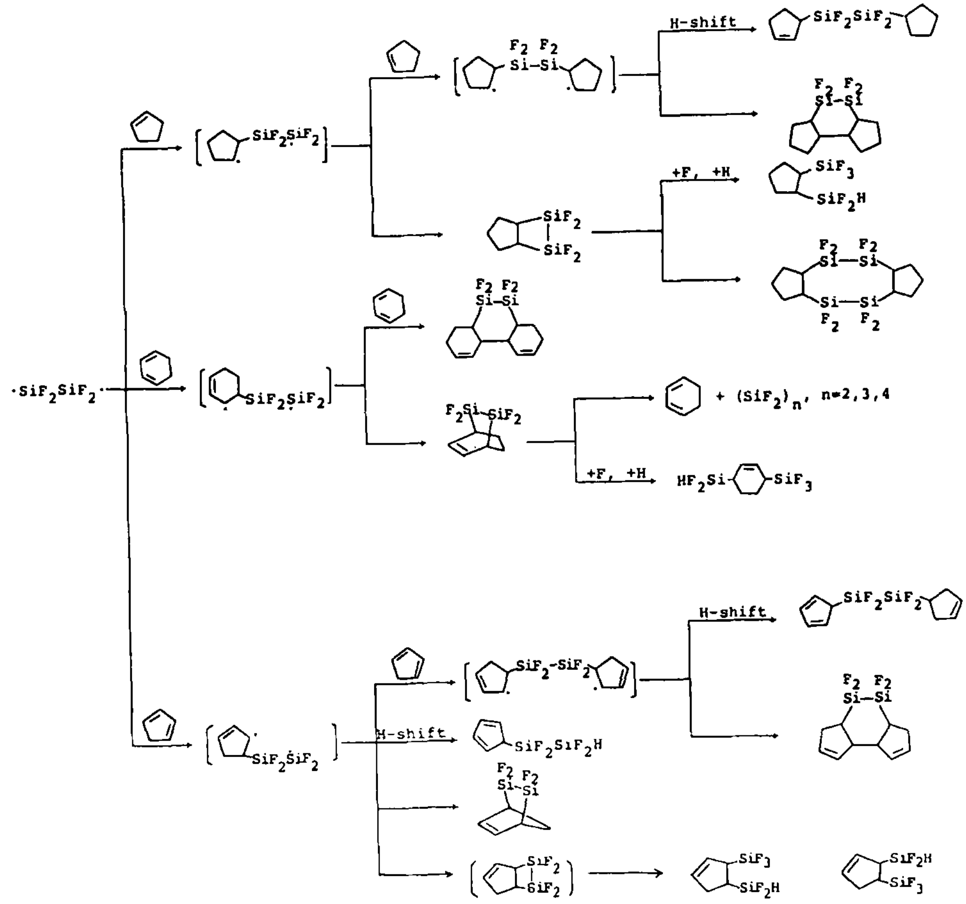
SCHEME 8


SiF2 + CH3CH=CH2
-196°C
SiF2
CH3CH-CH2-SiF2 n
F
dimerization
-H
H
CH2=CHCH2SiF3
CH3CH2CH2SiF3
CH2=CHCH2SiF2SiF2CH2CH2CH3
trans- and cis-

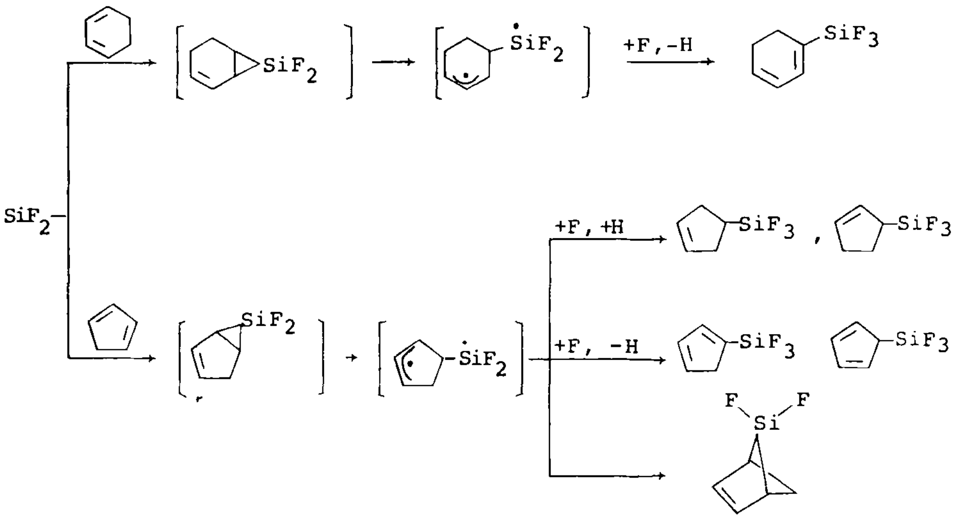
SCHEME 9

The cocondensation reactions with cyclopentene, cyclohexa-1,3-diene, and cyclopentadiene give structurally interesting products which are shown in Schemes 10 and 11 (*61, 78*). Since products involving both SiF_2 and $—SiF_2SiF_2—$ are obtained, it is quite possible that both silirane and $\cdot SiF_2SiF_2\cdot$ mechanisms are involved. For the latter mechanism, Scheme 10 summarizes the three reactions involved. Scheme 11 illustrates the reactions involving monomeric SiF_2.

The gas-phase reaction of cyclopentadiene gives the same products involving monomeric SiF_2 units (Table IV). These are the products from genuine difluorosilylene reactions, quite parallel to the chemistry of other silylenes.



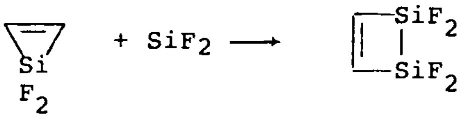
SCHEME 10



SCHEME 11

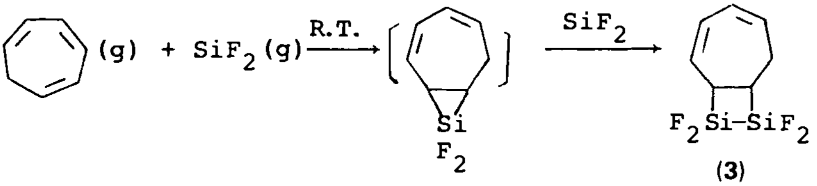
Reasonable as the mechanisms seem to be, a closer examination of the reaction scheme immediately reveals that all products involving two SiF_2 units can be explained equally well by the mechanism involving silirane intermediates, which dimerize either directly or followed by hydrogen-shift to form the observed products. The strategy used to differentiate these two mechanisms for insertion products in the reaction of vinyl flouride was simple: choosing a product, $CH_2{=}CHSiF_2SiF_3$, which could not possibly be formed via dimerization of the silirane intermediate, only to prove that it could not be formed by sequential insertion of SiF_2 either.

A similar strategy faces difficulty in the case of addition products. The only products that could not be formed by dimerization of the corresponding silirane intermediates are the four-membered ring compounds (disilacyclobutanes in the reactions of alkenes and disilacyclobutenes in the case of alkynes). But these four-membered ring compounds may well be formed by further insertion of difluorosilylene into intermediate three-membered silacycles, for example:



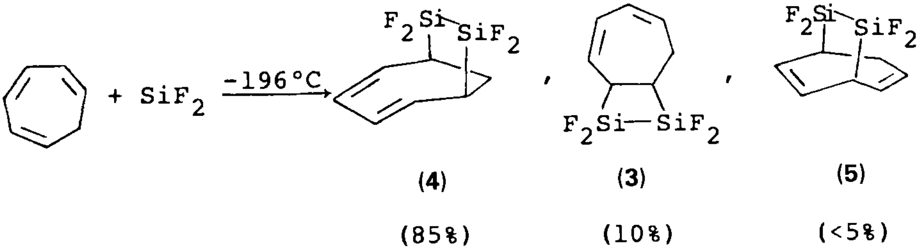
Although this type of reaction has not been observed experimentally with difluorosilylene, it is a well accepted reaction pathway in the chemistry of dimethylsilylene (*2, 6, 92*).

In the gas-phase reaction of difluorosilylene with cycloheptatriene (*94*), in addition to a small amount of unidentified products, compound (**3**) was obtained as the major product. Since only monomeric SiF_2 is involved in the gas phase, the formation of (**3**) is best viewed as the result of further insertion of SiF_2 into the initially formed silirane. This is the first experimental evidence for such insertion as far as difluorosilylene is concerned.



(61)

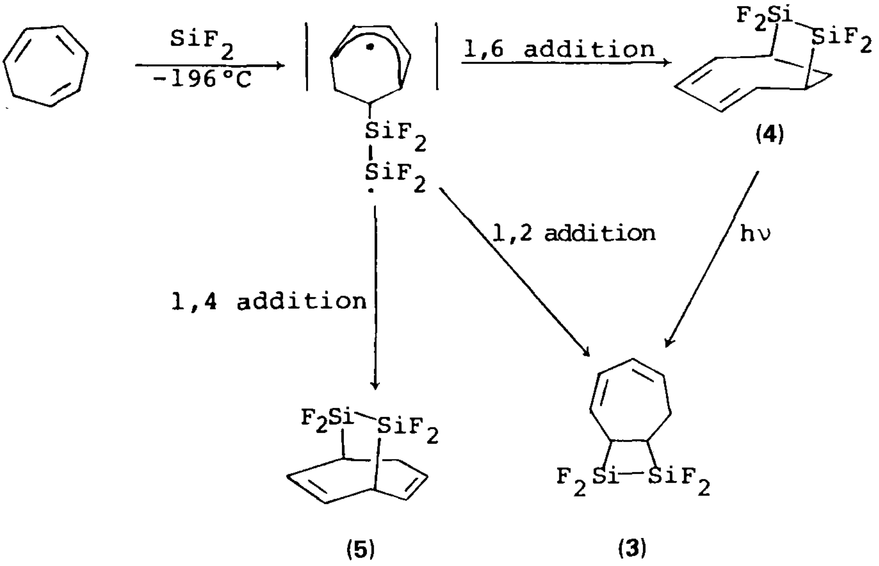
When the reaction was carried out under cocondensation conditions (*94*), three products, (**3**), (**4**), and (**5**), were obtained [Eq. (62)]. The major product was compound (**4**), and compound (**5**) was found only in trace abundance.



(62)

While compound (**3**) obtained in the cocondensation reaction may still be formed through the contribution from the silirane mechanism, just as it is formed in the gas phase, the formation of (**4**) and (**5**) cannot be rationalized with the same reaction mechanism. The fact that compound (**4**) was found to be the major product in the cocondensation reaction strongly indicates that the reaction proceeds via the diradical mechanism shown in Scheme 12. Compounds (**3**) and (**4**) are both thermally stable. It is interesting to note that compound (**4**) can be converted into compound (**3**) in *n*-hexane solution by UV irradiation.

One more type of reaction worth mentioning is that with isonitriles (*53*). This can be best illustrated by the reaction with methyl isocyanide.



SCHEME 12

The reaction did not produce any volatile product involving the SiF_2 group (except the polymeric products which contained SiF_2 units); instead, CH_4, C_2H_4, C_3H_6, C_3H_8, and CH_3CN were obtained in a total yield of 46%. Most interestingly, the isomerization of the starting material to methyl cyanide and a flash of chemiluminescence were observed at low temperatures during the reaction. Both phenomena appeared to accompany the evolution of a large quantity of methane gas as the cocondensate started to warm above −196°C. The reaction has been proposed to proceed by the mechanism of Eqs. (63-1)–(63-5).

$$\mathrm{CH_3{-}N{\equiv}C} + \mathrm{SiF_2} \xrightarrow{-196\,^{\circ}\mathrm{C}} \cdot\mathrm{CH_3} + [\mathrm{N{\equiv}C{-}\dot{S}iF_2}]$$

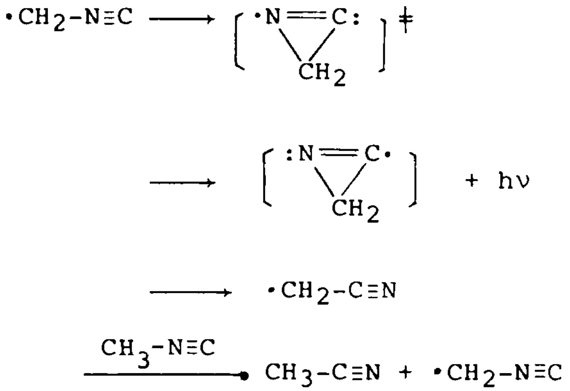
$$\downarrow$$

$$\text{involved in polymers} \qquad (63\text{-}1)$$

$$\uparrow$$

$$\cdot\mathrm{CH_3} \xrightarrow{\mathrm{CH_3{-}N{\equiv}C}} \mathrm{CH_4} + \cdot\mathrm{CH_2{-}N{\equiv}C} \qquad (63\text{-}2)$$

$$\xrightarrow{\qquad} \mathrm{C_2H_6},\ \mathrm{C_2H_4},\ \mathrm{C_3H_6},\ \mathrm{C_3H_8} \qquad (63\text{-}3)$$



(63-4)

(63-5)

The key steps in this mechanism are the initial attack of SiF_2 [Eq. (63-1)] and the hydrogen abstraction of CH_3NC by methyl radicals at low temperature [Eq. (63-2)]. The former resembles the reaction pattern of triplet carbenes; the latter had been demonstrated experimentally to be an extremely facile process at low temperatures (*97*).

At this point, we feel that the "difference" between the silirane mechanism and the diradical mechanism has been overemphasized in the past. In fact, the silirane intermediate may be considered as a special case in the $(SiF_2)_n$ homologue with $n = 1$.

If so, one most important question yet to be answered in the chemistry of difluorosilylene is the spin states of the reacting monomeric SiF_2 generated by various methods. The formation of silirane as an initial step in addition reactions is consistent with the chemistry of singlet SiF_2, which is in agreement with the spectroscopic studies in Margrave's earlier work (*73, 80*). An *ab initio* calculation also showed that SiF_2 has a singlet ground state (*114*). On the other hand, a number of chemical observations have suggested the participation of triplet SiF_2 in some reactions (*53, 95, 117*). It is obvious that more work along this line, preferably quantitative, is required to clarify the basic confusion in the chemistry of difluorosilylene.

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