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Cycloaddition Reactions of Tetrafluorodisilacyclobutene with 1,3-Butadienes Mediated by Metal Carbonyls. 1. 1,1-Addition via Hydrogen Migration

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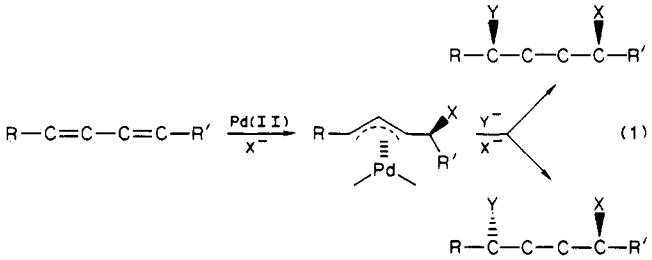
The cycloaddition reactions of 1,1,2,2-tetrafluoro-1,2-disilacyclobutene with 1,3-butadiene and its derivatives were studied. The reactions were carried out photochemically in the presence of iron pentacarbonyl. Products from the unusual metal-mediated 1,1-addition were characterized, and the reaction mechanism is discussed.

Regio- and stereo-controlled addition to 1,3-conjugated dienes has always been an interesting subject. The specificity can be achieved by the mediation of transition-metal complexes.[1,2] For example, the Pd(II)-catalyzed 1,4-acetoxychlorination of 1,3-dienes proceeds via a (η^3-allyl)palladium intermediate (eq 1).[2]

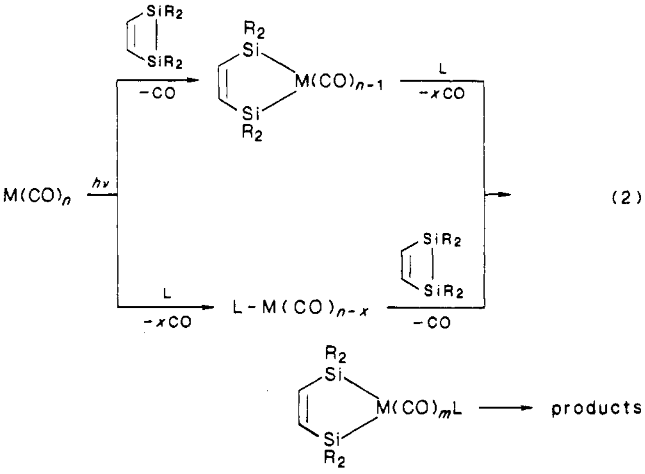


Importantly, the stereochemistry of the attack of the second nucleophile can be controlled in some cases so as to proceed either from the opposite side (trans attack) or from the same side (cis attack) of the metal atom. It is believed that if the attacking reagent could also be bonded to the metal, the intramolecular attack would probably show more regio- and stereoselectivity.

Metal carbonyls and metal phosphine complexes have been reported to catalyze cycloaddition of 1,2-disilacyclobutenes with unsaturated organic molecules.[3,4] In general, such reactions are believed to proceed either via oxidative addition by the disilacyclobutene or via complexation of the unsaturated organic ligand, with resulting formation of the intermediate X (eq 2).

Intermediates analogous to X have also been proposed in the rationalization of other metal-mediated reactions such as hydrosilylation but have rarely been isolated.[5,6]

We recently reported the cycloaddition reactions between 1,1,2,2-tetrafluorodisilacyclobutene (1) and cyclohexadiene mediated by iron pentacarbonyl and tungsten hexacarbonyl.[7] In the both reactions intermediates analogous to X were isolated. In the Fe-mediated reaction both isomers of the 1,2-addition product were obtained whereas the W-mediated reaction yielded only one isomer. The difference in reaction pathways was explained by the different structures of the reaction intermediates which were determined by single-crystal X-ray diffraction.[7]



X

R = CH_3, F; L = olefins, alkynes, x = 1; L = dienes, x = 2; $m = n - x - 1$

With all key steps involved in the coordination sphere of the central metal, one wonders if it is possible to fine tune the structures of the intermediates (the geometry of the complex, electronic properties of the metal, steric effects of the substituents on 1,3-dienes, etc.) to affect the reaction pathways.

In an attempt of thoroughly understanding the correlation between the reaction pathways and the structures of reaction intermediates, a systematic study of the cycloaddition reactions between 1 and various systems of conjugate dienes was carried out. This paper reports the results of the reactions with butadiene, 2-methyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, *trans*-1,3-pentadiene, 2,4-dimethyl-1,3-pentadiene, and 2,5-dimethyl-1,3-hexadiene, mediated by $Fe(CO)_5$ under photochemical conditions.

Results and Discussion

The results of the cycloaddition reactions of 1 with various butadienes mediated by iron pentacarbonyl are summarized in Table I.

When the reactions of 1 with various 1,3-butadienes were carried out under photochemical conditions and in the presence of iron pentacarbonyl, unexpected types of products were observed. Instead of the products from 1,4- and 1,2-additions, alkylidenedisilacyclopentenes (2) and disilacyclopentenylalkenes (3) were obtained (eq 3). Compounds **2a**/**2b**, **2c**/**2d**, **2e**/**2f**, **2g**/**2h**, and **3a**/**3b** existed in isomeric pairs. All attempts to separate these mixtures of air-sensitive products are not successful.

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[1] Bäckvall, J. E. *Acc. Chem. Res.* **1983**, *16*, 335.

[2] Bäckvall, J. E.; Nystrom, J. E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 3676.

[3] Sakurai, H.; Kobayashi, T.; Nakadaira, Y. *J. Organomet. Chem.* **1978**, *162*, C 43.

[4] Liu, C. S.; Cheng, C. W. *J. Am. Chem. Soc.* **1975**, *97*, 6746.

[5] Schroeder, M. A.; Wrighton, M. S. *J. Organomet. Chem.* **1977**, *128*, 345.

[6] Mitchener, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 975.

[7] Lin, C. H.; Lee, C. Y.; Liu, C. S. *J. Am. Chem. Soc.* **1986**, *108*, 1323.

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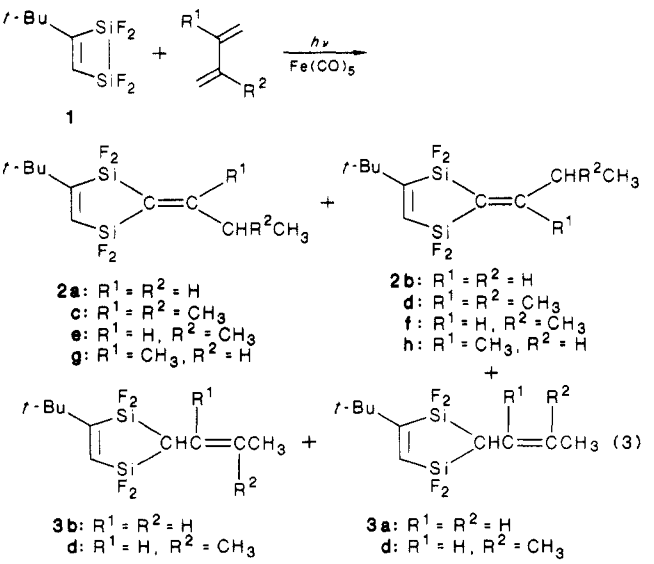
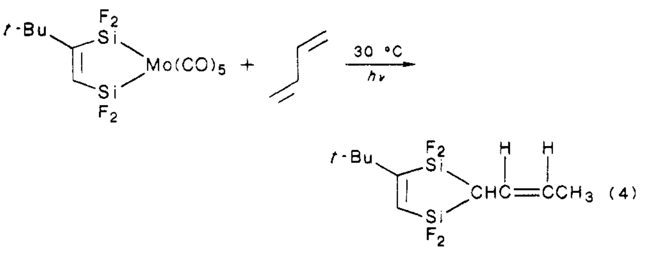


Nonetheless, structure identification was possible. Both the mass spectra and the elemental analyses of these isomer pairs suggest the proposed molecular formula.

The characteristic spectral feature of the compounds designated by **2** is the disilacyclopentene ring in which there is an sp^2 carbon without a hydrogen attached but strongly coupled with four fluorines. For example, the ^{13}C NMR spectrum of a 3:4 mixture of **2a** and **2b** shows a multiplet at δ 117.51 for that carbon (Figure 1). In addition to the extremely low-field peak at δ 179, which is the characteristic resonance region for *t*-BuC=CHSiF$_2$–,[8] there is another peak at very low field at δ 173.44. This peak is shown by the ^{13}C{^{1}H}$_{CW}$ spectrum to be due to a carbon atom with one hydrogen attached and can only be assigned to the sp^2 carbon β to two vinyl SiF$_2$ groups,[8] namely, *C*=C(SiF$_2$–)$_2$. On the basis of the empirical formula previously derived,[8] chemical shifts of this carbon in all members of the **2** family can be calculated. The shifts are in good agreement with the observed values (Table II).

For compounds designated by **3** the key spectral feature is a saturated CH in the disilacyclopentene ring. The ^{13}C NMR spectra of these isomer pairs not only show these features clearly but also fit the rest of the corresponding molecular structures perfectly. The ^{1}H and ^{19}F NMR spectra are also consistent with the proposed structures. However, one needs a pure sample to ensure the structural assignment.

Fortunately, it is possible to obtain pure **3a** by using molybdenum carbonyl as the mediator in the photochemical reaction kept strictly at 30 °C (eq 4).[9]



3a

The ^{1}H NMR spectrum fits the structure of **3a** but is not sufficiently informative. The ^{13}C NMR spectrum of **3a** (Figure 2) shows in addition to the complex peak at extremely low field (δ 179.0) for *t*-BuC=CHSiF$_2$–, three sp^2 CH peaks at δ 140.92, 128.80, and 117.77. The peak at δ 140.92 is strongly coupled with fluorines and is assigned to *t*-BuC=*C*HSiF$_2$–. The other two are assigned to C-7 and C-6, respectively. The key structural feature, carbon-5, is shown clearly at δ 13.65 as an sp^3 carbon coupled with two SiF$_2$ groups. The ^{19}F{^{1}H}$_{BB}$ NMR spectrum of **3a** shows four doublets of doublets of doublets at 134.38, 136.40, 138.65, and 141.74 ppm, respectively. This also fits the structure. All these spectral features seem to make the assignment of structure unequivocal.

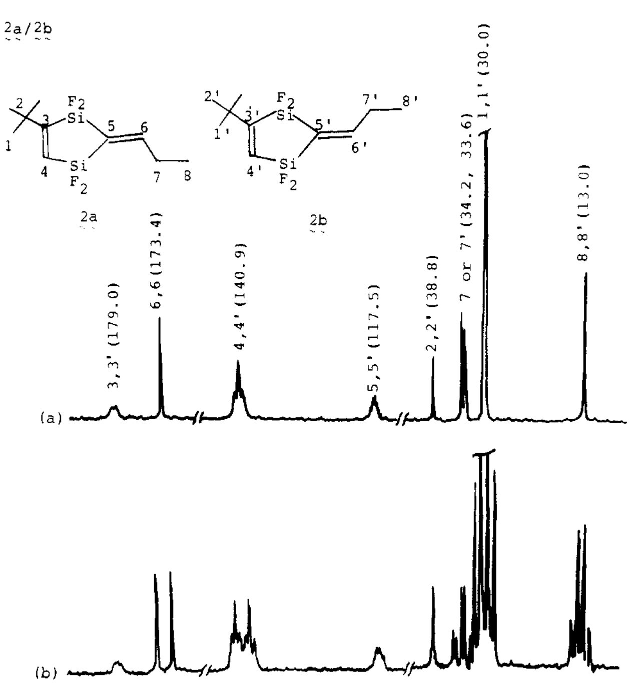


Figure 1. (a) ^{13}C{^{1}H}$_{BB}$ and (b) ^{13}C{^{1}H}$_{CW}$ spectra of a 3:4 mixture of **2a**/**2b**.

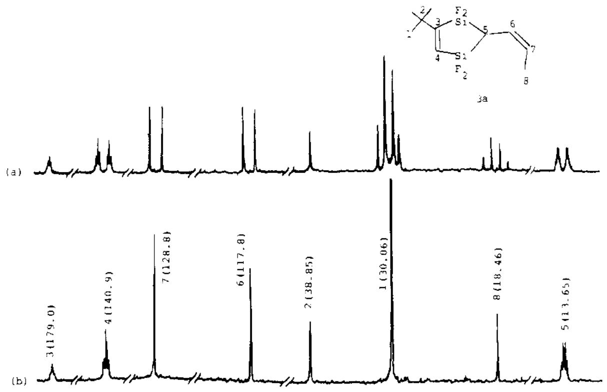


Figure 2. (a) ^{13}C{^{1}H}$_{CW}$ and (b) ^{13}C{^{1}H}$_{BB}$ spectra of compound **3a**.

It is interesting to note that the members of these isomer pairs show almost identical ^{1}H and ^{13}C NMR spectra (for example, only C-7 of **2a** and **2b** showed a difference in chemical shift; see Figure 1) but show very different ^{19}F chemical shifts. Besides, all ^{19}F{^{1}H}$_{BB}$ spectra of the compounds designated by **2** show AA′BB′ patterns whereas those of **3** family show first-order doublets for the four fluorines. These spectral features prove to be diagnostic for the particular structures.

The structural analysis described above is further supported by the case of compound **3c**, which can also be obtained in pure form, because in this case there is only one isomer possible.

When Fe(CO)$_5$ was used in the reaction between **1** and 2,3-dimethyl-1,3-butadiene, no **3c** was observed (the only

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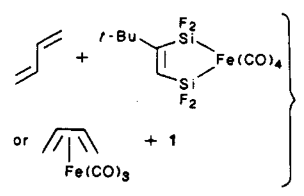
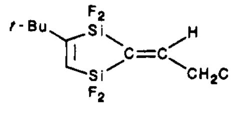
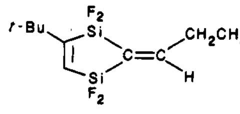
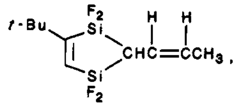
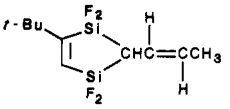
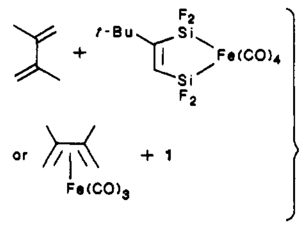
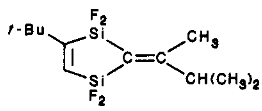
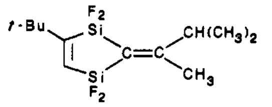
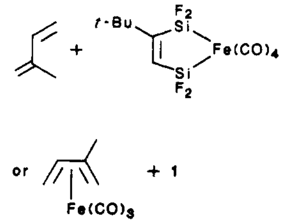
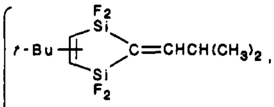
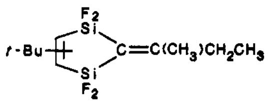
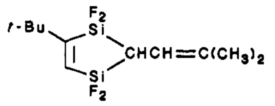
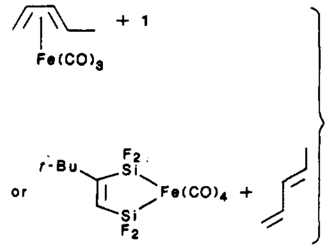
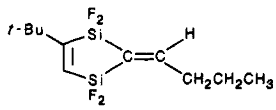
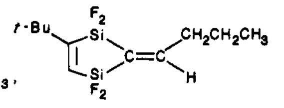
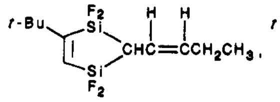
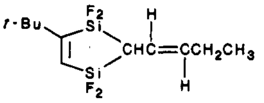
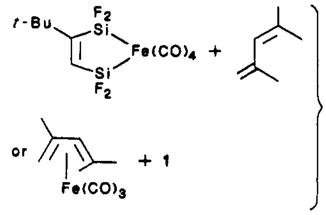
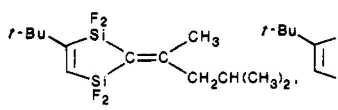
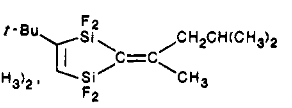
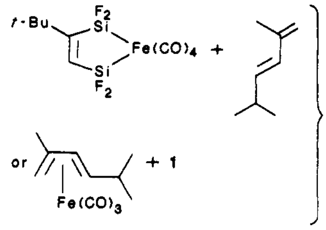
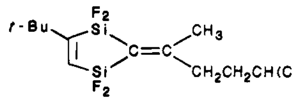
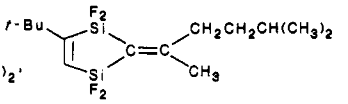
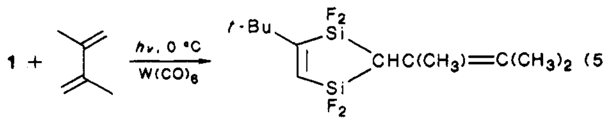
[8] Hseu, T. H.; Chi, Y.; Liu, C. S. *J. Am. Chem. Soc.* **1982**, *104*, 1594.

[9] Lee, C. Y. Ph.D. Thesis, National Tsing Hua University, 1986.

Table I. Reactions of 1 with Various Dienes Mediated by Iron Carbonyl

reactns	conditns	products
	60 °C, *hν*	 **2a**  **2b**  **3a**  **3b**
	50–70 °C, *hν*	 **2c**  **2d**
	*hν*, 0 °C *hν*, 30 °C	 **2e/2f**  **2g/2h**  **3d**
	30 °C, *hν*	 **2i**  **2j**  **3e**  **3f**
	30 °C, *hν*	 **2k**  **2l**
	−30 °C, *hν*	 **2m**  **2n**

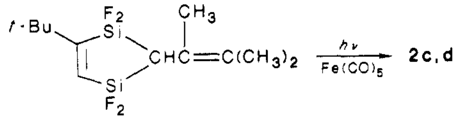
products were **2c** and **2d**). However, **3c** can be obtained by using W(CO)$_6$ at 0 °C (eq 5).[9]


(5)

3c

The ^{19}F{^{1}H}$_{BB}$ spectrum shows four doublets of doublets of doublets at 130.65, 133.05, 136.01, and 138.73 ppm. The ^{13}C NMR spectrum shows, in addition to the typical chemical shifts of the *t*-BuC=C– (δ 181.02), a triplet of triplets at δ 141.09 which further splits into a doublet in the ^{13}C{^{1}H}$_{CW}$ spectrum and two sp^2 carbons at δ 117.07 and 125.51 which remain singlets in the ^{13}C{^{1}H}$_{CW}$ spectrum. These features fit the structure of **3c** perfectly.

When **3c** was treated with Fe(CO)$_5$ under photochemical conditions, it isomerized quantitatively to **2c** and **2d**. This result explains why **3c** was not observed in reaction 3. It appears that a methyl group on C-2 of 1,3-butadiene would greatly facilitate the migration of the second hydrogen from C-1 (eq 6).



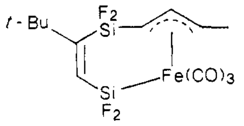
(6)

3c

In fact, the same products in reaction 3 can be obtained either by reaction 1 with (η^4-diene)tricarbonyliron or by reacting $(F_2Si(t\text{-}Bu)C{=}C(H)SiF_2\text{-})Fe(CO)_4$ with dienes. Scheme I scheme can be established experimentally.

(η^4-Diene)$Fe(CO)_3$ and $(F_2Si(t\text{-}Bu)C{=}C(H)SiF_2\text{-})Fe(CO)_4$ can be isolated. Intermediates Y for $R^1 = R^2 = H$, $R^1 = H$, $R^2 = CH_3$, and $R^1 = R^2 = CH_3$ were observed by ^{19}F NMR spectroscopy but were not isolated. The structure of Y is assured because, when *trans,trans*-2,4-hexadiene was used, the intermediate corresponding to Y, which showed an almost identical ^{19}F NMR spectrum, was isolated and the structure fully characterized.[10]

When the reaction with 1,3-butadiene was carried out at lower temperature (below -30 °C), two other intermediate species, **5** and **6**/**7**, were observed sequentially before the formation of final products **2a**, **2b**, **3a**, and **3b**.



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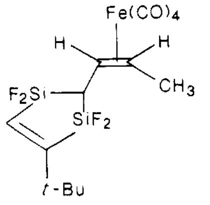

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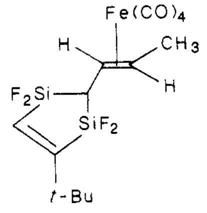
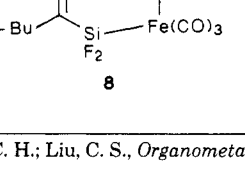


7

Compound **5** was characterized by its mass spectrum (M^+, *m*/*e* 408) and ^{19}F and ^{13}C NMR spectra. The ^{13}C NMR spectrum showed, in addition to the resonance of CO, two olefinic carbons, the *tert*-butyl carbons, one methyl carbon, and three CH carbons at δ 117.53, 70.25 and 91.35, respectively (Figure 3). These are typical resonances of the η^3-allyl moiety. The mass spectrum of **6**/**7** showed the molecular ion (M^+, *m*/*e* 436) and the expected fragments. The ^{13}C NMR spectrum showed that beside the resonances of the carbons of the $SiF_2(t\text{-}Bu)C{=}CHSiF_2$ moiety, carbonyl, and one CH_3, there were two CH carbons at δ 70.49 and 35.98, respectively. They are typical resonances of sp^2 carbons bonded to metals. At elevated temperatures, **5** was converted to **2a**/**2b** and **6**/**7**, and **6**/**7** was further converted to **2a**/**2b** and **3a**/**3b** quantitatively. An intermediate (**8**) analogous to **5** was also obtained in the reaction with 2,3-dimethyl-1,3-butadiene at -10 °C.



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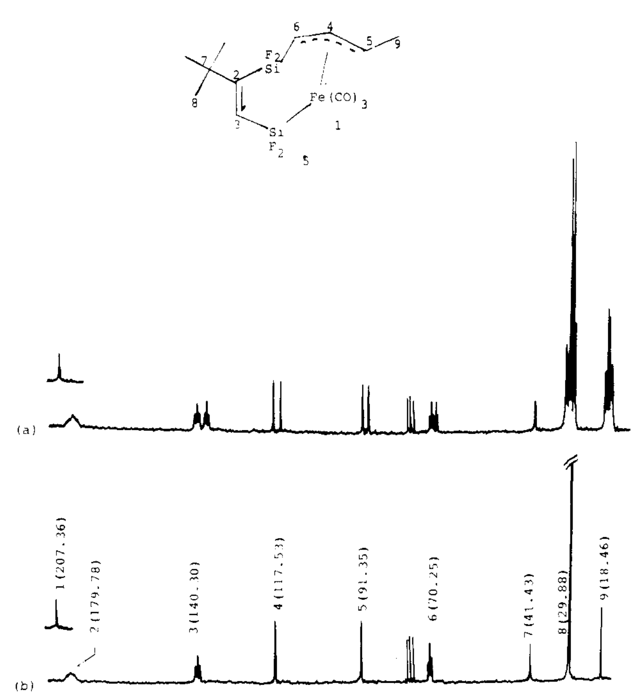
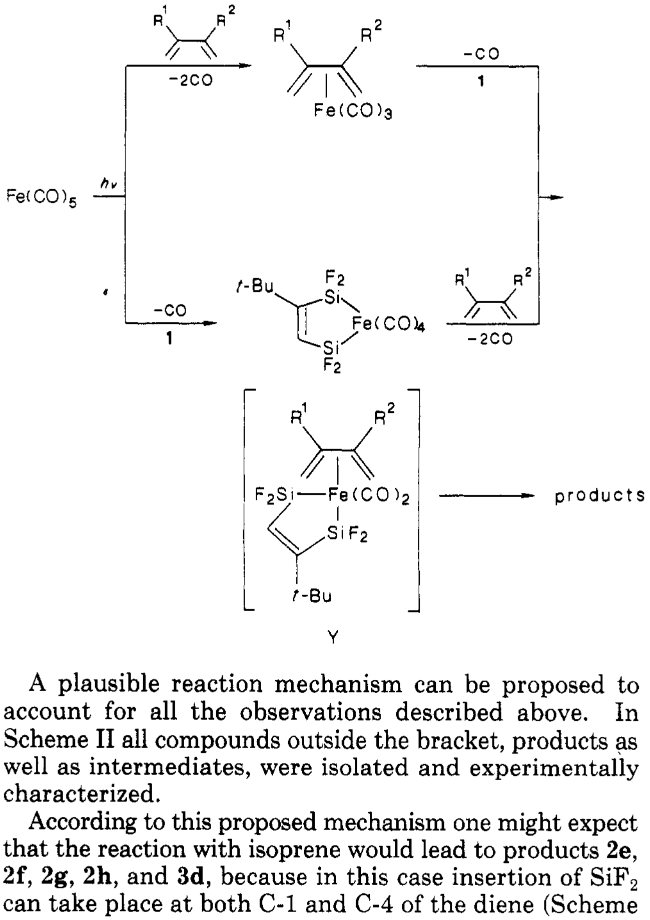


Figure 3. (a) $^{13}C\{^1H\}_{CW}$ and (b) $^{13}C\{^1H\}_{BB}$ spectra of compound **5**.

Scheme I



A plausible reaction mechanism can be proposed to account for all the observations described above. In Scheme II all compounds outside the bracket, products as well as intermediates, were isolated and experimentally characterized.

According to this proposed mechanism one might expect that the reaction with isoprene would lead to products **2e**, **2f**, **2g**, **2h**, and **3d**, because in this case insertion of SiF_2 can take place at both C-1 and C-4 of the diene (Scheme III).

Indeed, when isoprene was reacted with 1 under the same experimental conditions, the expected five products were obtained. Although these five compounds were not separated, the ^{19}F NMR spectrum of the mixture clearly shows four sets of AA′BB′ patterns characteristic for **2e**, **2f**, **2g**, and **2h** and one first-order spectrum characteristic for **3d**.

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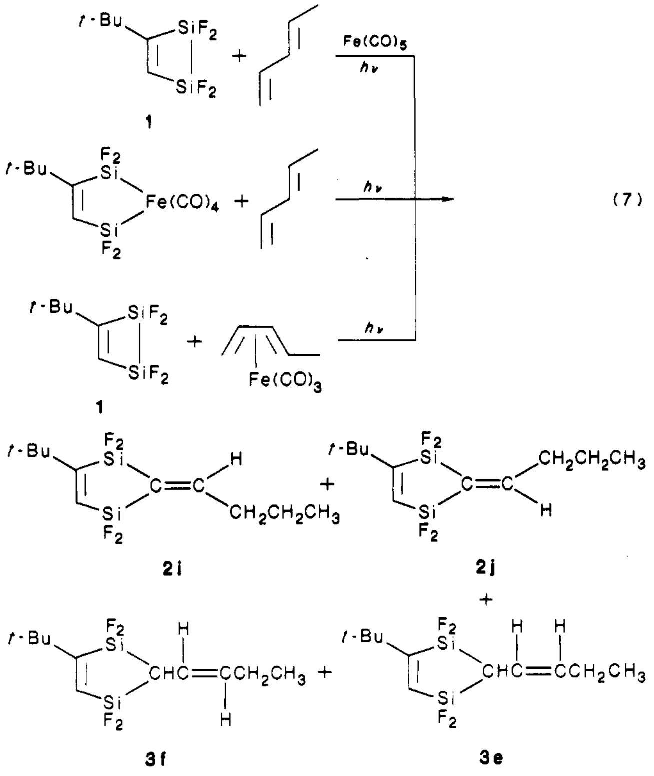
[10] Lee, C. Y.; Lin, C. H.; Liu, C. S., *Organometallics*, second of three papers in this issue.

The cycloaddition reactions of 1 to these three butadienes mediated by $Fe(CO)_5$ apparently proceeds via a very unusual 1,1-addition pathway.

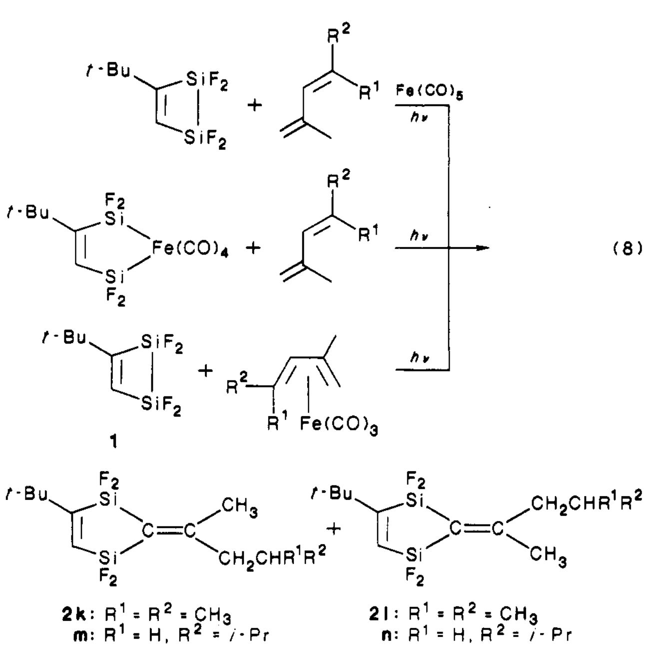
The effect of substituents on one terminal carbon of 1,3-butadienes was studied by the reaction of 1 with *trans*-1,3-pentadiene, 2,4-dimethyl-1,3-pentadiene, and 2,5-dimethyl-1,3-hexadiene. The reaction with *trans*-1,3-pentadiene can be carried out with either 1/1,3-pentadiene/$Fe(CO)_5$ or $(\overline{SiF_2(t\text{-Bu})C{=}C(H)SiF_2\text{-})F}(CO)_4$/1,3-pentadiene or 1/$(\eta^4\text{-}C_5H_8)Fe(CO)_3$; the same products **2i**/**2j** and **3e**/**3f** were obtained (eq 7).



(7)

Since no products from the addition to C-4 were observed, it is obvious that the silyl migration in the intermediate state strongly prefers the unsubstituted terminal carbon of the diene.

Secondly, 2,4-dimethylpenta-1,3-diene and *trans*-2,5-dimethylhexa-1,3-diene were used to compare the influence of the substituents at different carbons. The products **2k**/**2l** and **2m**/**2n**, respectively, showed nicely both the preference of addition to the unsubstituted terminal carbon and the enhanced tendency of the second hydrogen shift as a result of the methyl group on C-2. The latter influence resulted in the observation of only alkylidenedisilacyclopentenes (**2**) but not disilacyclopentenylalkenes (**3**) (eq 8).



(8)

Experimental Section

Vacuum distillation and chemical manipulations were carried out on vacuum lines at 10^{-3} torr. Photochemical preparations employed a 450-W medium-pressure Hg lamp. Dienes (Aldrich), $Fe(CO)_5$ (Merck), $M(CO)_6$ (M = Mo, W) (Strem), and $(\eta^4\text{-}C_4H_6)Fe(CO)_3$ (Strem) were used as received. The following compounds were prepared respectively according to the literatures published elsewhere: 1,[11] $(\overline{F_2Si(t\text{-Bu})C{=}C(H)SiF_2\text{-})M}(CO)_n$ ((M = Fe, n = 4; M = Cr, Mo, W, n = 5),[12,13] $(\eta^4\text{-diene})Fe(CO)_3$.[14,15]

Spectra. All mass spectra were recorded on a JEOL JMS-100 mass spectrometer operating at 12 eV. The NMR spectra were obtained from a JEOL JMX FX-100 spectrometer operating at 99.55, 93.65, and 25.0 MHz for ^1H, ^{19}F, and ^{13}C spectra, respectively, and a Bruker AM 400 spectrometer operating at 400.0, 376.5, and 100.0 MHz for ^1H, ^{19}F, and ^{13}C spectra, respectively. Chemical shifts of ^1H and ^{13}C NMR spectra were measured in δ values. ^{19}F NMR chemical shifts were measured in parts per million upfield from the internal standard CCl_3F. In the ^{13}C NMR data, the spectral multiplicity following each chemical shift is due to the coupling with heteronuclei, whereas the coupling patterns in $^{13}C\{^1H\}_{CW}$ are included in the parentheses.

Preparation of 2a, 2b, 3a, and 3b. Compounds **2a**/**2b** and **3a**/**3b** can be prepared photochemically by either reacting 1 with $(\eta^4$-1,3-butadiene)tricarbonyliron or reacting 1,3-butadiene with $(\overline{F_2Si(t\text{-Bu})C{=}C(H)SiF_2\text{-})Fe}(CO)_4$ or reacting 1 with 1,3-butadiene in the presence of $Fe(CO)_5$. A typical run is described as follows: 1 (5.0 mmol) and 10.0 mmol of $(\eta^4$-1,3-butadiene)tricarbonyliron were transferred into a quartz reaction tube filled with dry nitrogen. Dried and degassed *n*-pentane (10 mL) was used as the solvent. The reaction was carried out under irradiation at 60 °C. The reaction tube was subjected to degassing every 4–5 h. Compound 1 was completely consumed after 30 h. The solution was concentrated to a green liquid by pumping out solvent, which was heated at 120 °C for 20 min to remove $Fe_3(CO)_{12}$. Distillation under vacuum gave a yellowish liquid that contained in addition to **2a**, **2b**, **3a**, and **3b**, $(\overline{F_2Si(t\text{-Bu})C{=}C(H)SiF_2\text{-})Fe}(CO)_4$ and $(\eta^4$-diene)tricarbonyliron. $(\overline{F_2Si(t\text{-Bu})C{=}C(H)SiF_2\text{-})Fe}(CO)_4$ and $(\eta^4$-diene)tricarbonyliron were removed by adding PPh_3 in excess and heating the solution to 150–160 °C for 4 h, followed by vacuum distillation at 90 °C. On the basis of quantity of 1 used, the total yield was 35% (**2a**:**2b**:**3a**:**3b** = 8:8:3:3). When the mixture of **2a**/**2b** and **3a**/**3b** was subjected to further irradiation with $Fe(CO)_5$ at 100 °C for 72 h, **3a**/**3b** converted to **2a**/**2b** almost quantitatively (only a trace of **3a**/**3b** remained unchanged).

Preparation of 3a. A *n*-pentane solution containing 4.0 mmol of $(\overline{F_2Si(t\text{-Bu})C{=}C(H)SiF_2\text{-})Mo}(CO)_5$ and 5.0 mmol of 1,3-butadiene was degassed and irradiated under dry nitrogen atmosphere at 30 °C for 20 h. After removal of solvent, about 0.6 g of **3a** was obtained by distillation at 90 °C under vacuum. The yield based on the quantity of $(\overline{F_2Si(t\text{-Bu})C{=}C(H)SiF_2\text{-})Mo}(CO)_5$ used was 60%.

Anal. Calcd for **2a**/**2b** and **3a**/**3b**: C, 44.78; H, 6.00; F, 28.36. Found: C, 44.20; H, 6.19; F, 28.57. Mass spectrum of **2a**/**2b** and **3a**/**3b**: *m/e* 268 (M^+, $C_{10}H_{16}Si_2F_4^+$), 253 ($C_9H_{13}Si_2F_4^+$), 239

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[11] Liu, C. S.; Margrave, J. L.; Thompson, J. C. *Can. J. Chem.* **1972**, *50*, 465.

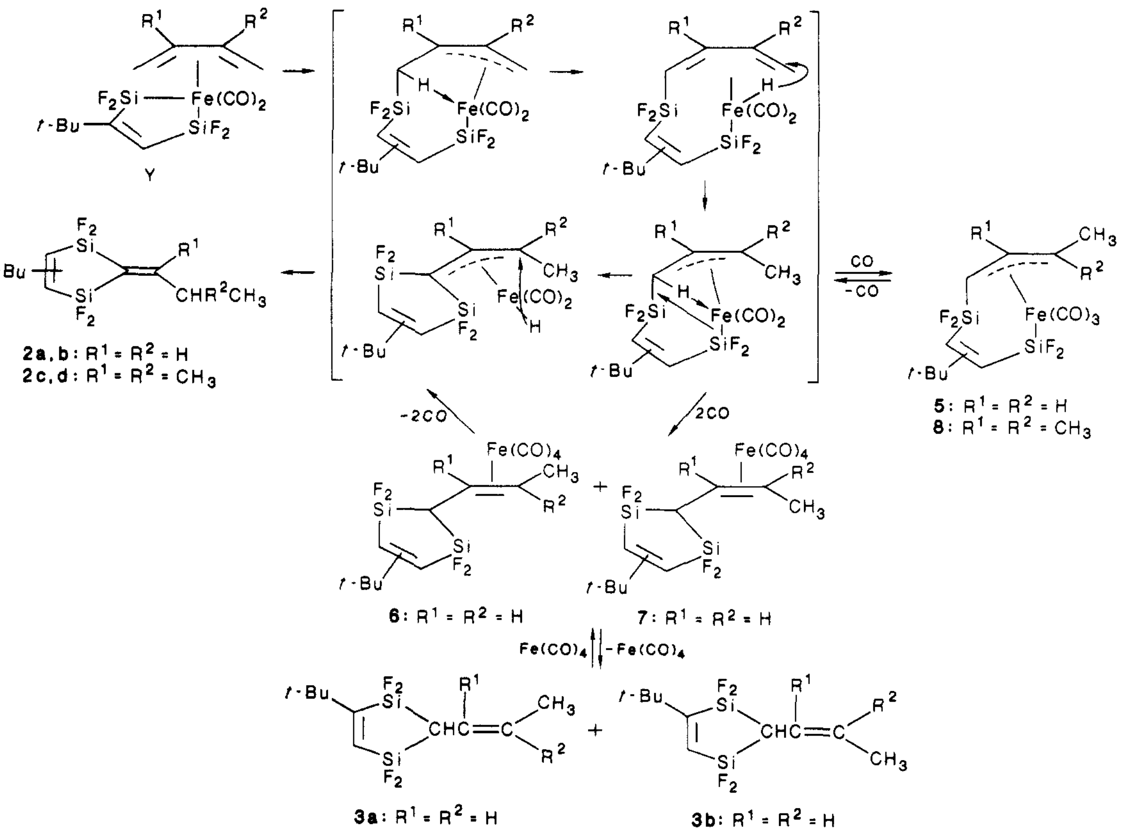
[12] Chi, Y.; Liu, C. S. *Inorg. Chem.* **1981**, *20*, 3456.

[13] Hseu, T. H.; Chi, Y.; Liu, C. S. *Inorg. Chem.* **1981**, *20*, 199.

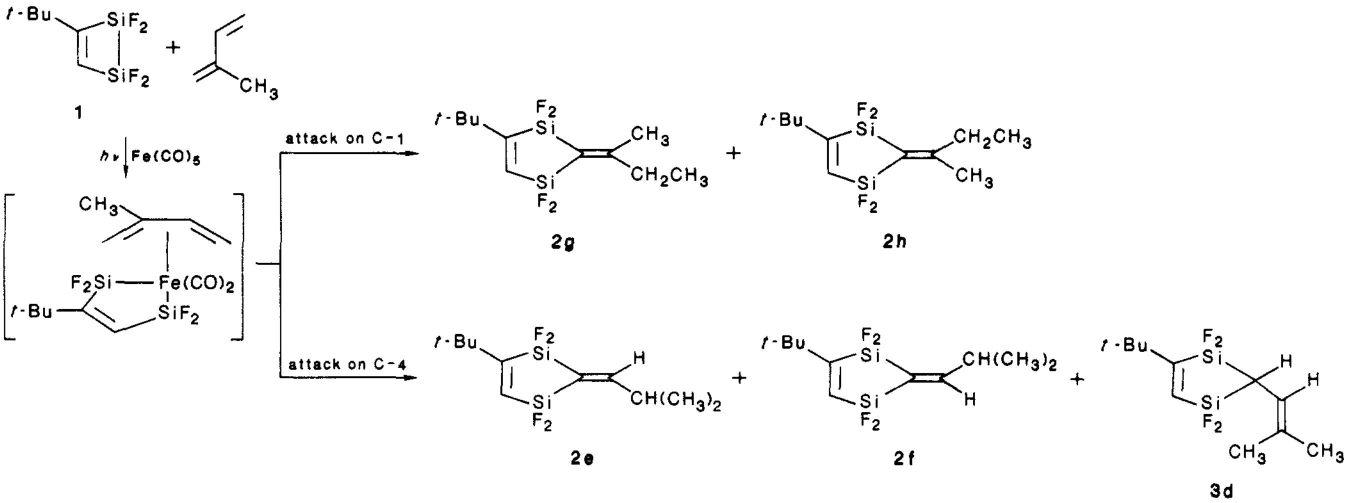
[14] Hallam, B. F.; Pauson, P. L. *J. Chem. Soc.* **1958**, 642.

[15] King, R. B.; Manuel, T. A.; Stone, F. G. A. *J. Inrog. Nucl. Chem.* **1961**, *16*, 233.

Scheme II



Scheme III



$(C_8H_{11}Si_2F_4^+)$ 226 $(C_7H_{10}Si_2F_4^+)$, 215 $(C_6H_{11}Si_2F_4^+)$, 57 $(C_4H_9^+)$. ^{1}H NMR of **2a**/**2b**: δ 1.05 (t), 3 H, $\mathrm{CH_2C}H_3$; 1.17 (s), 9 H, *t*-Bu; 2.33 (qn), 2 H, $\mathrm{C}H_2$; 6.73 (m), 1 H, $=\mathrm{C}H\mathrm{SiF_2}$; 7.19 (m), 1 H, $=\mathrm{C}H\mathrm{CH_2}$. ^{19}F{^{1}H} NMR of **2a**/**2b**: 135.55, 144.31; 138.22, 141.64 ppm (AA′BB′ for the two SiF$_2$ groups of **2a** and/or **2b**). ^{13}C NMR of **2a**/**2b**: δ 179.00 c (c), $=C(t\text{-Bu})\mathrm{SiF_2}$; 173.44 s (d), $=C\mathrm{HCH_2}$; 140.92 t (dt), $=C\mathrm{HSiF_2}$; 117.51 m (m), $(-\mathrm{SiF_2})_2C=$; 38.85 s (s), $(\mathrm{CH_3})_3\mathrm{C}$; 34.22 and 33.63 s (t), CH$_2$ of **2a** or **2b**; 30.06 s (q), $(C\mathrm{H_3})_3\mathrm{C}$; 13.01 s (q), CH$_3$.

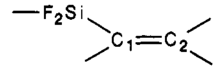
Anal. Calcd for **3a**: C, 44.78; H, 6.00; F, 28.36. Found: C, 44.30; H, 6.15; F, 28.60. Mass spectrum of **3a**: *m*/*e* 268 $(\mathrm{M^+}, C_{10}H_{16}Si_2F_4^+)$, 253 $(C_9H_{13}Si_2F_4^+)$, 239 $(C_8H_{11}Si_2F_4^+)$, 226 $(C_7H_{10}Si_2F_4^+)$, 215 $(C_6H_{11}Si_2F_4^+)$, 57 $(C_4H_9^+)$. ^{1}H NMR of **3a**: δ 1.17 (s), 9 H, *t*-Bu; 1.61 (d), 3 H, $=\mathrm{CHC}H$; 2.30 (m), 1 H, $\mathrm{C}H\mathrm{CH}=$; 5.37 (m), 2 H, $-H\mathrm{C}=\mathrm{C}H-$; 6.73 (tt), 1 H, $=\mathrm{CHSiF_2}$. ^{19}F{^{1}H} NMR of **3a**: 134.38, 136.40, 138.65, 141.74 ppm (ddd), four F of **3a**. ^{13}C NMR of **3a**: δ 179.00 m (m), $=\mathrm{C}(t\text{-Bu})\mathrm{SiF_2}$; 140.92 m (dm), $=C\mathrm{HSiF_2}$; 128.80, s (d), $=C\mathrm{HCH_3}$; 117.77 s (d), $\mathrm{CH}C\mathrm{H}=$; 38.85 s (s), $(\mathrm{CH_3})_3C$; 30.06 s (q), $(C\mathrm{H_3})_3\mathrm{C}$; 18.46 s (q), $C\mathrm{H_3}$; 13.65 m (dm), $(-\mathrm{SiF_2})_2\mathrm{CH}-$. By comparing the spectra, data of **3b** can be obtained.

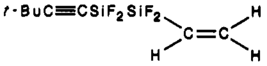
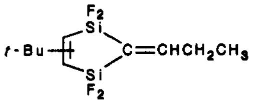
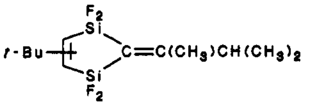
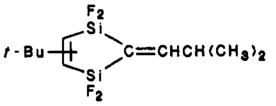
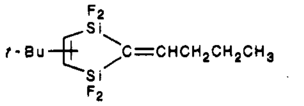
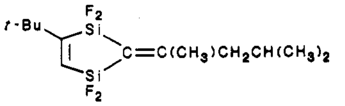
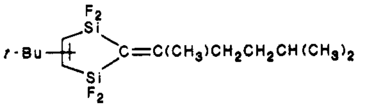
^{1}H NMR of **3b**: same as **3a**. ^{19}F NMR of **3b**: 132.99, 136.40, 139.71, 141.74 ppm (ddd), four F of **3b**. ^{13}C NMR of **3b**: same as **3a** except δ 125.86 s (d), $=C\mathrm{HCH_3}$, and δ 117.24 s (d), $\mathrm{CH}C\mathrm{H}=$.

Preparation of 2c/2d. Equimoles (4.0 mmol) of 1 and (η^4-2,3-dimethyl-1,3-butadiene)tricarbonyliron in 10 mL of *n*-pentane solution were irradiated under nitrogen atmosphere at 50–70 °C for 20 h. After removal of solvent and unreacted (η^4-diene)tricarbonyliron, 0.41 g of **2c**/**2d** was obtained by distillation under vacuum at 90 °C. The ratio of **2c**/**2d** was approximately 1:1. Total yield based on the quantity of 1 was 35%.

Anal. Calcd for **2c**/**2d**: C, 48.64; H, 6.76; F, 25.68. Found: C, 48.77; H, 6.59; F, 25.56. Mass spectrum of **2c**/**2d**: *m*/*e* 296 $(\mathrm{M^+}, C_{12}H_{20}Si_2F_4^+)$, 281 $(C_{11}H_{17}Si_2F_4^+)$, 253 $(C_9H_{13}Si_2F_4^+)$, 212 $(C_6H_8Si_2F_4^+)$, 83 $(C_6H_{11}^+)$, 57 $(C_4H_9^+)$. ^{1}H NMR of **2c**/**2d**: δ 0.95 (d), 6 H, $(\mathrm{C}H_3)_2\mathrm{CH}$; 1.14 (s), 9 H, *t*-Bu; 1.98 (s), 3 H, $=\mathrm{CC}H_3$; 2.88 (m), 1 H, *i*-Pr$\mathrm{C}H$; 6.68 (m), 1 H, $=\mathrm{C}H\mathrm{SiF_2}$. ^{19}F{^{1}H} NMR of **2c**/**2d**: 133.84, 141.21, 134.48, 140.46 ppm (AA′BB′ for the two SiF$_2$ groups

Table II. Experimental and Calculated[8] Chemical Shifts (δ) of Some Vinylsilanes and Alkylidenedisilacyclopentenes (2)



	C-1			C-2		
	obsd	calcd	Δ_1	obsd	calcd	Δ_2
$ClHC{=}CH\text{-}SiF_2SiF_2CH_2CH_2Cl$	123.7	122.6	+1.1	141.9	143.6	-1.7
	113.0	114.1	-1.1	168.1	167.0	+1.1
$CH_2{=}CHSiF_2SiF_3$	130.0	128.3	+1.7	142.8	140.3	+2.5
$CH_2{=}CHSiF_2CH{=}CH_2$	128.0	128.3	-0.3	140.0	140.3	-0.3
 **2a/2b**	117.5	117.6	-0.1	173.4	173.1	-0.3
 **2c/2d**	110.5	107.9	+2.6	189.5	190.9	-1.4
 **2e/2f**	115.0	115.8	-0.8	178.1	180.3	-2.2
 **2i/2j**	118.3	119.1	-0.8	171.4	171.6	-0.2
 **2k/2l**	114.4	112.7	+1.7	183.4	180.7	+2.7
 **2m/2n**	111.7	111.2	+0.5	184.2	182.2	+2.0

of **2c** and/or **2d**). ^{13}C NMR of **2d/2d**: δ 189.49 s (s), $(\text{-}SiF_2)_2C{=}C$; 180.40 c (c), $={C}(t\text{-}Bu)SiF_2$; 140.39 tt (dtt), $=CHSiF_2$; 110.86 m (m), $(\text{-}SiF_2)_2C{=}C$; 44.29, 43.24 s (d), $(CH_3)_2CH$ of **2c** and **2d**; 38.79 s (s), $(CH_3)_3C$; 30.06 s (q), $(CH_3)_3C$ and $=CCH$; 21.33 s (q), $(CH_3)_2CH$.

Preparation of 2g/2h, 2e/2f, and 3d. *n*-Pentane solution (10 mL) containing 4.0 mmol of 1 and 4.0 mmol of (η^4-diene)tricarbonyliron (R_1 = H, R_2 = CH_3) was irradiated under dry nitrogen atmosphere at 30 °C for 20 h. After removal of solvent and unreacted (η^4-diene)tricarbonyliron, about 0.6 g of colorless liquid was obtained by distillation at 90 °C under vacuum. The yield based on the quantity of 1 used was 55%. The colorless liquid contained **2g**, **2h**, **2e**, **2f**, and **3d** in the ratio of 1:1:6:7:5.

Anal. Calcd for **2e/2f**, **2g/2h**, and **3d**: C, 46.811; H, 6.38; F, 26.95. Found: C, 46.62; H, 6.50; F, 26.33. Mass spectrum of **2g/2h**, **2e/2f**, and **3d**: *m/e* 282 (M^+, $C_{11}H_{18}Si_2F_4^+$), 267 ($C_{10}H_{15}Si_2F_4^+$), 252 ($C_9H_{12}Si_2F_4^+$), 215 ($C_6H_{11}Si_2F_4^+$), 57 ($C_4H_9^+$). ^1H NMR of **2g/2h**, **2e/2f**, and **3d**: δ 1.09 (d), $\text{-}CH(CH_3)_2$ of **2g/2h**; 1.15 (s), *t*-Bu of all; 1.59 and 1.69 (s), $=C(CH_3)_2$ of **3d**; 1.85 (c), $(\text{-}SiF_2)_2CH$ of **3d**; 2.43 (m), $\text{-}CH(CH_3)_2$ of **2e/2f**; 5.03 (d), $\text{-}CH{=}C(CH_3)_2$ of **3d**; 6.77 (m), $=CHSiF_2$ of all; 7.11 (m), $(\text{-}SiF_2)_2C{=}CH$ of **2e/2f** (because of the low abundance, signals of **2g/2h** were not resolved). $^{19}F\{^1H\}$ NMR of **2e/2f**: 133.52, 136.62, 139.71, 142.92 ppm (AA′BB′ patterns for the two SiF_2 groups of **2e** and/or **2f**). $^{19}F\{^1H\}$ NMR of **2g/2h**: 134.16, 134.60, 140.68, 141.32 ppm (AA′BB′ patterns for the two SiF_2 groups of **2g** and/or **2h**). $^{19}F\{^1H\}$ NMR of **3d**: 131.55, 134.45 (ddd), $=CHSiF_2$; 137.36, 140.46 ppm (ddd), $=C(t\text{-}Bu)SiF_2$. ^{13}C NMR of **2e/2f**: δ 181.40 m (m), $=C(t\text{-}Bu)SiF_2$; 178.12 s (d), $(\text{-}SiF_2)_2C{=}CH\text{-}$; 140.92 m (dm), $=CHSiF_2$; 115.02 m (m), $(\text{-}SiF_2)_2C{=}CH$; 40.31, 39.78 s (d), $\text{-}CH(CH_3)_2$ of **2e** or **2f**; 38.79 s (s), $(CH_3)C$; 30.00 s (q), $(CH_3)_3C$; 21.74 s (q), $\text{-}CH(CH_3)_2$. ^{13}C NMR of **3d**: δ 181.40 m (m), $=C(t\text{-}Bu)SiF_2$; 140.92 m (dm), $=CHSiF_2$; 133.95 s (s) $\text{-}CH{=}C(CH_3)_2$; 110.39 s (d), $\text{-}CH{=}C(CH_3)_2$; 38.79 s (s), $(CH_3)_3C$; 30.00 s (q), $(CH_3)_3C$; 25.78, 18.16 s (q), $\text{-}CH{=}C(CH_3)_2$; 10.37 m (dm), $\text{-}(SiF_2)_2CH\text{-}$ (^{13}C NMR of **2g/2h** was not observed because of low concentration).

Preparation of 3c. *n*-Pentane solution (10 mL) containing 0.4 mmol of 1, 0.6 mmol of 2,3-dimethyl-1,3-butadiene, and 0.6 mmol of $W(CO)_6$ was irradiated under dry nitrogen at 0 °C for 10 h. After removal of solvent, 0.32 mmol of **3c** was obtained by vacuum distillation at 90 °C. The yield based on the quantity of 1 used was 80%. **3c** could also be prepared by reacting 1 with $(F_2\overline{Si(t\text{-}Bu)C{=}C(H)SiF_2\text{-})W}(CO)_5$ under similar conditions.

Anal. Calcd for **3c**: C, 48.64; H, 6.76; F, 25.68. Found: C, 48.70, H, 6.61; F, 25.57. mass spectrum of **3c**: *m/e* 296 (M^+, $C_{12}H_{20}Si_2F_4^+$), 281 ($C_{11}H_{17}Si_2F_4^+$), 253 ($C_9H_{13}Si_2F_4^+$), 212 ($C_6H_8Si_2F_4^+$), 83 ($C_6H_{11}^+$), 57 ($C_4H_9^+$). ^1H NMR of **3c**: δ 1.19 (s), 9 H, *t*-Bu; 2.10 (s), 9 H, $=CCH_3$; 2.3 (c), 1 H, $(SiF_2)_2CH$; 6.5 (m), 1 H, $=CH$. $^{19}F\{^1H\}$ NMR of **3c**: 130.65 (ddd), 133.05 (ddd), $=CHSiF_2$; 136.01 (ddd), 138.73 ppm (ddd), $=C(t\text{-}Bu)SiF_2$. ^{13}C NMR of **3c**: δ 181.02 tt (tt), $=C(t\text{-}Bu)$; 141.09 tt (dtt), $=CHSiF_2$; 125.51 s (s), $=C(CH_3)_2$; 117.07 s (s), $(CH_3)_2C{=}C(CH_3)$; 38.61 s (s), $(CH_3)_3C$; 29.30 s (q), $(CH_3)_3C$; 20.04 s (q), $=C(CH_2)_3$; 16.70 c (dc), $CH(SiF_2\text{-})_2$.

Isomerization of 3c. A *n*-pentane solution (10 mL) containing 1.0 mmol of **3c** and 5.0 mmol of $Fe(CO)_5$ was irradiated at room temperature for 50 h. After filtration and concentration, the solution was subjected to fractional distillation under vacuum. Equimoles of **2c** and **2d** were collected at 90 °C quantitatively. When the reaction was carried out at −30 °C and followed by ^{19}F NMR, no intermediates or products other than **2c** and **2d** were found during irradiation.

Preparation of Intermediates 5. A *n*-pentane solution (10 mL) containing 4.0 mmol of **1** and 4.0 mmol of $(\eta^4\text{-}C_4H_6)Fe(CO)_3$ was irradiated under nitrogen atmosphere at −30 °C for 24 h. The reacting solution was subjected to degassing every 4 h. After filtration and removal of solvent and excess $(\eta^4\text{-}C_4H_6)Fe(CO)_3$, a dark red liquid containing 80% of **5** and 20% of $(F_2Si(t\text{-}Bu)C{=}C(H)SiF_2{-})Fe(CO)_4$ was obtained. $(F_2Si(t\text{-}Bu)C{=}C(H)SiF_2{-})Fe(CO)_4$ could be removed by prolonged pumping at room temperature, but at considerable expense of **5**. The yield of **5** was 48% on the basis of the quantity of **1** used. When **5** was heated to 120 °C, it converted to **2a**, **2b**, **3a**, and **3b** (**2a**:**2b**:**3a**:**3b** = 8:8:3:3) quantitatively.

Mass spectrum of **5**: *m/e* 408 (M^+, $C_{10}H_{16}Si_2F_4Fe(CO)_3^+$), 380 ($C_{10}H_{16}Si_2H_4Fe(CO)_2^+$), 352 ($C_{10}H_{16}Si_2F_4Fe(CO)^+$), 324 ($C_{10}H_{16}Si_2F_4Fe^+$), 268 ($C_{10}H_{16}Si_2F_4^+$), 253 ($C_9H_{13}Si_2F_4^+$), 57 ($C_4H_9^+$). $^{19}F\{^1H\}$ NMR of **5**: 89.97 and 105.46 (d), $=CHSiF_2$; 129.44 and 137.50 ppm (d), $=C(t\text{-}Bu)SiF_2$. ^{13}C NMR of **5**: δ 207.36 s (s), CO; 179.78 c (c), $=C(t\text{-}Bu)SiF_2$; 140.30 t (dt), $=CHSiF_2$; 117.53 s (d), $CH{\dashv}CH{\dashv}CH$; 91.35 s (d), ${\dashv}CHCH_3$; 70.25 t (dt), SiF_2CHCH; 41.43 s (s), $(CH_3)_3C$; 29.88 s (q), $(CH_3)_3C$; 18.46 s (q), CH_3.

Preparation of Intermediates 6/7. A *n*-pentane solution (10 mL) containing 6.0 mmol of **1** and 6.0 mmol of $(\eta^4\text{-}C_4H_6)Fe(CO)_3$ was irradiated under nitrogen atmosphere at 50–70 °C for 12 h. The reaction mixture was degassed every 4 h during the irradiation. After removal of solvent and excess $(\eta^4\text{-}C_4H_6)$ $Fe(CO)_3$, a colorless liquid was obtained by distillation under vacuum. *n*-Pentane (5 mL) and 0.4 mL of $Fe(CO)_5$ were added to this colorless liquid, and the solution was irradiated at −30 °C for 3 days. After filtration the filtrate was subjected to trap-to-trap distillation on a vacuum line. The fraction collected at 0 °C contained 0.13 g (0.3 mmol) of **6**/**7** with relative abundance approximately 1:1. The yield based on the quantity of **1** used was 5%. (The fraction passing through the trap of 0 °C collected at −50 °C contained 0.44 g of **2a**/**2b**, yield 27%.) A 1:1 mixture of **6**/**7** could also be prepared by irradiating 5.0 mmol of **2a** and 8.0 mmol of $Fe(CO)_5$ in a *n*-pentane solution at −30 °C for 3 days. The yield based on **2a** was 95%.

Mass spectrum of **6**/**7**: *m/e* 436 (M^+, $C_{10}H_{16}Si_2F_4Fe(CO)_4^+$), 408 ($C_{10}H_{16}Si_2F_4Fe(CO)_3^+$), 380 ($C_{10}H_{16}Si_2F_4Fe(CO)_2^+$), 352 ($C_{10}H_{16}Si_2F_4Fe(CO)^+$), 324 ($C_{10}H_{16}Si_2F_4Fe^+$), 268 ($C_{10}H_{16}Si_2F_4^+$), 253 ($C_9H_{13}Si_2F_4^+$), 57 ($C_4H_9^+$). $^{19}F\{^1H\}$ NMR of **6**/**7**: 117.85, 132.40; 126.67, 146.17 (ddd), four **F** of **6** or **7**; 119.71, 141.37; 124.66, 139.36 ppm (ddd), four F or **7** or **6**. ^{13}C NMR of **6**/**7**: δ 207.36 s (s), CO; 181.46 m (m), $=C(t\text{-}Bu)SiF_2$; 141.21 t (dt), $=CHSiF_2$; 70.49 s (d), $=CHCH_3$; 38.96 s (s), $(CH_3)_3C$; 36.45 and 34.98 s (d), $CH{=}CHCH_3$ of **6** or **7**; 30.18 s (q), $(CH_3)_3C$; 18.22 s (q), CH_3; 13.00 m (dm), $(\text{-}SiF_2)_2CH$.

Preparation of Intermediate 8. A *n*-pentane solution (10 mL) containing 6.0 mmol of **1** and 6.0 mmol of (η^4-2,3-dimethyl-1,3-butadiene)tricarbonyliron was irradiated under dry nitrogen atmosphere at −10 °C for 30 h. After removal of solvent and prolonged pumping to remove unreacted reactants, about 50 mg of **8** was obtained as a brown liquid. The yield based on the quantity of **1** was about 2%. When **8** was heated above 120 °C, it converted to **2c**/**2d** quantitatively.

Mass spectrum of **8**: *m/e* 436 (M^+, $C_{12}H_{20}Si_2F_4Fe(CO)_3^+$), 408 ($C_{12}H_{20}Si_2F_4(CO)_2^+$), 380 ($C_{12}H_{20}Si_2F_4e(CO)^+$), 352 ($C_{12}H_{20}Si_2F_4Fe^+$), 296 ($C_{12}H_{20}Si_2F_4^+$), 281 ($C_{11}H_{17}Si_2F_4^+$), 253 ($C_9H_{13}Si_2F_4^+$), 57 ($C_4H_9^+$). $^{19}F\{^1H\}$ NMR of **8**: 94.28 (d), 101.03 (d), $=CHSiF_2$; 127.05 (d), 131.13 ppm (d), $=C(t\text{-}Bu)SiF_2$.

Preparation of 2i, 2j, 3e, 3f, 2k, 2l, 2m, and 2n. General Procedures. A solution of 2.0 mmol of $(F_2Si(t\text{-}Bu)C{=}C(H)SiF_2{-})Fe(CO)_4$ and 4.0 mmol of the respective diene in 10 mL of *n*-pentane in a quartz Schlenk tube was irradiated at −30 °C or 30 °C (see Table I) for 3–7 days to exhaust compound $(F_2Si(t\text{-}Bu)C{=}C(H)SiF_2{-})Fe(CO)_4$. The solution was then concentrated, and the residue was distilled under vacuum at 80–90 °C to give the products. In case that unreacted $(F_2Si(t\text{-}Bu)C{=}C(H)SiF_2{-})Fe(CO)_4$ and/or side reaction product $(\eta^4\text{-dienes})Fe(CO)_3$ was present, further purification was carried out by heating the distillate with excess PPh_3 to 150–160 °C for 4 h, followed by vacuum distillation. Yield was based on the compound $(F_2Si(t\text{-}Bu)C{=}C(H)SiF_2{-})Fe(CO)_4$ consumed. These compounds could also be prepared by reacting **1** with respective $(\eta^4\text{-dienes})Fe(CO)_3$ under similar conditions.

(i) **2i**, **2k**, **3e**, and **3f** (molar ratio 6:6:1:1): yield 70%, colorless liquid. Anal. Calcd for **3i**/**3j** and **4e**/**4f**: C, 46.81; H, 6.38; F, 26.95. Found: C, 46.78; H, 6.45; F, 26.22. Mass spectrum of **2i**/**2j** and **3e**/**3f**: *m/e* 282 (M^+, $C_{11}H_{18}Si_2F_4^+$), 267 ($C_{10}H_{15}Si_2F_4^+$), 252 ($C_9H_{12}Si_2F_4^+$) 215 ($C_6H_{11}Si_2F_4^+$), 68 ($C_5H_8^+$), 57 ($C_4H_9^+$). ^1H NMR of **2i** and **2j** (sample containing over 85% of **2i**/**2j** can be obtained by prolonged irradiating the mixture with $Fe(CO)_5$: δ 0.94 (t), 3 H, CH_2CH_3; 1.17 (s), 9 H, *t*-Bu; 1.54 (c), 2 H, CH_2CH_3; 2.35 (q), 2 H, $=CHCH_2$; 6.80 (m), 1 H, $=CHSiF_2$; 7.26 (m), 1 H, $=CHCH_2$ (last two assignments confirmed by H–H decoupling). $^{19}F\{^1H\}$ NMR of **2i** and **2j**: 135.66, 144.27; 138.41, 142.00 ppm (AA′BB′ patterns for the two SiF_2 groups of **2i** and **2j**). ^{13}C NMR of **2i** and **2j**: δ 180.94 m (m), $=C(t\text{-}Bu)SiF_2$; 171.44 s (d), $=CHCH_2$; 140.39 tt (dtt), $=CHSiF_2$; 118.30 m (m), $=C(SiF_2)_2$; 42.36 and 41.72 s (t), $=CHCH_2$ of **2i** or **2j**; 38.38 s (s), $C(CH_3)_3$; 29.65 s (q), $C(CH_3)_3$; 21.62 s (t), CH_2CH_3; 13.54 s (q), CH_2CH_3. $^{19}F\{^1H\}$ NMR of **3e** and **3f** (obtained by comparing the spectra): 131.99, 133.31, 134.91, 136.40 (double intensity), 137.58 (double intensity), 138.97 ppm (dd), four F of **3e** and **3f**. ^{13}C NMR of **3e** and **3f** (obtained by comparing the spectra): δ 180.94 m (m), $=C(t\text{-}Bu)$; 140.49 tt (dtt), $=CHSiF_2$; 134.88 and 133.06 s (d), $=CHCH_2$ of **3e** or **3f**; 115.02 s (d), $CHCH{=}$; 38.38 s (s), $C(CH_3)_3$; 29.65 s (q), $C(CH_3)_3$; 26.02 s (t), CH_2CH_3; 13.54 s (q), CH_2CH_3, 13.50 m (dm), $CH(SiF_2)_2$.

(ii) **2k** and **2l** (molar ratio 3:1): yield 80%, colorless liquid. Anal. Calcd for **2k**/**2l**: C, 50.32; H, 7.10; F, 24.52. Found: C, 50.45; H, 7.33; F, 24.21. mass spectrum of **2k** and **2l**: *m/e* 310 (M^+, $C_{13}H_{22}Si_2F_4^+$), 295 ($C_{12}H_{19}Si_2F_4^+$), 268 ($C_{10}H_{16}Si_2F_4^+$), 253 ($C_9H_{13}Si_2F_4^+$), 212 ($C_6H_8Si_2F_4^+$), 96 ($C_7H_{12}^+$), 57 ($C_4H_9^+$). ^1H NMR of **2k** and **2l**: δ 0.82 (d), 6 H, $CH(CH_3)_2$; 1.09 (s), 9 H, *t*-Bu; 1.76 (c), 1 H, $CH(CH_3)_2$; 1.95 (s) 3 H, $=C(CH_3)CH_2$; 2.14 (d), 2 H, CH_2; 6.60 (m), 1 H, $=CHSiF_2$. $^{19}F\{^1H\}$ NMR of **2k** and **2l**: 133.77, 142.29; 135.85, 140.35 ppm (AA′BB′ patterns for the two SiF_2 groups of **2k** and **2l**). ^{13}C NMR of **2k** and **2l**: δ 183.39 s (s), $=CCH_2$; 180.98 m (m), $=C(t\text{-}Bu)SiF_2$; 141.09 tt (dtt), $=CHSiF_2$; 114.43 m (m), $=C(SiF_2)_2$; 55.14 and 54.14 s (t), CH_2 of **2k** or **2l**; 38.96 s (s), $C(CH_3)_3$; 30.35 s (q), $C(CH_3)_3$ and $=C(CH_3)CH_2$; 28.01 s (d), CH; 22.79 s (q), $CH(CH_3)_2$.

(iii) **2m** and **2n** (molar ratio 1:1): yield 68%, colorless liquid. Mass spectrum of **2m** and **2n**: *m/e* 324 (M^+, $C_{14}H_{24}Si_2F_4^+$), 309 ($C_{13}H_{21}Si_2F_4^+$), 296 ($C_{12}H_{20}Si_2F_4^+$), 281 ($C_{11}H_{18}Si_2F_4^+$), 268 ($C_{10}H_{16}Si_2F_4^+$), 215 ($C_6H_{11}Si_2F_4^+$), 110 ($C_8H_{14}^+$), 57 ($C_4H_9^+$). ^1H NMR of **2m** and **2n**: δ 0.94 (d), 6 H, $CH(CH_3)_2$; 1.19 (s) 9 H, *t*-Bu; 1.50 (c), 3 H, $CH_2CH(CH_3)_2$; 2.13 (s), 3 H, $=C(CH_3)CH_2$; 2.36 (c), 2 H, $C(CH_3)CH_2$; 6.73 (m), 1 H, $=CHSiF_2$. $^{19}F\{^1H\}$ NMR of **2m** and **2n**: 135.22, 142.20; 135.89, 141.55 ppm (AA′BB′ patterns for the two SiF_2 groups of **2m** and **2n**). ^{13}C NMR of **2m** and **2n**: δ 184.22 s (s), $=C(CH_3)CH_2$; 180.06 t (t), $=C(t\text{-}Bu)SiF_2$; 139.98 m (dm), $=CHSiF_2$; 111.68 m (m), $=C(SiF_2)_2$; 43.36 and 37.97 s (t), CH_2CH of **2m** or **2n**; 38.26 s (s), $C(CH_3)_3$; 42.42 s (t)8, CH_2CH_2CH; 29.71 s (q), $C(CH_3)_3$ and $CH_3C{=}$; 28.54 s (d), $-CH$; 22.38 s (q), $CH(CH_3)_2$.

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Registry No. **1**, 36091-97-1; **2a**, 109034-53-9; **2b**, 109034-54-0; **2c**, 109034-56-2; **2d**, 109034-57-3; **2e**, 109307-44-0; **2f**, 109307-45-1; **2g**, 109307-46-2; **2h**, 109307-47-3; **2i**, 109307-48-4; **2j**, 109307-49-5; **2k**, 109307-52-0; **2l**, 109307-53-1; **2m**, 109283-96-7; **2n**, 109283-95-6; **3a**, 109064-32-6; **3b**, 109034-55-1; **3c**, 109283-40-1; **3d**, 109283-39-8; **3e**, 109307-50-8; **3f**, 109307-51-9; **5**, 109284-68-6; **6**, 109284-67-5; **7**, 109362-51-8; **8**, 109284-69-7; $F_2Si(t\text{-}Bu)C{=}CHSiF_2Fe(CO)_4$, 78514-11-1; $F_2Si(t\text{-}Bu)C{=}CHSiF_2Mo(CO)_5$, 75311-40-9; $W(CO)_6$, 14040-11-0; $\overline{F_2Si(t\text{-}Bu)C{=}CHSiF_2}W(CO)_5$, 109283-41-2; $Fe(CO)_5$, 13463-40-6; (η^4-1,3-butadiene)tricarbonyliron, 12078-32-9; 1,3-butadiene, 106-99-0; (η^4-2,3-dimethyl-1,3-butadiene)tricarbonyliron, 31741-56-7; (η^4-2-methyl-1,3-butadiene)tricarbonyliron, 32731-93-4; 2,3-dimethyl-1,3-butadiene, 513-81-5; (*E*)-1,3-pentadiene, 2004-70-8; (*E*)-(η^4-1,3-pentadiene)tricarbonyliron, 32732-71-1; 2,4-dimethyl-1,3-pentadiene, 1000-86-8; (η^4-2,4-dimethyl-1,3-pentadiene)tricarbonyliron, 12264-19-6; (*E*)-2,5-dimethyl-1,3-hexadiene, 927-98-0; (*E*)-(η^4-2,5-dimethyl-1,3-hexadiene)tricarbonyliron, 32732-63-1.

Cycloaddition Reactions of Tetrafluorodisilacyclobutene with 1,3-Butadienes Mediated by Metal Carbonyls. 2. Direct Cycloaddition vs. Isomerization

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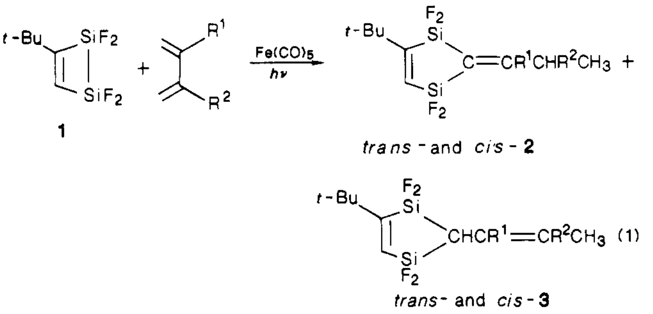
A systematic study of the effect of substituents at both terminal carbons of 1,3-dienes is carried out in the cycloaddition reactions with 1,1,2,2-tetrafluoro-1,2-disilacyclobutene mediated by transition-metal carbonyls. Correlation between the structures of intermediates and reaction pathways is established. Discussion is made in terms of direct cycloaddition vs. isomerization.

We recently reported the novel cycloaddition reactions between 1,1,2,2-tetrafluorodisilacyclobutene (1) and various conjugated dienes mediated by transition-metal carbonyls.[1,2] In the Fe-mediated reactions of 2,3-substituted butadiene derivatives, very unusual 1,1-addition reactions occurred where two Si added to the same carbon (C-1) and the hydrogens were shifted from C-1 to C-4 and C-3.[2] Products corresponding to the usual 1,2 or 1,4-addition[3] reactions were not found in these reactions (eq 1).

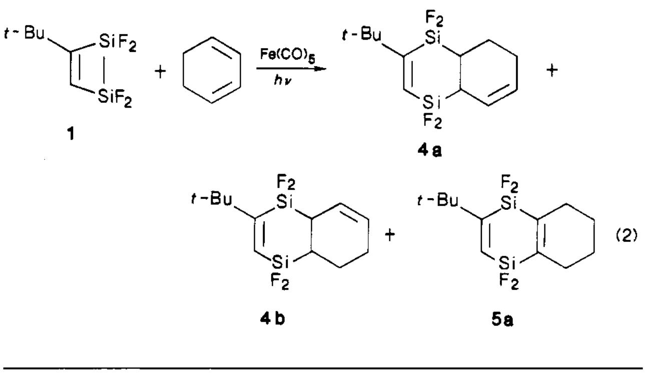


1

trans-and *cis*-2

trans- and *cis*-3

One particular case of 1,4-disubstituted dienes, namely, 1,3-cyclohexadiene, was studied;[1] products from direct 1,2-addition (4a,b) as well as H-shift isomerization (5a) were obtained (eq 2).



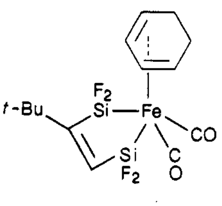
1

4a

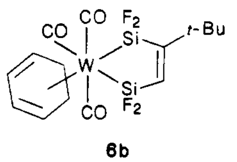
4b

5a

It was believed that in all these related reactions a π-complex of disilametallacycle existed as the intermediate,[4-6] the electronic and steric structures of which determined the reaction pathways following the decomposition of such an intermediate. In the case of the reaction of cyclohexadiene, such intermediates (6a,b) were isolated and the structures have been determined by X-ray diffraction experiment.[1]



6a



6b

This paper reports the results of direct addition vs. isomerization (via H shift) in the M-mediated (M = Fe, Cr, Mo, W) cycloaddition reactions between 1 and 1,3-butadienes with both terminal carbons substituted.

Results and Discussion

The experimental conditions and reaction products of the reactions of 1 with *trans,trans*-2,4-hexadiene, *trans,-cis*-2,4-hexadiene, 2,5-dimethyl-2,4-hexadiene, and cyclohexadiene are summarized in Table I. Two major types of product were obtained, 1,4-disilacyclohexenes and 1,4-

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