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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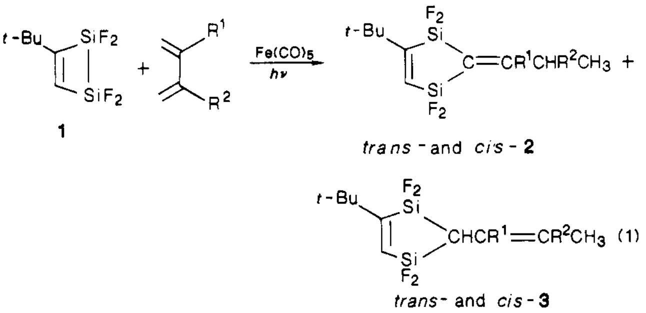
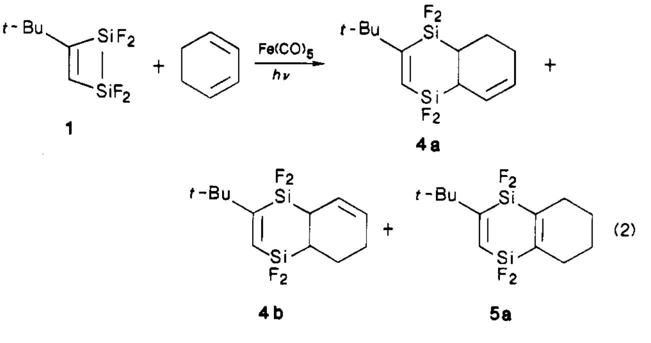
Received April 3, 1987

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.

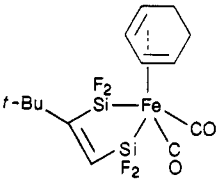
We recently reported the novel cycloaddition reactions between 1,1,2,2-tetrafluorodisilacyclobutene (1) and various conjugated dienes mediated by transition-metal carbonyls.[1,2] In the Fe-mediated reactions of 2,3-substituted butadiene derivatives, very unusual 1,1-addition reactions occurred where 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).



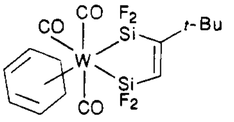
One particular case of 1,4-disubstituted dienes, namely, 1,3-cyclohexadiene, was studied;[1] products from direct 1,2-addition (4a,b) as well as H-shift isomerization (5a) were obtained (eq 2).



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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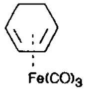
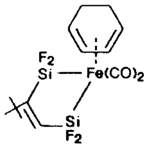
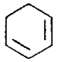
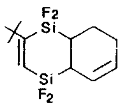
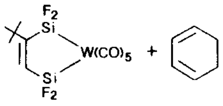
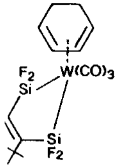
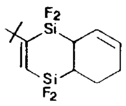
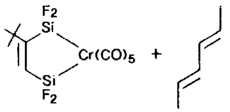
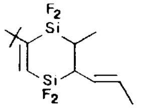
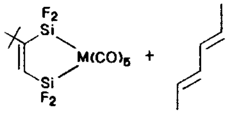
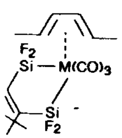
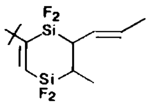
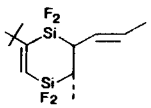
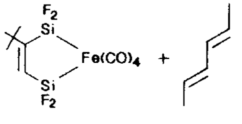
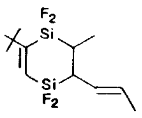
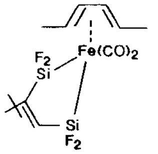
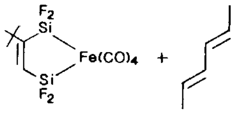
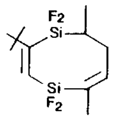
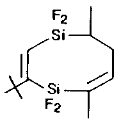
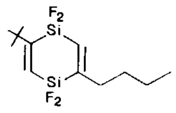
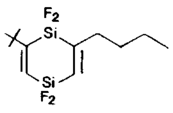
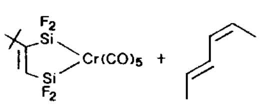
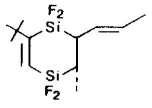
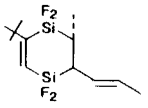
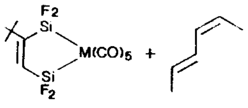
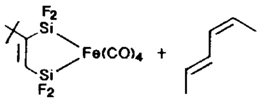
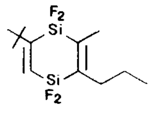
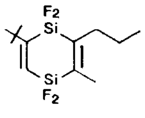
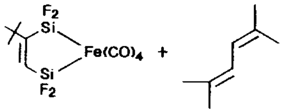
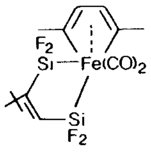
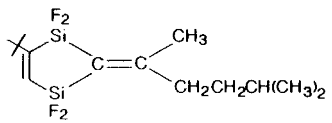
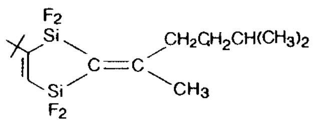
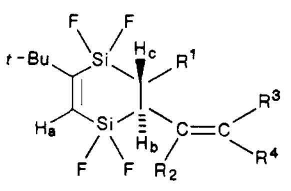
Table I. Products from the Reactions of 1 with Various Dienes Mediated by Metal Carbonyl

reactns	conditns	products
1 + 	$h\nu$, 0 °C	 **6a**
1 +  + **6a** (catalyst)	100 °C	 **4a**
	$h\nu$, 0 °C	 **6b**
6b decomposition	150 °C	 **4b**
	$h\nu$, 0 °C	 **4c**,  (trace)
 M = Mo, W	$h\nu$, −30 °C	**4c**
	$h\nu$, −50 °C	 **6e**: M = Mo **g**: M = W
	$h\nu$, 0 °C	**4c**,  **4d**,  **4e** (trace)
	$h\nu$, −30 °C	 **4c**  **6c**
	$h\nu$, 30 °C	 **8a**  **8b**
6c decomposition	70 °C	 **5c**  **5d**
	$h\nu$, 0 °C	 **4e**  **4f**
 M = Mo, W	$h\nu$, −30 °C	**4e**
	90 °C or $h\nu$, 90 °C	**4e**, **4f**, **4c** (trace)
	$h\nu$, −30 °C	**4e**
 or  + 1	$h\nu$, −30 °C $h\nu$, 60 °C	 **5e**  **5f**
	$h\nu$, −30 °C	 **6d**
6d decomposition	150 °C	 **11a**  **11b**

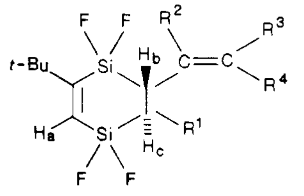
disilacyclohexadienes, designated as **4** and **5**, respectively.

Among the compounds in the **4** family, **4a**, **4b**, **4c**, and **4e** can be prepared in pure form. Other members of the **4** family exist in isomer mixtures. While the mass spectra and elemental analyses suggest the proposed molecular formula, the structure identification is not so straightforward.

Taking an isomer pair in the general form of the **4** family for example, the only difference between the two forms is the relative positions of the *tert*-butyl group and the vinyl group attached to the ring.



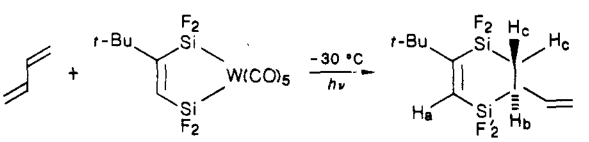
a



b

The ^1H and ^{13}C NMR spectra are in general entirely consistent with both structures so are not very helpful. The strategy used to solve the problem can be described as follows: (i) the ^{19}F NMR spectrum with selective decoupling of H_a, i.e., $^{19}F\{^1H\}_{H_a}$, will show which SiF_2 group locates near H_a, (ii) the ^{19}F NMR spectrum with selective decoupling of the allylic proton, i.e., $^{19}F\{^1H\}_{H_b}$, will tell which SiF_2 is closer to the vinyl group, and (iii) to conclude that the structure is **a** if the same SiF_2 locates in the neighborhood of both H_a and H_b. On the other hand, if H_a is closer to one SiF_2 group and H_b is closer to the other, the structure is **b**.

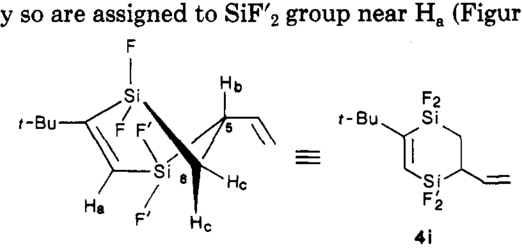
One other factor further complicates the case. On closer inspection of the molecular model of 1,4-disilacyclohex-2-ene, one immediately finds that each of the equatorially bonded atoms at C-5 and C-6 of the six-membered ring forms a W-shaped relationship with one of the fluorines four bonds away. If a hydrogen atom is bonded at the equatorial position, the four-bond W-shape H–F coupling constants $^4J_{H-F}$ may be comparable in size to the three-bond coupling constants $^3J_{H-F}$. Take the simplest case **4i**, for example. Compound **4i** can be prepared by reacting 1,3-butadiene with disilametallacycle $(F_2Si(t\text{-}Bu)C{=}C(H)SiF_2\text{-})W(CO)_5$ photochemically at –30 °C (although the Fe-mediated reaction yielded predominately products of 1,1-addition[2]) (eq 3).



(3)

4i

Compound **4i** shows in its ^{19}F NMR spectrum four complex resonances of equal intensity at 138.6, 139.5, 138.9, and 141.5 ppm. The $^{19}F\{^1H\}_{H_a}$ selective proton decoupling shows that the former two change only slightly so are assigned to SiF_2 group which is close to the *tert*-butyl group, whereas the latter two change much more significantly so are assigned to SiF'_2 group near H_a (Figure 1b).



4i

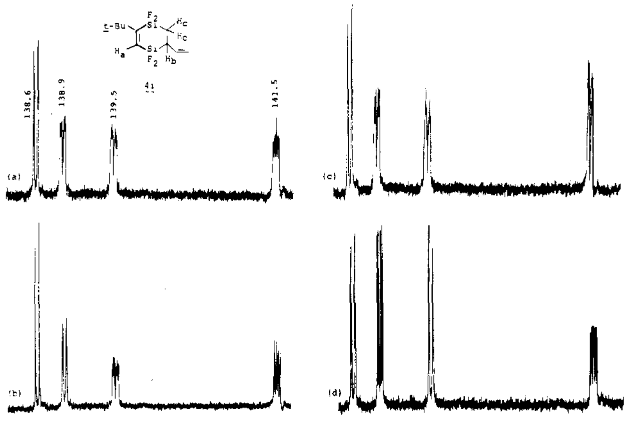


Figure 1. (a) ^{19}F, (b) $^{19}F\{^1H\}_{H_a}$, (c) $^{19}F\{^1H\}_{H_b}$, and (d) $^{19}F\{^1H\}_{H_c}$ spectra of compound **4i**.

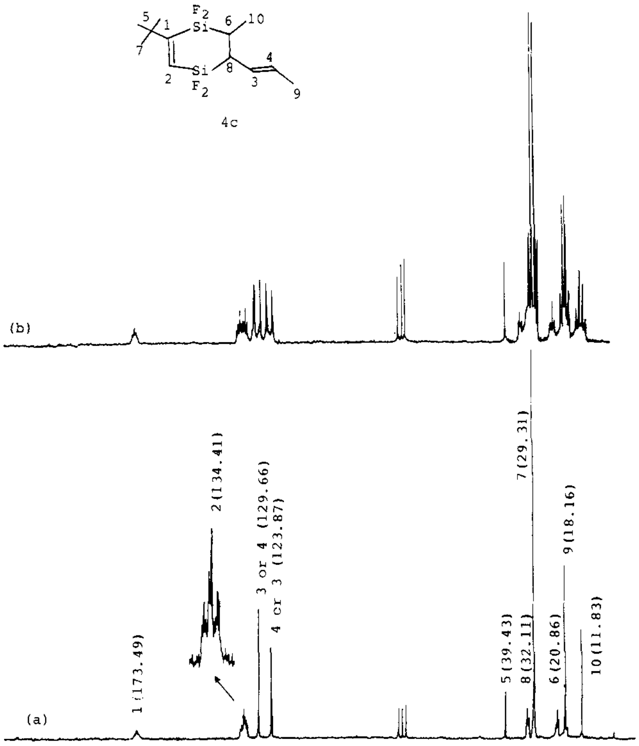
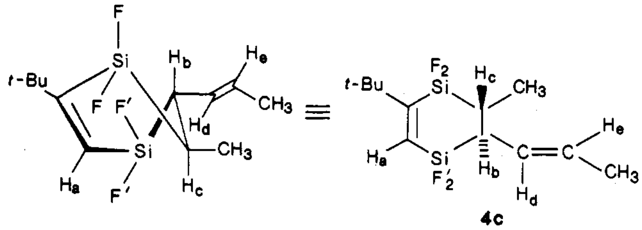


Figure 2. (a) $^{13}C\{^1H\}_{BB}$ and (b) $^{13}C\{^1H\}_{CW}$ spectra of compound **4c**.

When H_b is decoupled selectively, the $^{19}F\{H\}_{H_b}$ spectrum (Figure 1c) shows that a coupling of 9 Hz has been removed from the resonance at 141.5 ppm (F'). When H_c is decoupled selectively, both resonance at 139.5 (F) and 138.9 ppm (F') are simplified (Figure 1d). The former loses a coupling of 9 Hz whereas the latter loses a coupling of 3 Hz. Since the decoupling of H_c affects both F and F', one of the two effects must have come from a W-shaped long-range coupling. If 9 Hz is attributed to the three-bond coupling between H_b–F' and H_c–F whereas 3 Hz is attributed to the four-bond W-shaped coupling between H_c–F' (this will be discussed in more detail later), the structure is **4i** as shown.

In the case of compound **4c** the ^{13}C NMR spectrum fits the structure perfectly but no conclusion can be drawn because it fits the structure of **4d** equally well (Figure 2). The ^1H NMR spectrum shows at δ 5–6 an AB system with a coupling of 15.7 Hz, which indicates H_d and H_e are trans to each other. The key problem, the position of the *tert*-butyl group relative to that of the vinyl group, remains unsettled.

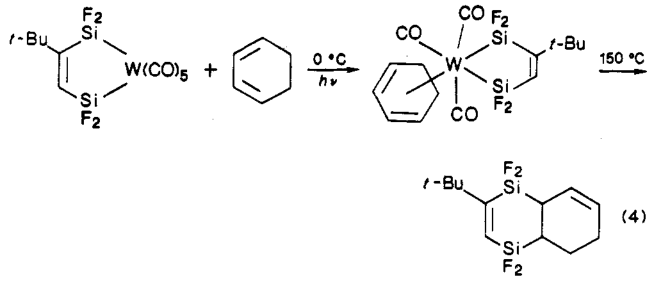


4c

The ^{19}F NMR spectrum shows four complex resonances at 137.39, 139.59, 144.20, and 147.30 ppm. The ^{19}F{^{1}H}$_{H_a}$ spectrum shows the resonances at 137.39 and 139.59 ppm have larger coupling with H_a and therefore are assigned to SiF$'_2$ (Figure 3b). A two-dimensional COSY NMR shows that H_b and H_c are strongly coupled so they are trans to each other. A NOESY experiment further shows that H_b and H_c are spacially far apart. The conclusion is that H_b and H_c both occupy the axial positions and no W-shape bonding relationship between H_b/H_c and the fluorines is possible in this molecule. Whatever $J_{H_b\text{-}F}$ and/or $J_{H_c\text{-}F}$ observed in this case must be due to the three-bond coupling.

The ^{19}F{^{1}H}$_{H_b}$ and ^{19}F{^{1}H}$_{H_c}$ NMR spectra are shown in parts c and d of Figure 3, respectively. It is clear that H_b couples strongly with the F$'$ at 139.59 ppm and H_c couples strongly with the F at 147.30 ppm, both with $^3J_{H\text{-}F}$ = 9 Hz. Now we conclude that the structure is **4c**.

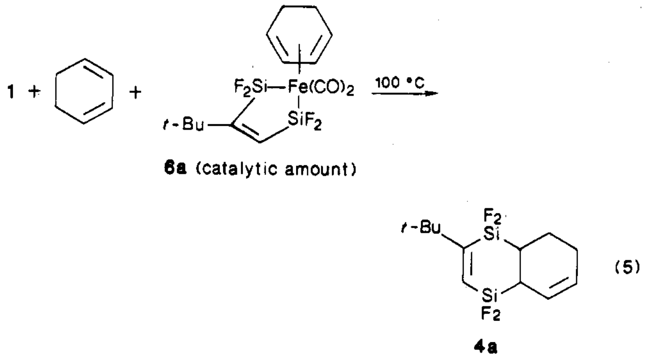
The structures of other members of the **4** family are determined by the same procedures as described above. These spectral analyses are further confirmed in the case of **4b**, the product from the reaction of cyclohexadiene (eq 4).



(4)

4b

The structure of **4b** is consistent with that derived from the analysis of the crystal structure of the intermediate **6b** from which **4b** is resulted.[1] Since the structure of **4b** is certain, the structure of its isomer **4a** is also unequivocal. Compound **4a** in 95% purity can be obtained by the catalytic reaction described (eq 5).



4a

In all these cases where the structure determination is unequivocal, the three-bond coupling $^3J_{H\text{-}F}$ is larger than the four-bond W-shape coupling $^4J_{H\text{-}F}$. In fact, all compounds in the **4** family thus identified show that $^3J_{H\text{-}F}$ has values in the range of 7–14 Hz whereas the $^4J_{H\text{-}F}$ values range from 3 to 7 Hz.

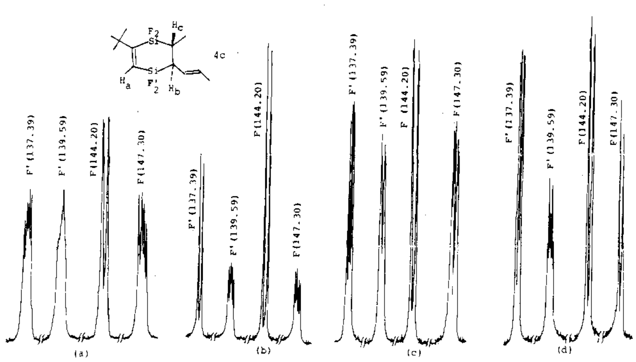


Figure 3. (a) ^{19}F, (b) ^{19}F{^{1}H}$_{H_a}$, (c) ^{19}F{^{1}H}$_{H_b}$, and (d) ^{19}F{^{1}H}$_{H_c}$ NMR spectra of compound **4c**.

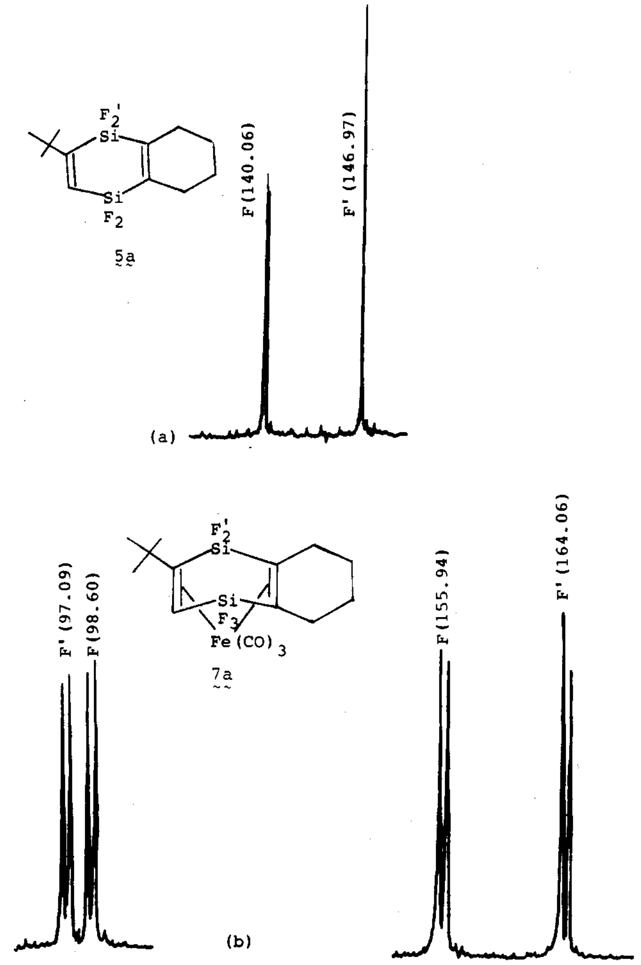
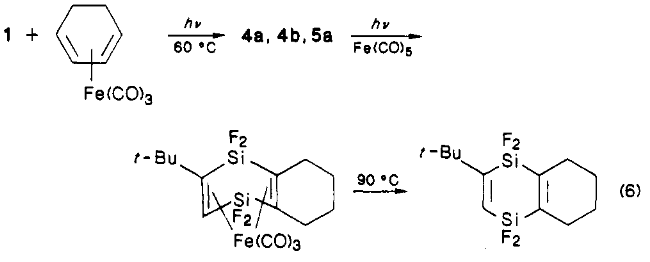


Figure 4. (a) ^{19}F NMR spectrum of **5a**. (b) ^{19}F{^{1}H} NMR spectrum of compound **7a**.

The other class of products is the derivatives of 1,4-disilacyclohexa-2,5-diene, designated by **5**. Although most compounds in **5** family exist in isomer mixtures, the redistilled samples from each reaction do show satisfactory results of elemental analyses and mass spectra which support the proposed molecular formula.

Compound **5a** can be obtained in pure form. Its purification can be achieved via complexation with iron pentacarbonyl (eq 6).

The ^{19}F{^{1}H} NMR spectrum of **5a** shows two resonances at 140.06 and 146.97 ppm, indicating the two fluorine atoms in each SiF$_2$ group are equivalent (Figure 4a). The ^{13}C NMR spectrum of **5a** shows four sp^2 carbons with strong fluorine coupling at δ 174.23, 150.75, 149.81, and 134.59, respectively (Figure 5a). These spectral features fit the characteristics of the structure of **5a**. It is partic-

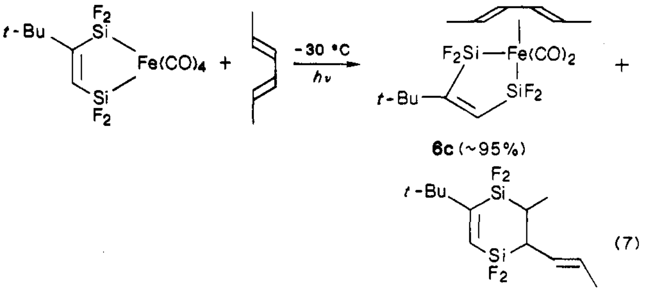


7a **5a**

ularly interesting to note that on complexing with Fe(CO)$_3$, the ^{19}F{^{1}H}$_{BB}$ NMR spectrum changes to two sets of AX patterns, indicating the two fluorine atoms in each SiF$_2$ become nonequivalent (Figure 4b). This is the natural consequence of the boat-form configuration of the 1,4-disilacyclohexa-2,5-diene ring as required by the two olefin–Fe bondings in complex **7a**. The ^{13}C NMR spectrum of **7a** shows large upfield shifts of the resonances of the four sp^2 carbons (shifted to 122.53, 96.52, 86.56, and 50.33 ppm, respectively; Figure 5b), which is a strong evidence that the four olefin carbons are bonded to the metal. Furthermore, the coupling patterns of these carbons in the spectrum of **5a** are all triplets due to coupling with groups of two equivalent fluorines whereas those in the spectrum of **7a** show doublets of doublets of doublets of doublets, as the consequence of being coupled with four nonequivalent fluorines.

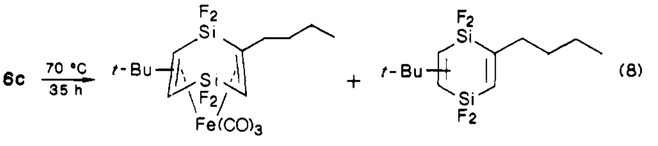
In the reactions of *trans,trans*-2,4-hexadiene, 2,5-dimethyl-2,4-hexadiene, and 1,3-cyclohexadiene, reaction intermediates **6a–h** were isolated. The structures of these relatively stable intermediates are determined by the mass spectra, elemental analysis, and NMR spectroscopy. In the cases of **6a** and **6b** single-crystal x-ray diffraction experments were carried out to confirm the structures.[1]

It was found that under different experimental conditions the reaction of *trans,trans*-2,4-hexadiene with ($\overline{\text{SiF}_2(t\text{-Bu})\text{C}{=}\text{C(H)SiF}_2\text{-})}\text{Fe(CO)}_4$ resulted in different results. When reacted photochemically at −30°, the diene–disilametallacycle intermediate **6c** was obtained as the overwhelmingly major product (>95% relative yield) (eq 7).



4c

Intermediate **6c** could be obtained in pure form by recrystallization. When **6c** was subjected to thermal decomposition at 70 °C, products **5c**/**5d** and **7c**/**7d** and trace amount of an unidentified product were obtained (eq 8).

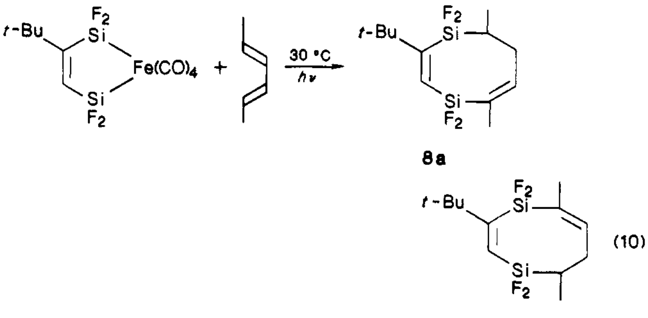


7c/7d **5c/5d**

The isomer pair **7c**/**7d** could be separated from the product mixture by fractional distillation. When a sample of **7c**/**7d** was heated at 150 °C for 30 min, **5c** and **5d** were obtained quantitatively. When the mixture of **5c**/**5d** was treated with Fe(CO)$_5$ photochemically at −30 °C, the reverse reaction occurred and **7c**/**7d** was recovered (eq 9).

$$\text{7a/7d} \underset{\text{Fe(CO)}_5,\ h\nu,\ -30\ °\text{C}}{\overset{150\ °\text{C},\ -\text{Fe(CO)}_3}{\rightleftarrows}} \text{5c/5d} \qquad (9)$$

However, when ($\overline{\text{SiF}_2(t\text{-Bu})\text{C}{=}\text{C(H)SiF}_2\text{-})}\text{Fe(CO)}_4$ and *trans,trans*-2,4-hexadiene were irradiated at 30 °C, the major products obtained were neither **5c**/**5d** nor **4c** but the eight-membered ring compounds **8a**/**8b** (eq 10).



8b

An attempt was made to follow the reaction process by ^{19}F NMR at 0 °C. The first change of the spectrum was the appearance of the spectra that were assigned to intermediates **9** and **6c** followed by the appearance of the spectra of **8a**/**8b** and a new spectrum assigned to another intermediate **10**. The spectrum of **6c**, showed up though in the early stage of the irradiation, was kept at rather low intensity (≤10% relative to the rest of the spectra.) At

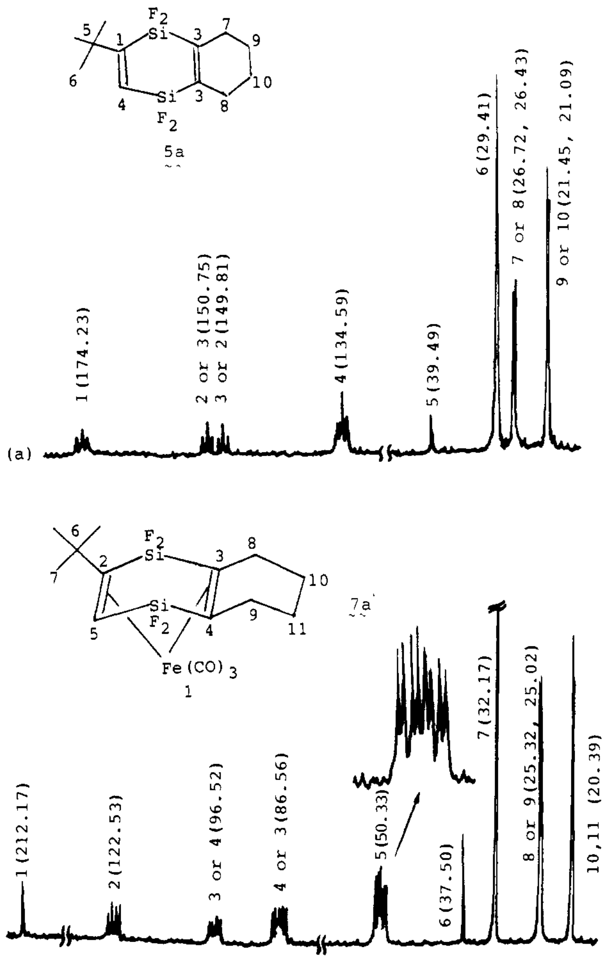
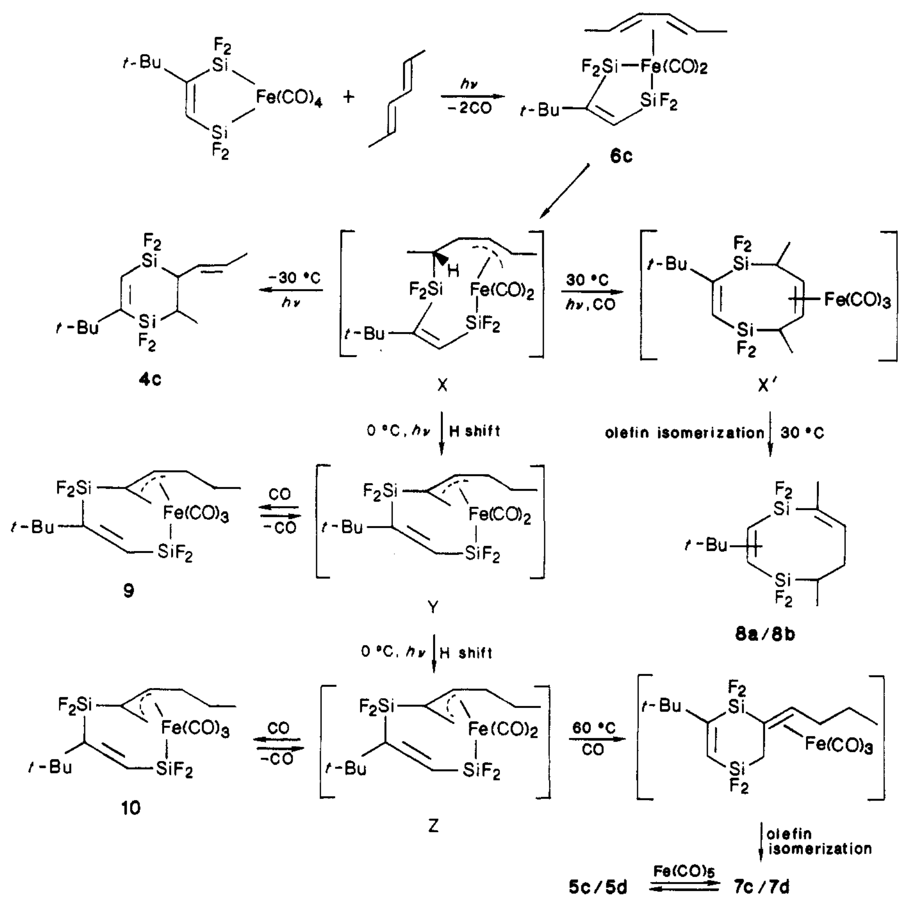


Figure 5. ^{13}C{^{1}H}$_{BB}$ spectra of (a) compound **5a** and (b) compound **7a**.

Scheme I



the time when $(\overline{\mathrm{SiF_2}(t\text{-Bu})\mathrm{C{=}C(H)SiF_2{-})Fe}}(\mathrm{CO})_4$ was completely consumed, the relative abundances of **8a**/**8b**, **9**, **10**, and **6c** were found to be 45:30:15:10, respectively.

Further irradiation on the solution of this composition resulted in the disappearance of the spectra of **6c** and **9** and simultaneous growth of that of **10**, while the abundance of **8a**/**8b** increased very little. Finally the solution was heated at 60 °C in a sealed tube for 8 h, it was found from the spectrum change that intermediate **10** had been converted completely to **7c**/**7d** while the abundance of **8a**/**8b** remained unchanged.

All these observations seem to support the reaction mechanism described in Scheme I.

The first silyl migration in the intermediate **6c** resulted in the formation of a η^3-complex X from which the second silyl group might react via three different pathways in a competitive manner: (i) 1,2-addition to form **4c** but only at low temperature and in a trace amount, (ii) 1,4-addition followed by olefin isomerization to form **8a**/**8b** via olefin complex X′, and (iii) formation of a series of η^3-complexes (Y, Z) via hydrogen shift isomerization before cyclization finally took place. Each of these 16-electron η^3-complexes during the reaction process might take in one CO to form the observable 18-electron counterparts, namely, **9** and **10**.

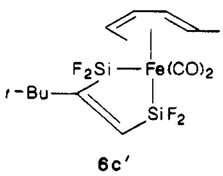
Apparently the sequence X → Y → Z was irreversible. Prolonged irradiation on the reaction mixture at 0 °C would result in complete conversion of **9** to **10** without an increase of **8a** and **8b**. The structures of **9** and **10** show that the $\mathrm{SiF_2}$ group adjacent to the *tert*-butyl group was involved in the initial attack. It is assumed that this structure was retained throughout the sequence from X to Z. As a consequence, when X was converted to the product of 1,2-addition at −30 °C, only **4c** was obtained (no **4d** was observed). When **10** was heated to 60 °C, the second silyl migration occurred and the subsequent olefin isomerization resulted into both isomers **5c** and **5d**. The formation of the isomeric pair of **8a**/**8b** from X was also due to the process of olefin isomerization of X′.

After the first silyl migration had taken place, the hydrogen atom on the diene terminal carbon in X should point toward the metal and the methyl group on the same carbon would point away from the metal. This configuration would facilitate the process of H migration to form Y. On abstraction of H the methyl group would turn to the "anti" position, thus providing a convenient configuration for further H migration to form **Z**.

It is interesting to note that because of the isomerization among the η^3-complexes, the cyclization that took place at Z was literally an "1,0-addition" (referred to the original skeleton of the butadiene).

For comparison with the results of the reaction with *trans,trans*-2,4-hexadiene, the reaction with *cis,trans*-2,4-hexadiene was studied under the same reaction conditions. It was thought that if the first silyl migration took place at the trans side of the diene, one would expect to observe similar results to those of the reaction of *trans,trans*-2,4-hexadiene.

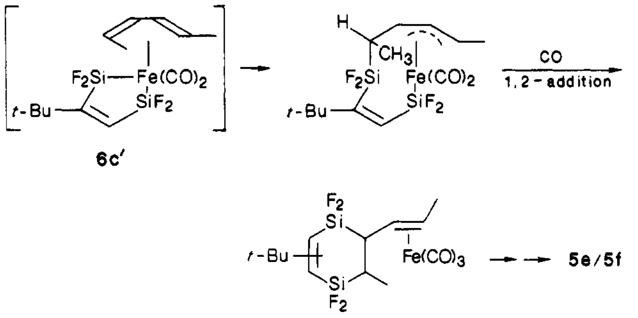
However, the reaction proceeded in quite a different manner. The diene–disilametallacycle intermediate **6c′** was not observed in the reaction even at −30°C.



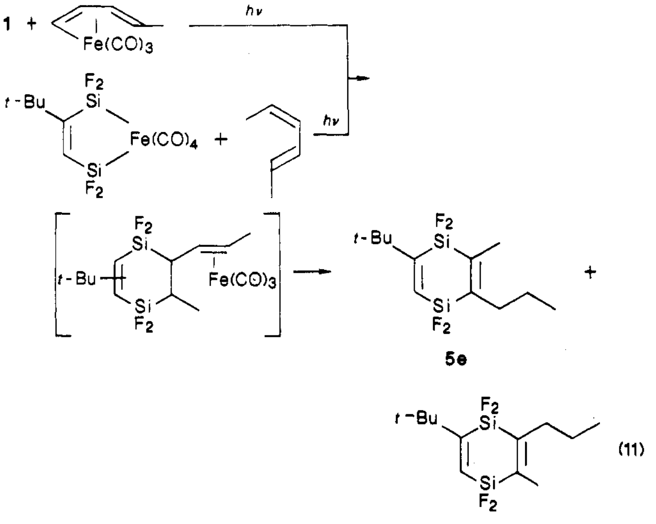
6c′

Secondly, products according to 1,4-addition (such as **8a**/**8b**) or "1,0-addition" (such as **5c**/**5d**) were not observed; instead, the main products were those from 1,2-

Scheme II



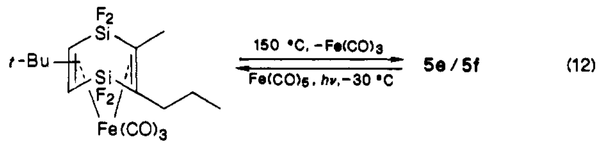
addition, followed by olefin isomerization, namely, **5e** and **5f** (eq 11).



(11)

5f

When the reactions were carried out at −30 °C, a small quantity of **7e**/**7f** was obtained in addition to **5e**/**5f**. On heating, **7e**/**7f** quantitatively converted to **5e**/**5f**. The reverse reaction could be effected by irradiating **5e**/**5f** with $Fe(CO)_5$ (eq 12).



(12)

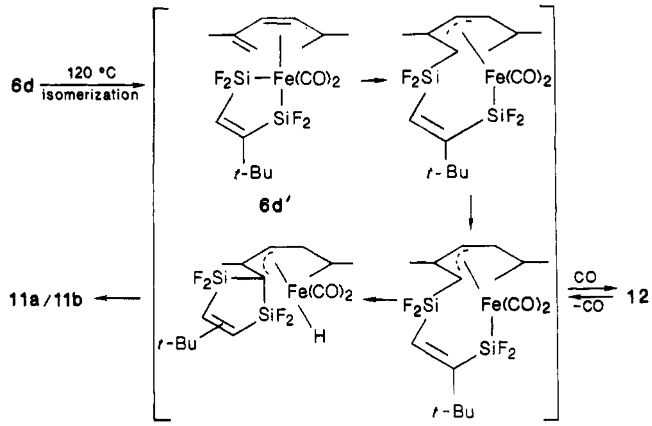
7e/**7f**

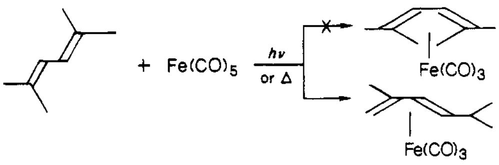
Since the results obviously differ from those of the reaction of *trans*, *trans*-2,4-hexadiene, it is perhaps safe to state that the first silyl migration took place at the cis side in the present case. This would suggest that the trans substituent brought about more steric hinderance than the cis substituent. It is consistent with the fact that the cis,trans intermidiate **6c′** was too unstable to be observed.

While **6c′** was not observed experimentally, there is no doubt about its existence. The first silyl migration on the cis side of **6c′** would result in the η^3-complex with the terminal H pointing away from the metal. This configuration would make the H migration, which was essential to the following isomerizations, very difficult to occur. One would therefore expect the second silyl migration to occur at carbon-2 of the coordinated butadiene (Scheme II).

In the reaction with 2,5-dimethylhexa-1,4-diene, with the steric hinderance of the four methyl groups attached on the terminal carbons of the butadiene, the formation of the corresponding η^4-complex was hampered, instead, a small quantity of the η^4-complex of 2,5-dimethylhexa-1,3-diene was obtained (eq 13).[11]

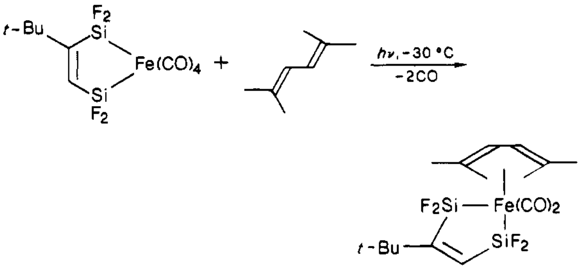
Scheme III





(13)

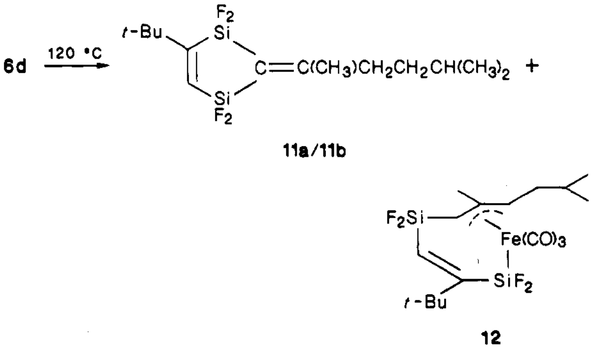
So the reaction was carried out by reacting $(\overline{SiF_2(t\text{-}Bu)C{=}C(H)SiF_2{-}})Fe(CO)_4$ and 2,5-dimethylhexa-2,4-diene photochemically at −30°C. Only one product, compound **6d**, was obtained as colorless crystals (eq 14).



(14)

6d

Compound **6d** remained unchanged on further irradiation. When heated to 120 °C, **6d** decomposed to **11a**/**11b** and a small quantity of **12** (eq 15). Compound **12** could be converted quantitatively to **11a**/**11b** on heating at 150 °C in a sealed tube.



(15)

12

It is quite obvious that the steric effect of the four methyl groups in **6d** hindered the silyl migration so that **6d** was stable up to 120 °C. Even at elevated temperatures, **6d** isomerized to **6d′** before silyl migration took place. Since one of the terminal carbons in the η^4 part of **6d′** was

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(11) (a) Emerson, G. F.; Mahler, J. E.; Kochhar, R.; Pettit, R. *J. Org. Chem.* **1964**, *39*, 3620. (b) Emerson, G. F.; Pettit, R. *Adv. Organomet. Chem.* **1964**, *1*, 1.

free from substitution, it was not surprising that the final products were the same as those from the reaction with 2,5-dimethylhexa-1,3-diene, namely, compounds **11a** and **11b**. The reaction mechanism is summarized in Scheme III.

Since isomerization took place in prior to silyl migration, the reaction proceeded via an 1,1-addition pathway as one would expect.

In all these reactions, it is obvious that after the attack of the first silyl group, direct cycloaddition (to form **4**) competes with isomerization via H migration (to form **2**, **3**, and **11a**/**11b**). The relatively more favored stability of a vinylsilyl moiety over an allylsilyl moiety must have contributed to the driving force for such H migration.[12,13]

Experimental Section

Vacuum distillation and manipulations were carried out on vacuum lines at 10^{-3} torr. Photochemical preparations employed a 450-W medium-pressure Hg lamp. Solvents were dried and distilled over calcium hydride. Dienes (Aldrich), $Fe(CO)_5$ (Merck), and $M(CO)_6$ (M = Cr, Mo, W) (Strem) were used as received. The following compounds were prepared respectively according to the literatures published elsewhere: 1,[7] ($F_2Si(t$-Bu)C=C(H)-SiF_2–)$M(CO)_n$ (M = Fe, *n* = 4; M = Cr, Mo, W, *n* = 5),[8,9] (η^4-diene)$Fe(CO)_3$.[10]

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.

Preparations of 6c, 6d, 6e, 6f, 6g, and 6h. A solution of 2.0 mmol of ($F_2Si(t$-Bu)C=C(H)SiF_2–)$M(CO)_n$ (M = Fe for **6c** and **6d**; M = Mo for **6e** and **6f**; M = W for **6g** and **6h**) and 4.0 mmol of diene (*trans,trans*-2,4-hexadiene for **6c**, **6e**, and **6g**; 2,5-dimethylhexa-2,4-diene for **6d**, **6f**, and **6h**) in a 10 mL of *n*-pentane in a quartz Schlenk tube was irradiated (–30 °C and 10 days for **6c**; –50 °C and 3 h for **6e** and **6g**; –30 °C and 50 h for **6d**; –50 °C and 3 h for **6f** and **6h**). Crystals of **6c**, **6e**, **6g**, and **6d** were collected by filtration. **6c** and **6d** were purified by recrystallization from *n*-pentane-benzene (volume ratio 1:1 for **6c** and 3:1 for **6d**). **6f** and **6h** were obtained as reddish solids that decomposed on warming to 0 °C. The yield based on ($F_2Si(t$-Bu)C=C(H)-SiF_2–)$M(CO)_n$ consumed was 60% for **6c**, 45% for **6e** and **6g**, 55% for **6f**, and approximately 30–40% for **6f** and **6h**.

Mass spectrum of **6c**: 408 (M^+, $C_{12}H_{20}Si_2F_4Fe(CO)_2{}^+$), 380 ($C_{12}H_{20}Si_2F_4(CO)^+$), 352 ($C_{12}H_{20}Si_2F_4Fe^+$), 296 ($C_{12}H_{20}Si_2F_4{}^+$), 281 ($C_{11}H_{17}Si_2F_4{}^+$), 194 ($C_6H_{10}Fe(CO)_2{}^+$), 166 ($C_6H_{10}Fe(CO)^+$), 138 ($C_6H_{10}Fe^+$), 82 ($C_6H_{10}{}^+$), 57 ($C_4H_9{}^+$). ^1H NMR of **6c**: δ 1.03 (d), 6 H, =CHCH_3; 1.18 (s), 9 H, *t*-Bu; 1.60 (c), 2 H, =C*H*CH$_3$; 4.58 (d), 2 H, =C*H*C*H*=; 7.18 (m), 1 H, =C*H*SiF$_2$. $^{19}F\{^1H\}$ NMR of **6c**: 92.03 and 96.98 (d), =CHSIF_2; 102.53 and 107.64 ppm (d), =C(*t*-Bu)SiF_2. (Assignments confirmed by comparing with a nondecoupled spectrum). ^{13}C NMR of **6c**: δ 203.32 s (s), *C*O; 187.43 m (m), =*C*(*t*-Bu)SiF$_2$; 150.94 m (dm), =*C*HSiF$_2$; 92.40 and 91.52 s (d), =*C*H*C*H=; 90.23 and 89.53 s (d), =*C*HCH$_3$; 39.37 s (s), *C*(CH$_3$)$_3$; 30.35 s (q), C(*C*H$_3$)$_3$; 20.04 and 18.63 s (q), =CH*C*H$_3$.

Mass spectrum of **6e**: *m/e* 476 (M^+, $C_{15}H_{20}O_3Si_2F_4Mo^+$); 448 ($C_{14}H_{20}O_2Si_2F_4Mo^+$); 420 ($C_{13}H_{20}OSi_2F_4Mo^+$); 215 ($C_6H_{11}Si_2F_4{}^+$); 57 ($C_4H_9{}^+$). $^{19}F\{^1H\}$ NMR of **6e**: 87.43 and 88.68 (t), F_2Si(*t*-Bu)C=; 74.63 and 75.11 ppm (t), F_2SiCH=; $^4J_{F,F}$ = 1.5 Hz. ^1H NMR of **6e**: δ 1.1 (s), 9 H, *t*-Bu; 1.04 (d), 6 H, =CHCH_3; 1.5 (m), 2 H, =C*H*CH$_3$; 4.6 (m), 2 H, C*H*=C*H*; 7.24 (m), 1 H, F$_2$SiC*H*=.

Mass spectrum of **6g**: *m/e* 564 (M^+, $C_{15}H_{20}O_3Si_2F_4W^+$); 536 ($C_{14}H_{20}O_2Si_2F_4W^+$); 508 ($C_{13}H_{20}OSi_2F_4W^+$); 480 ($C_{12}H_{20}Si_2F_4W^+$); 215 ($C_6H_{11}Si_2F_4{}^+$); 57 ($C_4H_9{}^+$). ^{19}F NMR of **6g**: 85.24 and 86.57 (t), F_2Si(*t*-Bu)C=; 77.65 and 78.92 ppm (t), F_2SiCH=; $^4J_{F,F}$ = 1.5 Hz.

Mass spectrum of **6d**: *m/e* 436 (M^+, $C_{14}H_{24}Si_2F_4Fe(CO)_2{}^+$), 408 ($C_{14}H_{24}Si_2F_4(CO)^+$), 380 ($C_{14}H_{24}Si_2F_4Fe^+$), 324 ($C_{14}H_{24}Si_2F_4{}^+$), 222 ($C_8H_{14}Fe(CO)_2{}^+$), 215 ($C_6H_{11}Si_2F_4{}^+$), 194 ($C_8H_{14}Fe(CO)^+$), 166 ($C_8H_{14}Fe^+$), 110 ($C_8H_{14}{}^+$), 95 ($C_7H_{11}{}^+$). ^1H NMR of **6d**: υ 1.24 (s), 9 H, *t*-Bu; 1.60 (s), 6 H, =C(CH_3), anti; 1.76 and 1.80 (s), 2 H, =C*H*C*H*; 3.36 (s), 6 H, =C(CH_3), syn; 7.12 (m), 1 H, =C*H*SiF$_2$. $^{19}F\{^1H\}$ NMR of **6d**: 97.77 and 98.32 (d), =CHSiF_2; 107.54 and 109.50 ppm (d), =C(*t*-Bu) SiF_2. 1^3C NMR of ^6d: δ 202.20 s (s), *C*O; 187.28 m (m), =*C*(*t*-Bu)SiF$_2$; 150.70 m (dm), =*C*HSiF$_2$; 120.41 and 119.35 s (s), =*C*(CH$_3$)$_2$; 85.60 and 85.08 s (d), =*C*H*C*H=; s (s), *C*(CH$_3$)$_3$; 30.94 s (q), C(*C*H$_3$)$_3$; 30.29, 30.06, 23.03, and 22.79 s (q), =C(*C*H$_3$).

Mass spectrum of **6f**: *m/e* 504 (M^+, $C_{17}H_{24}O_3Si_2F_4Mo^+$); 476 ($C_{16}H_{24}O_2Si_2F_4Mo^+$); 448 ($C_{15}H_{24}OSi_2F_4Mo^+$); 420 ($C_{14}H_{24}Si_2F_4Mo^+$); 215 ($C_6H_{11}Si_2F_4{}^+$); 57 ($C_4H_9{}^+$). $^{19}F\{^1H\}$ NMR of **6f**: 99.4 and 102.3 (t), F_2Si-C(*t*-Bu); 85.6 and 86.6 ppm (t), F_2Si-CH=; $^4J_{F,F}$ = 1.5 Hz.

Mass spectrum of **6h**: m/e 592 (M^+, $C_{17}H_{24}O_3Si_2F_4W^+$); 564 ($C_{16}H_{24}O_2Si_2F_4W^+$); 536 ($C_{15}H_{24}OSi_2F_4W^+$); 508 ($C_{14}H_{24}Si_2F_4W^+$); 215 ($C_6H_{11}Si_2F_4{}^+$); 57 ($C_4H_9{}^+$). ^{19}F NMR of **6h**: 87.56 and 88.35 (t), F_2Si(*t*-Bu)C=; 77.98 and 79.23 ppm (t), F_2Si-CH=; $^4J_{F,F}$ = 1.5 Hz.

Preparation of 8a and 8b. A solution of 2.0 mmol of ($F_2Si(t$-Bu)C=C(H)SiF_2–)$Fe(CO)_4$ and 6.0 mmol of *trans*,-*trans*-2,4-hexadiene in 10 mL of *n*-pentane in a quartz Schlenk tube was irradiated at 30 °C over 15 days to exhaust ($F_2Si(t$-Bu)C=C(H)SiF_2–)$Fe(CO)_4$. The solution was concentrated and distilled under vacuum at 80 °C to give 1.2 mmol (45% yield) of **8a** and **8b** (molar ratio 3:1).

Anal. Calcd for **8a**/**8b**: C, 48.64; H, 6.67; F, 25.68. Found: C, 48.47; H, 6.43; F, 25.32. Mass spectrum of **8a** and **8b**: *m/e* 296 (M^+, $C_{12}H_{20}Si_2F_4{}^+$), 281 ($C_{11}H_{17}Si_2F_4{}^+$), 267 ($C_{10}H_{15}Si_2F_4{}^+$), 254 ($C_9H_{14}Si_2F_4{}^+$), 239 ($C_8H_{11}Si_2F_4{}^+$), 226 ($C_7H_{10}Si_2F_4{}^+$), 212 ($C_6H_8Si_2F_4{}^+$), 168 ($C_4H_7Si_2F_3{}^+$), 149 ($C_4H_7Si_2F_2{}^+$), 129 ($C_4H_6Si_2F^+$), 82 ($C_6H_{10}{}^+$), 57 ($C_4H_9{}^+$). ^1H NMR of **8a** and **8b**: δ 1.08 (br s), 12 H, *t*-Bu and –CH(CH_3); 1.52 (d), 3 H, =C(CH_3); 1.96 (c), 3 H, –C*H*(CH$_3$)CH_2–; 6.44 (m), 2 H, =C*H*CH$_2$ and =C*H*SiF$_2$. $^{19}F\{^1H\}$ NMR of **8a** and **8b**: 129.33 (dd), 136.18 (d), 144.45 (d), 151.53 (dd), four F of **8a** or **8b**; 135.18, 135.27, 136.17, 144.68 ppm (dd), four F of **8a** or **8b**. ^{13}C NMR of **8a** and **8b**: δ 173.73 m (m), =*C*(*t*-Bu)SiF$_2$; 148.06 and 146.19 s (d), =*C*HCH$_2$ of **8e** or **8f**; 134.24 m (dm), =*C*HSiF$_2$; 130.72 t (t), =*C*(CH$_3$); 39.55 s (s), *C*(CH$_3$)$_3$; 29.41 s (q), C(*C*H$_3$)$_3$ and =C(*C*H$_3$); 22.38 s (t), =CH*C*H$_2$–; 19.33 t (m), –*C*H(CH$_3$); 14.82 and 14.36 s (q), –CH(*C*H$_3$) of **8a** or **8b**.

Preparation of Compounds of the 4 Family. The family 4 compounds were prepared by reactions of (F_2SiCH=C(*t*-Bu)SiF_2–)$M(CO)_5$ (M = Cr, Mo, W) with the respective dienes.

General Procedure. A solution of 2.0 mmol of (F_2SiCH=C-(*t*-Bu)SiF_2–)$M(CO)_5$ and 4.0 mmol of the respective diene in a 10 mL of *n*-pentane in a quartz Schlenk tube was irradiated to exhaust compound (F_2SiCH=C(*t*-Bu)SiF_2–)$M(CO)_5$. The solution was then concentrated and subjected to distillation under vacuum at 80–90 °C to give the products. Yield was based on the quantity of (F_2SiCH=C(*t*-Bu)SiF_2–)$M(CO)_5$ consumed.

(i) **4c**: yield 40%; colorless liquid obtained by irradiating (F_2SiCH=C(*t*-Bu)SiF_2)-$Cr(CO)_5$ with *trans,trans*-2,4-hexadiene at –30 °C for 48 h. Anal. Calcd for **4c**: C, 48.64; H, 6.76; F, 25.68. Found; C, 48.88; H, 6.54; F, 25.99. Mass spectrum of **4c**: *m/e* 296 (M^+, $C_{12}H_{20}Si_2F_4{}^+$); 281 ($C_{11}H_{17}Si_2F_4{}^+$); 215 ($C_6H_{11}Si_2F_4{}^+$); 57 ($C_4H_9{}^+$). ^1H NMR of **4c**: δ 1.08 (c), 1 H, F$_2$SiC*H*CH$_3$; 1.1 (s), 9 H, *t*-Bu; 1.15 (c), 3 H, F$_2$SiCHCH_3; 1.6 (d), 3 H, C=CHCH_3; 2.0 (s), 1 H, F$_2$SiC*H*C=C; 5.2 (dq), 1 H, C=C*H*CH$_3$; 5.6 (dd), 1 H, C*H*=CHCH$_3$; 6.5 (c), 1 H, F$_2$SiC*H*=; $J_{HC=CH}$ = 15.7 Hz. $^{19}F\{^1H\}$

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NMR of **4c**: 137.39, 139.59; 144.20, 147.30 ppm (d) (AA′XX′ pattern for the two SiF_2 group). ^{13}C NMR of **4c**: δ 11.83 s (q), $F_2SiCH\mathit{C}H_3$; 20.86 t (dt), $F_2Si\mathit{C}HCH_3$, 18.16 s (q), $=CH\mathit{C}H_3$; 29.31 s (q), $(\mathit{C}H_3)_3C$; 32.11 t (dt), $F_2Si\mathit{C}HCH=$; 39.43 s (s), $(CH_3)_3\mathit{C}$; 123.87, 129.66 s (d), $-H\mathit{C}=\mathit{C}HCH_3$; 134.41 tt (dtt), $F_2Si\mathit{C}H=$; 173.49 m (m), $F_2Si(t\text{-Bu})\mathit{C}=$.

(ii) **4c** and **4d**: yield 95%, colorless liquid obtained by keeping **6e** at 0 °C for 5 h. The ^1H and ^{13}C NMR spectra of **4d** are apparently the same as those of compound **4c**. Only the ^{19}F NMR spectrum shows the difference. $^{19}F\{^1H\}$ NMR of **4d**: 139.0, 142.08; 143.59, 145.5 ppm (d) (AA′XX′ pattern for the two SiF_2 group).

(iii) **4e**: yield 40%, colorless liquid obtained by irradiating $(F_2SiCH=C(t\text{-Bu})SiF_2-)Cr(CO)_5$ with *cis,trans*-2,4-hexadiene at −30 °C for 24 h. Anal. Calcd for **4e**: C, 48.64; H, 6.76; F, 25.68. Found: C, 48.52; H, 6.89; F, 25.54. Mass spectrum of **4e** is very similar to that of compound **4c** or **4d**. Also, the ^1H and ^{13}C NMR spectra of **4e** are apparently the same as those of compound **4c**. Only the ^{19}F NMR spectrum shows difference. $^{19}F\{^1H\}$ NMR of **4e**: 136.4, 136.9; 141.98, 143.39 ppm (d) (AA′XX′ pattern for the two SiF_2 group).

(iv) **4e** and **4f**: yield 40%, colorless liquid obtained by irradiating $(F_2SiCH=C(t\text{-Bu})SiF_2-)M(CO)_5$ with *cis,trans*-2,4-hexadiene at 90 °C for 10 h. The mass spectrum and ^1H and ^{13}C NMR spectra of **4f** are very similar to those of compound **4c**, **4d**, **4e**. $^{19}F\{^1H\}$ NMR of **4f**: 136.4, 138.0; 140.8, 142.38 ppm (d) (AA′XX pattern for the two SiF_2 group).

(v) **4i**: yield 40%, colorless liquid obtained by irradiating $(F_2SiCH=C(t\text{-Bu})SiF_2-)W(CO)_5$ with butadiene at −30 °C for 15 h. Anal. Calcd for **4i**: C, 44.78; H, 6.00; F, 28.36. Found: C, 44.65; H, 6.21; F, 28.55. Mass spectrum of **4i**: *m/e* 268 (M^+, $C_{10}H_{16}Si_2F_4^+$), 253 ($C_9H_{13}Si_2F_4^+$), 215 ($C_6H_{11}Si_2F_4^+$), 57 ($C_4H_9^+$). ^1H NMR of **4i**: δ 1.2 (s), 9 H, *t*-Bu; 1.4 (c), 2 H, $F_2SiC\mathit{H}_2-$; 2.0 (c), 1 H, $F_2SiC\mathit{H}-$; 4.9–5.8 (ABC), 3 H, $\mathit{H}_2C=C\mathit{H}-$; 6.5 (tt), 1 H, $F_2SiC\mathit{H}=$. $^{19}F\{^1H\}$ NMR of **4i**: 138.6 (d), 139.5 (dd); 138.9 (d), 141.5 ppm (dd) (AA′XX′ pattern for the two SiF_2 groups). ^{13}C NMR of **4i**: δ 10.06 t (tt), $F_2Si\mathit{C}H_2$; 24.3 t (dt), $F_2Si\mathit{C}H-$; 29.02 s (q), $(\mathit{C}H_3)_3C$; 39.17 s (s), $(CH_3)_3\mathit{C}$; 115.2 s (t), $H_2\mathit{C}=CH-$; 134.5 s (d), $H_2C=\mathit{C}H-$; 134.9 tt (dtt), $F_2Si\mathit{C}H=$; 173.0 tt (tt), $=\mathit{C}(t\text{-Bu})SiF_2$.

Preparation of Compounds of the 5 and 7 Families. Preparation of 5c/5d. A solution of 4.0 mmol of **6c** in 5 mL of isooctane was degassed and sealed in a tube. After being heated at 70 °C for 30 h, the resulting brown liquid was heated at 150 °C for one more hour. The distillate collected at 120 °C was found to contain a mixture of **5c** and **5d** (molar ratio 1:1, yield 76% based on **6c** used).

Anal. Calcd for **5c**/**5d**: C, 48.64; H, 6.76; F, 25.68. Found C, 48.55; H, 6.95; F, 25.89. Mass spectrum of **5c** and **5d**: *m/e* 296 (M^+, $C_{12}H_{20}Si_2F_4^+$), 281 ($C_{11}H_{17}Si_2F_4^+$), 254 ($C_8H_{14}Si_2F_4^+$), 83 ($C_6H_{11}^+$), 57 ($C_4H_9^+$). ^1H NMR of **5c** and **5d**: δ 0.91 (t), 3 H, $-CH_2C\mathit{H}_3$; 1.17 (s), 9 H, *t*-Bu; 1.40 (c), 4 H, $-(C\mathit{H}_2)_2CH_3$; 2.17 (c), 2 H, $-C\mathit{H}_2(CH_2)_2CH_3$; 6.60 (m), 2 H, $=C\mathit{H}SiF_2$. $^{19}F\{^1H\}$ NMR of **5c**: 135.59 (t), $=C(n\text{-Bu})SiF_2$; 143.47 ppm (t), $=(t\text{-Bu})Si\mathit{F}_2$. $^{19}F\{^1H\}$ NMR of **5d**: 137.66 (t), $=CHSi\mathit{F}_2$; 142.55 ppm (t), $=C(t\text{-Bu})SiF_2$. ^{13}C NMR of **5c** and **5d**: δ 173.49 m (m), $=C(t\text{-Bu})SiF_2$; 164.53 and 163.88 tt (tt), $=C(n\text{-Bu})SiF_2$ of **5c** or **5d**; 138.28, 137.46, 135.17, 133.83, tt (dtt), $=CH(SiF_2)$ of **5c** and **5d**; 39.26 s (s), $\mathit{C}(CH_3)_3$; 38.09 s (t), $=C(\mathit{C}H_2)-$; 29.47 s (t), $-\mathit{C}H_2CH_2CH_3$; 29.18 s (q), $C(\mathit{C}H_3)_3$; 22.15 s (t), $\mathit{C}H_2CH_3$; 13.59 s (q), $-CH_2\mathit{C}H_3$.

Preparation of 5e/5f and 5a. A 5-mL isooctane solution containing 1.0 mmol of compound **4** (**4c**, **4d**, **4e**, or **4f** for **5e**/**5f**; **4a** or **4b** for **5a**) and 3.0 mmol of $Fe(CO)_5$ was degassed, sealed in a quartz Schlenk tube, and irradiated at 50–70 °C for 72 h. After filtration and removal of solvent, compounds **5e**/**5f** were obtained by distillation at 90 °C under vacuum. The yield based on the quantity of 4 consumed was 60% for **5e**/**5f** (molar ratio 2:3) and 75% for **5a**.

Mass spectrum of **5e** and **5f**: *m/e* 296 (M^+, $C_{12}H_{20}Si_2F_4^+$), 281 ($C_{11}H_{17}Si_2F_4^+$), 215 ($C_6H_{11}Si_2F_4^+$), 83 ($C_6H_{11}^+$), 57 ($C_4H_9^+$). ^1H NMR of **5e** and **5f**: δ 0.95 (t), 3 H, $CH_2C\mathit{H}_3$; 1.17 (s), 9 H, *t*-Bu; 1.48 (c), 2 H, $C\mathit{H}_2CH_3$; 1.94 (s), 3 H, $=CC\mathit{H}_3$; 2.32 (c), 2 H, $=CC\mathit{H}_2$; 6.62 (m), 1 H, $=C\mathit{H}SiF_2$. $^{19}F\{^1H\}$ NMR of **5e** and **5f**: 137.79, 139.47 (t), $=C(CH)SiF_2$; 143.22, 146.14 ppm (t), $=C(t\text{-Bu})SiF_2$. ^{13}C NMR of **5e** and **5f**: δ 172.79 m (m), $=\mathit{C}(t\text{-Bu})SiF_2$; 153.75 m (m), $PrC=$; 149.41 m (m), $=\mathit{C}(CH_3)SiF_2$; 134.94 and 134.42 tt (dtt), $=\mathit{C}HSiF_2$ of **5e** or **5f**; 39.26 s (s), $\mathit{C}(CH_3)_3$; 32.05 s (t), $\mathit{C}H_2CH_2CH_3$; 29.82 s (q), $=C\mathit{C}H_3$; 29.24 s (q), $C(\mathit{C}H_3)_3$; 21.74 and 21.50 s (t), $\mathit{C}H_2CH_3$ of **5e** or **5f**; 14.18 s (q), $CH_2\mathit{C}H_3$.

Structure identification of **5a** has been reported previously.[1]

Preparation of 7a. A *n*-pentane solution containing 1.0 mmol of **5a** and 5.0 mmol of $Fe(CO)_5$ was degassed, sealed, and irradiated at −30 °C for 7 days. After the solution was filtered and concentrated, compound **7a** was obtained by distillation at 120–140 °C under vacuum. The yield based on the quantity **5a** used was 60%.

Mass spectrum of **7a**: *m/e* 434 (M^+, $C_{12}H_{18}Si_2F_4Fe(CO)_3^+$), 406 ($C_{12}H_{18}Si_2F_4(CO)_2^+$), 378 ($C_{12}H_{18}Si_2F_4Fe(CO)^+$), 350 ($C_{12}H_{18}Si_2F_4Fe^+$), 294 ($C_{12}H_{18}Si_2F_4^+$), 279 ($C_{11}H_{15}Si_2F_4^+$), 215 ($C_6H_{11}Si_2F_4^+$), 57 ($C_4H_9^+$). $^{19}F\{^1H\}$ NMR of **7a**: 97.09, 164.06 (d), $=C(t\text{-Bu})Si\mathit{F}_2$; 98.60, 155.94 ppm (d), $=CHSi\mathit{F}_2$. ^{13}C NMR of **7a**: δ 212.17 s (s), CO; 122.53 ddd (ddd), $=\mathit{C}(t\text{-Bu})SiF_2$; 96.52 and 86.56 ddd (ddd), $CH_2\mathit{C}=\mathit{C}CH_2$; 50.33 ddd (dddd), $=\mathit{C}HSiF_2$; 37.50 s (s), $(CH_3)_3\mathit{C}$; 32.17 s (q), $(\mathit{C}H_3)_3C$; 25.32 and 25.02 s (t), $-\mathit{C}H_2CH_2CH_2\mathit{C}H_2$; 20.39 s (t), $-\mathit{C}H_2\mathit{C}H_2$.

Preparation of 7c and 7d. A solution of 4.0 mmol of **6c** in 0.5 mL of isooctane was degassed and sealed in a tube. After being heated at 70 °C for 30 h, the resulting brown liquid was subjected to fractional distillation under vacuum. Distillate of 80 °C, a colorless liquid, was found to contain **5c**, **5d**, and an unidentified compound (molar ratio 3:3:2, relative yield 24%); the distillate of 120 °C, a brown viscous liquid, was found to contain **7c** and **7d** (molar ratio 1:1, relative yield 76%). When the mixture of **7c**/**7d** was heated at 150 °C for 1 h in a sealed tube, it converted quantitatively to the mixture of **5c** and **5d** (molar ratio 1:1).

Mass spectrum of **7c** and **7d**: 436 (M^+, $C_{12}H_{20}Si_2F_4Fe(CO)_3^+$), 408 ($C_{12}H_{20}Si_2F_4Fe(CO)_2^+$) 380 ($C_{12}H_{20}Si_2F_4Fe(CO)^+$), 352 ($C_{12}H_{20}Si_2F_4Fe^+$), 296 ($C_{12}H_{20}Si_2F_4^+$), 281 ($C_{11}H_{17}Si_2F_4^+$), 254 ($C_9H_{14}Si_2F_4^+$), 83 ($C_6H_{11}^+$), 57 ($C_4H_9^+$). $^{19}F\{^1H\}$ NMR of **7c**: 92.08 and 162.48 (d), $=C(t\text{-Bu})SiF_2$; 94.87 and 153.63 ppm (d), $=C(n\text{-Bu})Si\mathit{F}_2$. $^{19}F\{^1H\}$ NMR of **7d**: 90.91 and 162.73 (d), $=C(t\text{-Bu})SiF_2$; 96.87 and 155.94 ppm (d), $=CHSi\mathit{F}_2$. ^{13}C NMR of **7c** and **7d**: δ 211.63 s (s), $\mathit{C}O$; 103.40, 98.54, 84.53, 74.25 m (m), $=\mathit{C}(t\text{-Bu})SiF_2$ and $=\mathit{C}(n\text{-Bu})SiF_2$ for **7c** and **7d**; 60.24 m (dm), $=\mathit{C}H$ of **7c** and **7d**; 37.88 s (s), $\mathit{C}(CH_3)_3$; 36.10, 35.65 s (t), $=CH\mathit{C}H_2-$ for **7c** and **7d**; [illegible]84 s(q), $C(\mathit{C}H_3)_3$; 23.39, 29.13 s (t), $-\mathit{C}H_2\mathit{C}H_2CH$ 14.49 s (q $CH_2\mathit{C}H_3$

Reaction between $(F_2Si(t\text{-Bu})C=C(H)SiF_2-)Fe(CO)_4$ and *trans,trans*-2,4-Hexadiene. A solution of 2.0 mmol of $(F_2SiCH=C(t\text{-Bu})SiF_2-)Fe(CO)_4$ and 3.0 mmol of *trans,trans*-2,4-hexadiene in 10 mL of *n*-pentane was degassed, sealed in a quartz Schlenk tube, and irradiated at 0 °C. The reaction was followed by ^{19}F NMR spectroscopy as described in the text. Two $(\eta^3\text{-}C_6H_{10})(C_6H_{10}Si_2F_4)Fe(CO)_3$ complexes, **9** and **10**, were involved as intermediates.

$^{19}F\{^1H\}$ NMR of **9**: 89.59 (d), 109.36 (d), $Si\mathit{F}_2$ bond to Fe; 134.94 (d), 140.96 ppm (d), $Si\mathit{F}'_2$ bond to $\eta^3\text{-}C_6H_{10}$.

$^{19}F\{^1H\}$ NMR of **10**: 100.72 (d), 120.10 (d), $Si\mathit{F}_2$ bond to Fe; 132.60 (d), 134.13 ppm (d), $Si\mathit{F}'_2$ bond to $\eta^3\text{-}C_6H_{10}$.

Preparation of 7e and 7f. A solution of 5.0 mmol of $Fe(CO)_5$ and 2.0 mmol of **5e**/**5f** in 20 mL of *n*-pentane in a quartz Schlenk tube was irradiated at −30 °C for 5 days to exhaust **5e** and **5f**. After filtration, quantitative **7e** and **7f** were obtained as brown viscous liquids after the solvent and excess $Fe(CO)_5$ were removed by pumping.

Mass spectrum of **7e** and **7f**: *m/e* 436 (M^+, $C_{12}H_{20}Si_2F_4Fe(CO)_3^+$), 408 ($C_{12}H_{20}Si_2F_4Fe(CO)_2^+$), 380 ($C_{12}H_{20}Si_2F_4Fe(CO)^+$), 352 ($C_{12}H_{20}Si_2F_4Fe^+$), 296 ($C_{12}H_{20}Si_2F_4^+$), 281 ($C_{11}H_{17}Si_2F_4^+$), 57 ($C_4H_9^+$). $^{19}F\{^1H\}$ NMR of **7e** and **7f**: 96.48, 99.72, 156.31, 157.50 ppm (d), four F of $=CHSi\mathit{F}_2$ of **7e** and **7f**; 92.58, 96.47, 165.38, 165.39 ppm (d), four F of $=C(t\text{-Bu})Si\mathit{F}_2$ of **7e** and **7f**. ^{13}C NMR of **7e** and **7f**: δ 211.99 s (s), $\mathit{C}O$; 101.19, 96.52, 91.38, 87.18, 80.64 m (m), $=\mathit{C}RSiF_2$ for **7e** and **7f**; 55.42 m (dm), $=\mathit{C}HSiF_2$; 37.68 s (s), $\mathit{C}(CH_3)_3$; 31.99 s (q), $C(\mathit{C}H_3)_3$ and $=C(SiF_2)\mathit{C}H_3$; 29.94 and 24.96 s (t), $\mathit{C}H_2\mathit{C}H_2$; 14.65 s (q), $CH_2\mathit{C}H_3$.

Preparation of 12. A solution of 2.0 mmol of **6d** in 5.0 mL of isooctane was degassed and sealed in a quartz tube. After irradiation at 30 °C for 1 week no detectable change was observed. When the solution was subjected to heating at 120 °C for 7 h, compound **6d** decomposed completely. Fractional distillation under vacuum gave 0.4 mmol (20% yield) of ($F_2Si(t\text{-}Bu)C{=}C(H)SiF_2$–)$Fe(CO)_4$ and 1.2 mmol (60% yield) of **11a/11b** at 90 °C. The fraction of 120 °C contained 0.2 mmol of a 1:1 mixture of **11a/11b** and compound **12** (5% yield). Identification of **11a/11b** has been described elsewhere.[2]

Mass spectrum of **12** and **11a/11b**: *m/e* 464 (M^+, $C_{14}H_{24}Si_2F_4Fe(CO)_3^+$), 436 ($C_{14}H_{24}Si_2F_4Fe(CO)_2^+$), 408 ($C_{14}H_{24}Si_2F_4Fe(CO)^+$), 380 ($C_{14}H_{24}Si_2F_4Fe^+$), 324 ($C_{14}H_{24}Si_2F_4^+$), 309 ($C_{13}H_{21}Si_2F_4^+$), 281 ($C_{11}H_{17}Si_2F_4^+$), 268 ($C_{10}H_{16}Si_2F_4^+$), 255 ($C_9H_{15}Si_2F_4^+$), 212 ($C_6H_8Si_2F_4^+$), 57 ($C_4H_9^+$). $^{19}F\{^1H\}$ NMR of **12**: 85.10 and 156.98 ppm (d), $=C(t\text{-}Bu)SiF_2$ bond to Fe; 128.76 and 129.72 ppm, AB pattern for $=CHSiF_2$ bond to η^3-C_8H_{14}.

Decomposition of 12. A solution of 0.1 mmol of **12** in 0.5 mL of isooctane in a tube was degassed and sealed. Heating at 150 °C for 1 h resulted in the complete decomposition of **12** to **11a/11b**. The solution was then distilled under vacuum at 90 °C, and **11a/11b** was obtained quantitatively.

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Registry No. **1**, 36091-97-1; **4a**, 100513-62-0; **4b**, 100485-82-3; **4c**, 109306-11-8; **4d**, 109283-89-8; **4e**, 109362-47-2; **4f**, 109428-75-3; **4i**, 109283-90-1; **5a**, 100485-83-4; **5c**, 109283-91-2; **5d**, 109283-92-3; **5e**, 109283-93-4; **5f**, 109283-94-5; **6a**, 100485-84-5; **6b**, 100513-64-2; **6c**, 109284-02-8; **6d**, 109284-03-9; **6e**, 109283-98-9; **6f**, 109283-99-0; **6g**, 109284-00-6; **6h**, 109284-01-7; **7a**, 100513-63-1; **7c**, 109284-05-1; **7d**, 109284-06-2; **7e**, 109284-07-3; **7f**, 109306-41-4; **8a**, 109283-88-7; **8b**, 109283-87-6; **9**, 109283-97-8; **10**, 109306-40-3; **11a**, 109283-96-7; **11b**, 109283-95-6; **12**, 109306-39-0; ($F_2Si(t\text{-}Bu)C{=}C(H)SiF_2$)-$Fe(CO)_4$, 78514-11-1; ($F_2Si(t\text{-}Bu)C{=}C(H)SiF_2$)$Mo(CO)_5$, 75311-40-9; ($F_2Si(t\text{-}Bu)C{=}C(H)SiF_2$)$W(CO)_5$, 109283-41-2; ($F_2Si(t\text{-}Bu)C{=}C(H)SiF_2$)$Cr(CO)_5$, 109284-04-0; $Fe(CO)_5$, 13463-40-6; (η^4-1,3-cyclohexadiene)$Fe(CO)_3$, 12152-72-6; *trans,trans*-2,4-hexadiene, 5194-51-4; *cis,trans*-2,4-hexadiene, 5194-50-3; 2,5-dimethylhexa-2,4-diene, 764-13-6; butadiene, 106-99-0; 1,3-cyclohexadiene, 592-57-4.

Cycloaddition Reactions of Tetrafluorodisilacyclobutene with 1,3-Butadienes Mediated by Metal Carbonyls. 3. Hydrogen Migration vs. Fluorine Migration[†]

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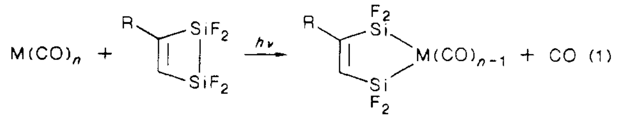
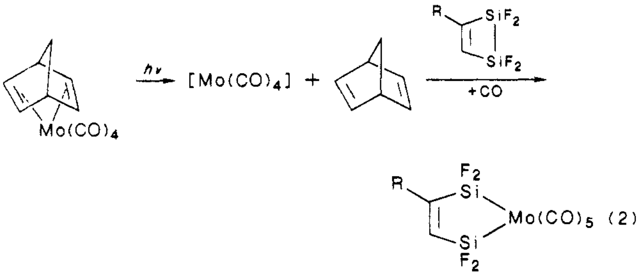
Cycloaddition reactions between 1,1,2,2-tetrafluoro-1,2-disilacyclobutene and various 1,3-butadiene derivatives mediated by VIB (6) transition-metal carbonyls are studied under photochemical conditions. The reactions proceed via an unusual 1,1-addition pathway in which hydride and fluoride migrations were observed to have occurred in the intermediates. The parallel reaction pattern of hydride vs. fluoride migration strongly suggests a common intermediate involving the metal-bonded disilabutadiene species.

The chemistry of vinyldisilanes has been a subject of considerable recent interest because of the possible involvement of silicon–carbon double-bonded species generated under photochemical conditions.[1,2] Disilacyclobutenes belong to a special class of vinyldisilane, reaction of which may involve disilabutadiene intermediates according to the study of some cycloaddition reactions.[3,4] Attempts to stabilize disilabutadiene intermediates by transition-metal carbonyls under photochemical conditions have so far been unsuccessful.[5,6] Such experiments resulted only in the formation of disilametallacycles. The structures of some of these compounds have been determined by single-crystal X-ray diffraction experiments (eq 1).[7,8] Even in the case where vacancy of two coordination sites is essentially guaranteed, no η^4-disilabutadiene complexes are obtained,[6,8] for example,[6] eq 2.



M = Fe, *n* = 5; M = Cr, Mo, W, *n* = 6



On the other hand, metal carbonyls and metal phosphine complexes have been reported to catalyze cycloaddition of disilacyclobutenes with unsaturated organic compounds, for example,[9,10] eq 3 and 4.

[†] In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13–18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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