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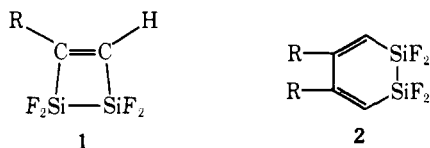
Cycloaddition of Disilacyclobutenes in the Presence of Nickel Tetracarbonyl

Chao-shiuan Liu*¹ and Chi-wen Cheng

Contribution from the Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan. Received January 14, 1975

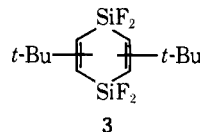
Abstract: 3-*tert*-Butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobut-3-ene (**1**), one of the products from the reaction between $(\text{CH}_3)_3\text{CC}\equiv\text{CH}$ and SiF_2 , is shown to undergo further cycloaddition to $(\text{CH}_3)_3\text{CC}\equiv\text{CH}$ in the presence of $\text{Ni}(\text{CO})_4$. The apparent function of $\text{Ni}(\text{CO})_4$ is to assist the cleavage of Si-Si bonds through $d \rightarrow d$ back π bonding to form chelate intermediates which react readily to form new cycloaddition products. These intermediates were isolated by reacting **1** directly with $\text{Ni}(\text{CO})_4$. An oxidative addition of the Si-Si bond to nickel resulted in the first well-characterized metal chelate with two silicon atoms bound to a metal atom. A reaction mechanism is proposed and is compared with those of other related catalytic systems.

The study of the addition reactions of the carbene-like difluorosilylene to unsaturated organic compounds has led to the synthesis of a series of unusual new organosilicon compounds.²⁻⁵ Our experiments on the addition reactions of a number of alkyne systems have established a plausible reaction mechanism which involved a reactive species SiF_2 - $(\text{SiF}_2)_n\text{SiF}_2$ ($n = 0, 1, 2 \dots$) on condensation of monomeric SiF_2 which is thermally generated according to the method of Timms et al.⁶ The assumption in our proposed mechanism is that the most reactive silicon-fluorine species toward these unsaturated molecules is a dimeric SiF_2 unit, which the ESR⁷ indicates is probably a diradical species. The dimeric species $\cdot\text{SiF}_2\text{SiF}_2\cdot$ reacts with alkynes $\text{RC}\equiv\text{CH}$ in the ratios of 1:1 and 1:2 to form, in addition to other products resulted from H migration, cyclic products **1** and **2**, respectively.



While this reaction mechanism accounts for all existing reaction data, there remains one alternative—that an intermediate formed between monomeric SiF_2 and the reagent molecule reacts so rapidly with other such intermediates to form silicon-silicon bonds that the products from the initial “monomeric intermediate” are not observed.

Our previous evidence was not really sufficient to distinguish between these two possibilities. However, if the latter mechanism was important in this type of reaction, one might expect, for example, in the reaction of $(\text{CH}_3)_3\text{CC}\equiv\text{CH}$ to find compounds such as **3** formed from linking two $(\text{CH}_3)_3\text{C}-\dot{\text{C}}\equiv\text{CH}-\dot{\text{S}}\text{iF}_2$ intermediates. Our previous results did not indicate that this type of product was formed in any significant yield. When a six-membered ring was formed, the spectral data⁴ seem to favor **2** ($\text{R} = t\text{-Bu}$) rather than **3**.



Based on the argument described above, it seemed to us that, if a compound with structure **3** could be synthesized and the spectral data compared with those of **2**, a more conclusive confirmation of the structures would greatly strengthen the reaction mechanism proposed previously.

We approached this problem by thinking of the possibility of a further cycloaddition of the four-membered ring compound **1** ($\text{R} = t\text{-Bu}$) to an alkyl-substituted alkyne $\text{RC}\equiv\text{CH}$. The silicon-silicon bond is known to be relatively weak (Si-Si bond energy 51 kcal/mol compared with 83 kcal/mol for C-C bond⁸) and is expected to be even weaker in a small ring compound involving a double bond such as **1**. If the Si-Si bond in compound **1** can be cleaved and the two Si atoms add to the alkyne molecule, compounds with structure **3** should be formed.

Experimental Section

Materials. 3,3-Dimethyl-1-butyne was prepared by the pinacol rearrangement reaction from acetone followed by chlorination and dehydrohalogenation.⁹ Nickel tetracarbonyl (99% purity) and metal silicon (98% purity) were commercially available products used without further purification.

Reactions. All reactions were carried out in a greaseless vacuum system. Silicon difluoride was generated and reacted with $(\text{CH}_3)_3\text{CC}\equiv\text{CH}$ as previously described.⁴ The volatile products were manipulated in the vacuum system and separated by trap-to-trap fractionation. 3-*tert*-Butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobut-3-ene (compound **1**, $\text{R} = t\text{-Bu}$), volatile at 0 °C, was collected at -22 °C. All the reactions between **1** and other reactants were carried out at room temperature in a tube sealed under the vapor pressure of the reactants at -196 °C.

Synthesis of 1,1,4,4-Tetrafluoro-1,4-disilacyclohexa-2,5-dienes. Approximately equimolar amounts of compound **1**, $(\text{CH}_3)_3\text{CC}\equiv\text{CH}$, and $\text{Ni}(\text{CO})_4$ were reacted in a sealed tube. A vigorous exothermic reaction occurred immediately as the frozen reactant mixture began to melt. The color changed from colorless

Table I. Ir Data for Compounds 1, 3a, 4a, and 4b

Compd	ν_{CH}	ν_{CO}	$\nu_{\text{C}=\text{C}}$	δ_{CH}	ν_{CC}	ν_{SiF}
1 ^a	2965 (w) 2910 (sh) 2878 (w)		1560 (m)	1420 (w) 1361 (w)	1212 (w)	986 (s) 947 (m) 832 (s)
3a	2978 (s) 2915 (m) 2878 (m)		1560 (m) 1538 (m)	1465 (m) 1365 (m)	1283 (m) 1230 (m) 1100 (m)	970 (m) 910 (s) 870 (s) 800 (s)
4a	2970 (s) 2910 (sh) 2878 (m)	2090 (s) 2040 (s)	1610 (m)	1480 (m) 1365 (m) 1290 (m)	1260 (w) 1222 (m) 1120 (m)	974 (m) 940 (s) 845 (s) 805 (s)
4a + 4b	2970 (s) 2910 (m) 2880 (m)	2120 (s) 2090 (s) 2070 (s) 2040 (s)	1610 (m)	1470 (m) 1365 (m) 1294 (w)	1255 (m) 1223 (s) 1117 (m)	965 (m) 890 (s) 840 (s) 810 (s)

^aCompound 1, ref 4.

to dark brown. The volatile reaction products were fractionated in the vacuum system, the more volatile fractions contained unreacted $\text{Ni}(\text{CO})_4$ and $(\text{CH}_3)_3\text{CC}\equiv\text{CH}$, and the least volatile fraction was a pale yellow liquid. This fraction contained compounds **3a** and **3b** (see text).

Reaction between $\text{Ni}(\text{CO})_4$ and 3-tert-Butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobut-3-ene (Compound 1). Equimolar proportions of the four-membered ring compound **1** and $\text{Ni}(\text{CO})_4$ were reacted in a sealed tube. The colorless mixture changed color on melting the condensate to yellow, brown, and finally reddish brown in about 1 hr. Volatile products were fractionated and four fractions were collected at -196 , -78 , -45 , and 0 °C. The most volatile portion contained mainly CO, and the fractions at -78 °C and -45 °C were found to be mixtures of unreacted reactants. The fraction collected at 0 °C was a pale brown liquid which contained the chelate compounds **4a** and **4b** (see text). It is highly moisture sensitive and decomposes at ca. 70 °C.

Spectra. ^1H and ^{19}F NMR spectra were obtained on a JEOL C 60HL- spectrometer operating at 60 and 56.4 MHz, respectively. Samples were sealed under vacuum with Me_4Si and CCl_3F as internal references. Infrared spectra were recorded on a Perkin-Elmer 337 spectrometer using 10-cm gas cell with KBr windows for gaseous samples and NaCl plates for liquid samples. Mass spectra were obtained on a Hitachi RMU 6 spectrometer.

Results and Discussion

The pale yellow liquid from the reaction between $\text{Ni}(\text{CO})_4$, $(\text{CH}_3)_3\text{CC}\equiv\text{CH}$, and the four-membered ring compound **1** has a molecular formula of $\text{C}_{12}\text{H}_{20}\text{Si}_2\text{F}_4$ suggested by its mass spectrum (m/e 296 M^+ , 119 $\text{C}_5\text{H}_{12}\text{SiF}^+$, 117 $\text{C}_5\text{H}_{10}\text{SiF}^+$, 104 $\text{C}_4\text{H}_9\text{SiF}^+$, 102 $\text{C}_4\text{H}_7\text{SiF}^+$, 85 SiF_3^+ , 69 C_3H_9^+ , 57 C_4H_9^+). The ir spectral data are summarized in Table I. The NMR data are shown in Table II.

The ^1H NMR spectrum showed a singlet at τ 8.80 and a partially resolved multiplet (apparently due to the overlap with another small multiplet at slightly higher field) centered at τ 3.40 with intensity ratio 9:1. The ^{19}F NMR spectrum showed two broad peaks at 135.5 and 143.3 ppm with intensity ratio 1:1 and four smaller broad peaks of equal intensity at 135.0, 138.1, 140.0, and 145.2 ppm. This fraction was subjected to further purification and one fraction which passed a trap at 0 °C after prolonged pumping was collected and the NMR spectra were compared with the previous ones. The multiplet in the ^1H spectrum is now fully resolved and the four less intense peaks in the ^{19}F spectrum disappear.

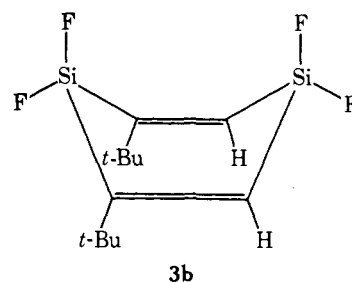
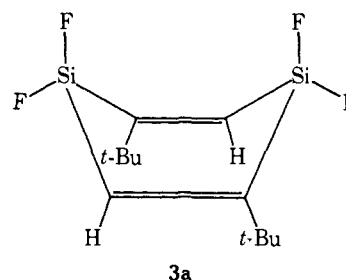
All these spectral data strongly support the conclusion that compounds of structure **3** are obtained. The former fraction contains a mixture of two possible isomers **3a** and **3b**, while the latter is mainly **3a**.

The ^{19}F NMR spectra are consistent with a "boat-form" conformation of **3a** and **3b**.¹⁰ The geminal fluorines are intrinsically different; therefore there are two different types

Table II. NMR Data for Compounds 1, 2, 3a, 3b, 4a, and 4b

Compd ^b	Chemical shift ^a		
	Vinyl H	<i>t</i> -Bu H	SiF
1	2.38 (t of t)	8.79 (s)	125.0 (c), 129.7 (c)
2	3.86 (m)	8.77 (s)	140.96 (c), 152.34 (c)
3a	3.38 (m)	8.80 (s)	135.5 (c), 143.3 (c)
3b	3.44 (m)	8.80 (s)	135.0 (c), 138.1 (c), 140.0 (c), 145.2 (c)
4a	2.73 (t, b)	8.75 (s)	136.4 (c), 137.1 (c)
4b	2.36 (t, b)	8.75 (s)	136.4 (c), 137.0 (c)

^ac = complex; s = singlet; t = triplet; m = multiplet; b = broad. τ units for ^1H ; PPM upfield of CCl_3F for ^{19}F . ^bCompounds **1** and **2**, ref 4.



of fluorine atoms in structure **3a**, while all four fluorine atoms are nonequivalent in structure **3b**.

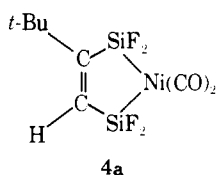
A comparison of the spectral data for compounds **2**, **3a**, and **3b** is made in Tables I and II. It is clear that the six-membered ring compound **2** obtained from the $(\text{CH}_3)_3\text{CC}\equiv\text{CH}/\text{SiF}_2$ reaction is definitely different from the present products. Bearing in mind the different ways these compounds are synthesized, the data of the former favor a structure with two SiF_2 units linked together, while the latter are consistent with a structure with two SiF_2 units being separated. This is the first time that we have obtained a compound in which two SiF_2 units are not linked together.

While the primary idea of this study was realized with the synthesis of compounds **3a** and **3b**, it is obvious that one

needs to know how these compounds are formed in the presence of $\text{Ni}(\text{CO})_4$.

Compound **1** did not react with $(\text{CH}_3)_3\text{CC}\equiv\text{CH}$ at room temperature. When the mixture was heated to 120°C in a sealed NMR tube for 16 hr, NMR peaks corresponding to **1** decreased in intensity and some new complex peaks appeared in the spectrum. The spectrum of $(\text{CH}_3)_3\text{CC}\equiv\text{CH}$ remained unchanged. The new spectrum resembles closely that of compound **1** after heating at 120°C for 16 hr alone. The products were not identified; however, it seems certain that no cycloaddition reaction occurred between **1** and $(\text{CH}_3)_3\text{CC}\equiv\text{CH}$.

No reaction was observed for the system $(\text{CH}_3)_3\text{CC}\equiv\text{CH}/\text{Ni}(\text{CO})_4$ up to 70°C . For the system $\text{Ni}(\text{CO})_4/\text{compound 1}$, however, a rapid reaction occurred at room temperature and a pale yellow liquid was obtained.¹¹ The pale yellow liquid was further separated into two fractions after exhaustive purification. By comparing the spectral data of the two, we conclude that the slightly more volatile fraction contained mainly compound **4a** and

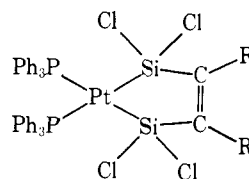


the other was a mixture of **4a** and some unidentified product **4b**. The ir and NMR spectral data are shown in Tables I and II.

Since compound **4a** was prepared in relatively pure form, its structure was further supported by mass spectrometry and elemental analysis (m/e 329MH^+ , $215\text{C}_6\text{H}_{11}\text{Si}_2\text{F}_4^+$, $187\text{C}_4\text{H}_7\text{Si}_2\text{F}_4^+$, 85SiF_3^+ , 67SiHF_2^+ , $57\text{C}_4\text{H}_9^+$, and 28CO^+). Anal. Calcd (for **4a**): C, 29.19; H, 3.06. Found: C, 29.08; H, 3.17. The most intense mass peak corresponds to $\text{C}_6\text{H}_{11}\text{Si}_2\text{F}_4^+$ (215) which may indicate that bonding between Si and Ni is weak. The highest mass peak corresponds to a molecular formula $\text{C}_6\text{H}_{11}\text{Si}_2\text{F}_4\text{Ni}(\text{CO})_2^+$ instead of the parent ion expected for compound **4a** (328). However, it seems unlikely that a product with the structure corresponding to $\text{C}_6\text{H}_{11}\text{Si}_2\text{F}_4\text{Ni}(\text{CO})_2$ would appear under the reaction conditions used. Besides, it is not impossible that compound **4a**, being weakly bonded between Ni and Si, could combine with an extra H when the chelate opened under the conditions that the mass spectrum was measured. We therefore assign the mass peak 329 as MH^+ .

Compared with the NMR data of compounds **1**, the ^1H chemical shifts are little changed whereas the ^{19}F chemical shifts are shifted to upfield by 7–10 ppm. This indicates that reaction occurred and a bond was formed between Ni and Si. The ir spectra of **4a** and the mixture of **4a** and **4b** in the region of CO stretching frequencies are compared; in the spectrum of **4a**, two of the four stretching bands of the mixture decrease in intensity and apparently only two of them are seen. All these results strongly support our structural assignment of the "chelate" compounds with two silicon atoms bound to nickel. The exact structure of **4b** is not certain since it has never been prepared in pure form and the spectral data are not conclusive.

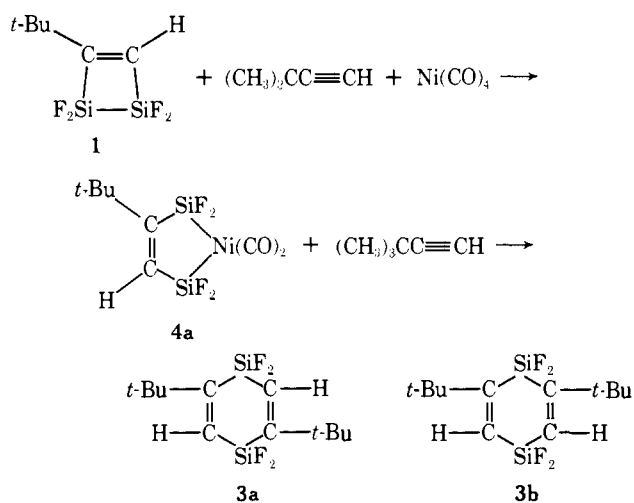
As far as the authors are aware, compound **4a** is the first well-characterized chelate compound with two silicon atoms as "donors". Only one other compound of similar structure has been found in the literature; Schmid and Balk¹² reported an unusual reaction between $\text{Pt}(\text{PPh}_3)_4$, Si_2Cl_6 , and $\text{RC}\equiv\text{CR}$ to give a chelate compound whose structure was based on the ir spectrum:



The bonding between the central metal and the silicon atoms in these compounds can be understood by a back π -bonding scheme of the d electrons of the metal donating to the empty 3d orbitals of the silicon atoms. This kind of bonding may be enhanced by the electron-withdrawing effect of the fluorine atoms attached to silicon.

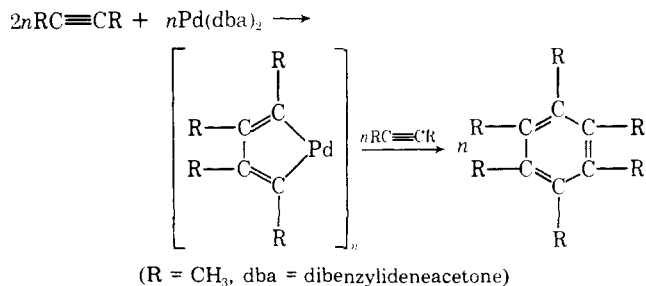
Additional chemical evidence comes from the study of the reactivity of these compounds. When either **4a** or a mixture of **4a** and **4b** was reacted with $(\text{CH}_3)_3\text{CC}\equiv\text{CH}$, the immediate products were found to be **3a** and **3b**.

Thus it is very likely that compound **1** and $(\text{CH}_3)_3\text{CC}\equiv\text{CH}$ undergo cycloaddition to form **3a** and **3b** in the presence of $\text{Ni}(\text{CO})_4$ via intermediates **4a** and perhaps **4b**:

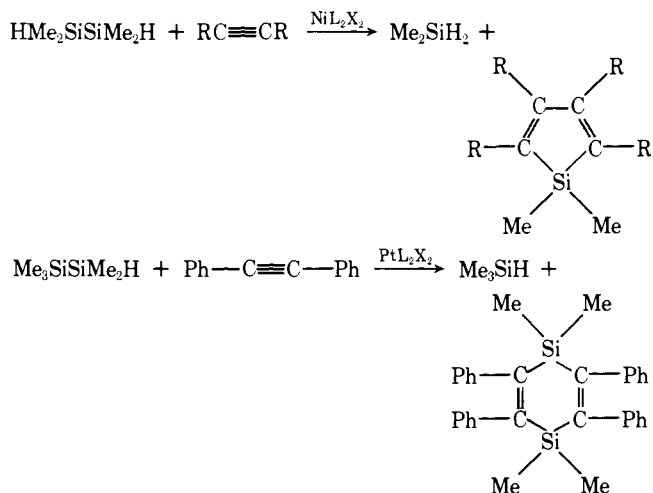


The function of $\text{Ni}(\text{CO})_4$ here is to form chelate intermediates with compound **1** through the assistance of back π bonding and thus cleave the relatively weak Si–Si bond in **1**, which is a necessary step toward further cycloaddition onto a $(\text{CH}_3)_3\text{CC}\equiv\text{CH}$ molecule. It is a "back π -assisted cycloaddition".

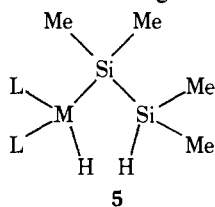
This catalytic reaction mechanism is almost certainly related to that of the cyclotrimerization of substituted acetylenes,^{13–15} and perhaps of many other polymerization processes.¹⁶ For example, Maitlis et al.¹⁴ reported the isolation of a Pd complex which was believed to be the intermediate in the Pd(0) catalyzed cyclotrimerization of dimethylacetylene:



All these reactions involve an initial oxidative addition to the coordinatively unsaturated metal complex in which the metal is in a low oxidation state, followed by the generation of the reactive species which are apparently "activated" via coordination.¹⁷ In our case, the oxidative addition to Ni involves the cleavage of the Si-Si bond which is essential for the formation of **3a** and **3b**. It is interesting to compare this reaction with the catalyzed cycloaddition reactions between acetylenes and methyl-substituted disilanes reported by Kumada and his coworkers:^{18,19}



In the latter case, the 1,4-disilacyclohexadiene was formed by linking two acetylene molecules through two separate SiMe_2 units as shown above whereas, in our case, due to the role of the dimeric Si_2F_4 species, a four-membered ring 1,2-disilacyclobutene was used as the starting reagent.²⁰ Kumada has proposed a reaction intermediate **5** to account for the products from the preceding reactions as well as a series of other related reactions between tetramethyldisilane and unsaturated organic molecules:¹⁸



The important feature of this suggestion is the addition of the Si-H bond to nickel which may generate the reactive dimethylsilylene species (probably bonded to the transition metal) by eliminating a dimethylsilane molecule. In our case, the involvement of any intermediate analogous to **5** is not likely.²¹ It is the Si-Si bond that undergoes oxidative addition to Ni, and the Si-Si cleavage is directly resulted. Similar oxidative addition reactions of O-O bonds to Ni(0) systems have been reported by Schott and Wilke.²²

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