under vacuum gave 0.4 mmol (20% yield) of $(F_2Si(t\text{-}Bu)C{=}C(H)SiF_2\text{-})Fe(CO)_4$ 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 $\eta^3\text{-}C_8H_{14}$.

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.

Acknowledgment. We thank the Chinese National Science Council for financial support of this work. C.-h.L. thanks the Nuclear Energy Research Institute for a research fellowship.

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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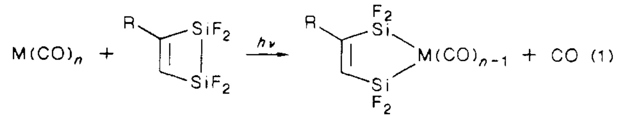
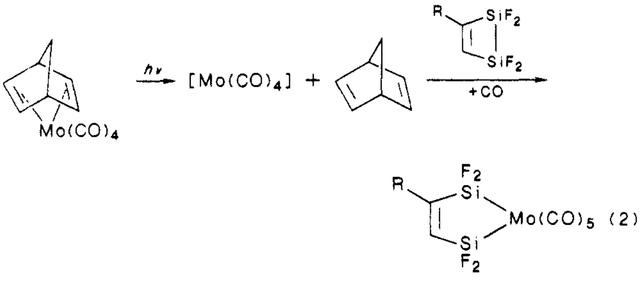
Received April 2, 1987

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.)

(1) (a) Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529 and references therein. (b) Gusel'nikov, L. E.; Nametkin, N. S.; Vdovin, V. M. *Acc. Chem. Res.* **1975**, *8*, 18 and references therein.

(2) Ishikawa, M.; Sugaya, T.; Kumada, M. *J. Am. Chem. Soc.* **1975**, *97*, 5923.

(3) Sakurai, H.; Nakadaira, Y. *J. Am. Chem. Soc.* **1976**, *98*, 7424.

(4) Barton, T. J.; Kilgour, T. A. *J. Am. Chem. Soc.* **1976**, *98*, 746.

(5) Liu, C. S.; Chi, Y. *Inorg. Chem.* **1981**, *20*, 3456.

(6) Liu, C. S. *NSC Symp Ser.* **1982**, *No. 4*, 279.

(7) Hseu, T. H.; Chi, Y.; Liu, C. S. *Inorg. Chem.* **1981**, *20*, 199.

(8) Lin, W. P.; Liu, C. S.; Wang, Y.; Lee, G. H. *J. Chin. Chem. Soc. (Taipei)* **1985**, *32*, 279.

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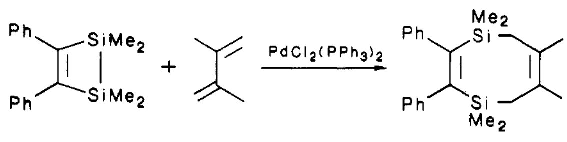
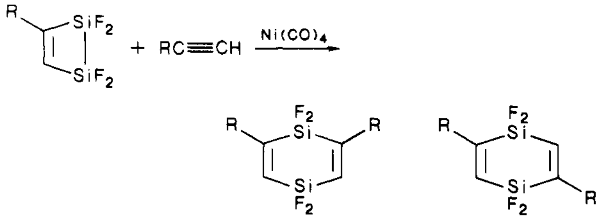


(3)



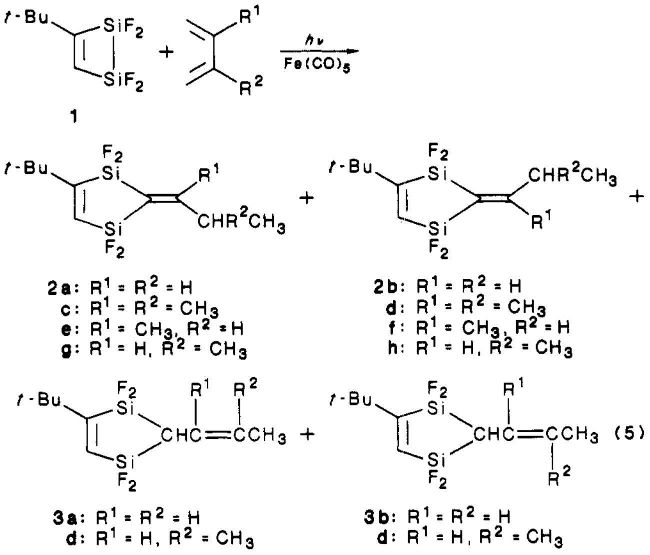
(4)

We recently reported the cycloaddition reactions between 3-*tert*-butyl-1,1,2,2-tetrafluorodisilacyclobutene (1) and cyclohexadiene mediated by iron pentacarbonyl and tungsten hexacarbonyl.[11] 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 that were determined by single-crystal X-ray diffraction.[11]

We have investigated as a model reaction cycloaddition between 1,3-butadienes and 1,1,2,2-tetrafluoro-1,2-disilacyclobutene with the hope that, should disilabutadiene exist at all, the reactions may proceed via certain intermediates that would reveal the existence of such species. This paper reports our results of the cycloaddition reactions mediated by group VI (6) metal carbonyls (M = Cr, Mo, W).

Results and Discussion

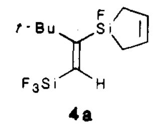
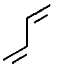
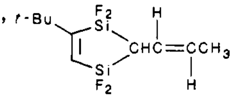
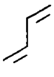
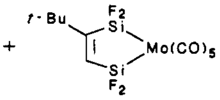
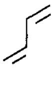
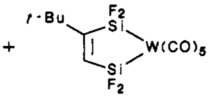
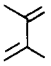
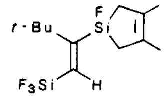
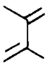
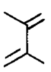
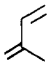
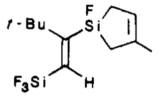
When the reactions of 3-*tert*-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobutene (1) with 1,3 butadienes were carried out under photochemical conditions and in the presence of iron pentacarbonyl, products of the unusual 1,1-addition reaction were obtained (eq 5).[12]

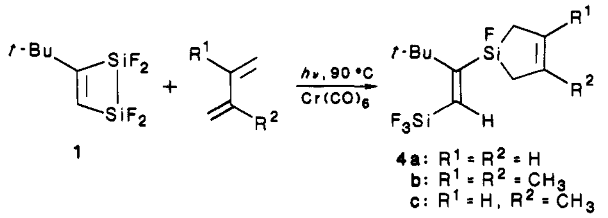


(5)

When group VI (6) metal carbonyls were used at room temperature, in addition to products 3 mentioned above, the photochemical reactions yielded a new type of product, (fluorosilyl)(trifluorosilyl)alkenes, designated by 4. Under controlled experimental conditions, it is possible to obtain 4 only. With $Cr(CO)_6$ as a catalyst, pure 4 can be prepared by reacting 1 with corresponding 1,3-dienes photochemically at 90 °C (eq 6). The products and reaction conditions are summarized in Table I.

Table I. Products from the Reaction of 1 with Dienes Mediated by VIB (6) Metal Carbonyl

reactns	conditns	products
 + 1 + $Cr(CO)_6$	90 °C	 **4a**
 + 1 + $Mo(CO)_6$	90 °C	**4a**,  **3a** (trace)
 + 	*hν*, 30 °C	**4a**
 + 	90 °C	**4a**
 + 1 + $Cr(CO)_6$	90 °C	 **4b**
 + 1 + $Mo(CO)_6$	90 °C	**4b**
 + 1 + $W(CO)_6$	90 °C	**4b**
 + 1 + $M(CO)_6$ M = Cr, Mo, W	90 °C	 **4c**



(6)

Compounds **4a**, **4b**, and **4c**, apparently formed in a process involving F migration, can be purified and fully characterized by mass spectrometry, elemental analysis, and ^1H, ^{19}F, and ^{13}C NMR spectroscopy. For example, the $^{19}F\{^1H\}_{BB}$ NMR spectrum of **4b** shows a doublet at 137.53 ppm and a quartet at 161.54 ppm with an intensity ratio of 3:1, two fluorosila groups are trans to each other because $^5J_{F,F'} = 20$ Hz. (All compounds with two fluorosila groups cis to each other synthesized in this laboratory have $^5J_{F,F'}$ in the range of 1–6 Hz.) The ^1H NMR spectrum shows a singlet at δ 1.10, a broadened peak at δ 1.5–1.8 which overlaps with a sharper peak at δ 1.7, and a quartet of doublets at δ 6.20, with an intensity ratio of 9:10:1. They are assigned to the *tert*-butyl group, two CH_2 and two CH_3 groups, and the olefin proton near SiF_3 ($=CHSiF_3$), respectively. That the coupling constant of the quartet ($^3J_{H\text{-}SiF} = 4$ Hz) is larger than that of the doublets ($^4J_{CH\text{-}SiF} = 2$ Hz) is strong evidence that the olefin hydrogen is

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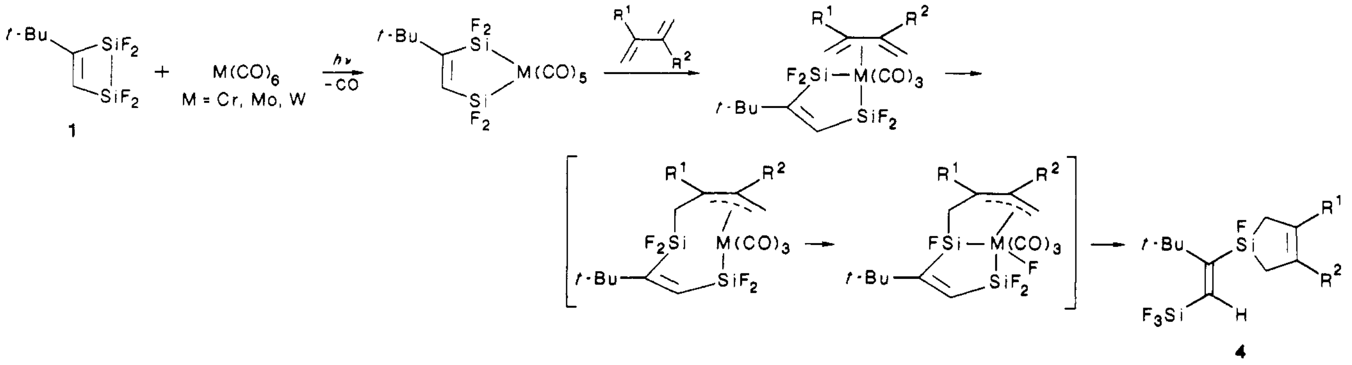
(9) Sakurai, H.; Kobayashi, T.; Nakadaira, Y. *J. Organomet. Chem.* **1978**, *162*, C43.

(10) Liu, C. S.; Cheng, C. W. *J. Am. Chem. Soc.* **1975**, *97*, 6746.

(11) Lin, C. H.; Lee, C. Y.; Liu, C. S. *J. Am. Chem. Soc.* **1986**, *108*, 1323.

(12) Lin, C. H.; Lee, C. Y.; Liu, C. S., *Organometallics*, first of four papers in this issue.

Scheme I



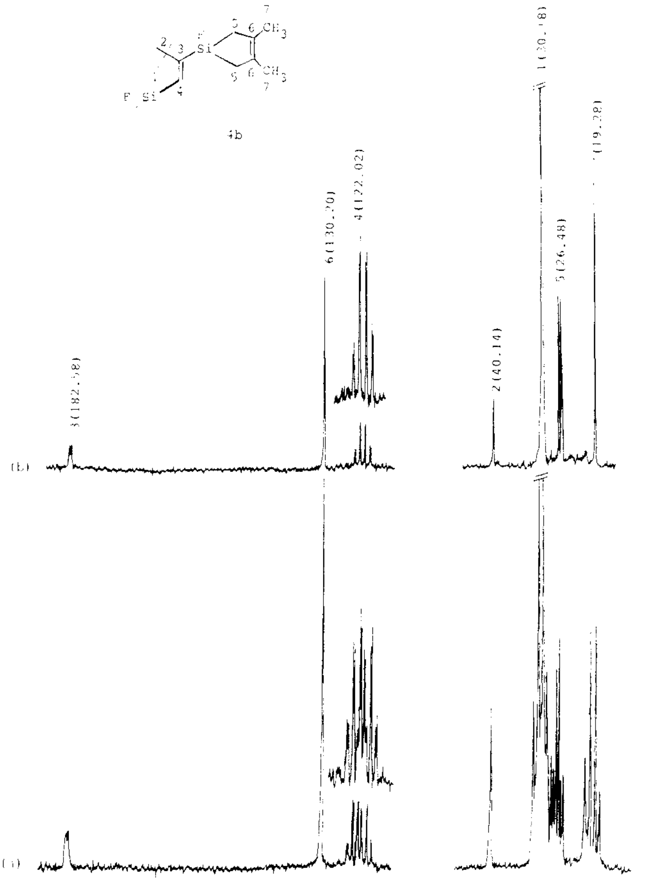


Figure 1. (a) $^{13}C\{^1H\}_{CW}$ and (b) $^{13}C\{^1H\}_{BB}$ spectra of compound **4b**.

adjacent to the SiF_3 group. The $^{13}C\{^1H\}_{CW}$ NMR spectrum is most informative since it shows a doublet (due to F coupling) of triplets (due to H coupling) for the two CH_2 carbons at δ 26.48 and a doublet (due to H coupling) of quartets (due to F coupling) for the CH carbon in the $=CHSiF_3$ moiety at δ 122.02 (Figure 1). The latter is consistent with the interpretation of the ^1H NMR spectrum described above.

These results indicate a very unusual fluorine migration from one silicon to the other assisted by the metal (Scheme I).

Considering compounds **3** which are formed from hydrogen migration from carbon-1 to carbon-4, that the fluorine migration proceeds alongside the hydrogen migration may suggest a common type of intermediate that allows both pathways to proceed in a parallel manner (Scheme II).

Intermediate species X, X_1, and X_2 involving η^3-allyl and η^3-silaallyl moieties are not expected to be stable under the

Scheme II

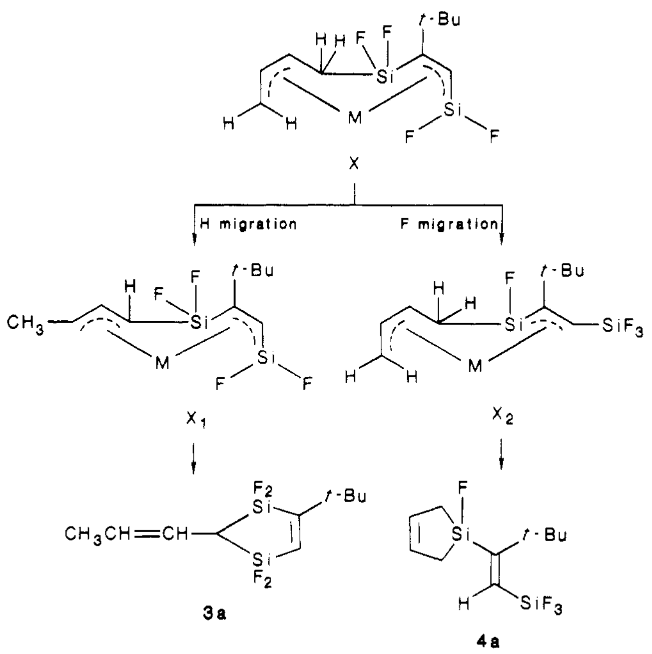
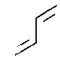
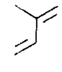
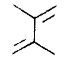


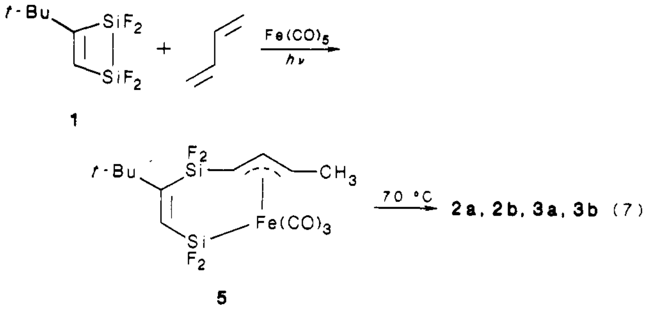
Table II. Products of the Cycloaddition Reactions between 1 and Various 1,3-Butadienes Mediated by $M(CO)_6$ (M = Cr, Mo, W)

butadiene	exptl conditns	product $Cr(CO)_6$	$Mo(CO)_6$	$W(CO)_6$
	hν, 0 °C	**3a**	**3a**	**3a**
	hν, 30 °C	**4a**, **3a** (trace)	**3a**, **4a** (trace)	**3a**
	hν, 0 °C	**4c**, **3d**	**3d**	**3d**
	hν, 30 °C	**4c**	**4c**, **3d**	**3d**
	hν, 0 °C	**4b**	**4b**, **3c**	**3c**
	hν, 30 °C	**4b**	**4b**, **3c**	**3c**

experimental conditions used. However, in the case of 1,3-butadiene with iron pentacarbonyl as mediator, we did observe the η^3-allyl intermediate, namely, compound **5**.[12]

Compound **5** can be viewed as the more stable form of X_1. When **5** was warmed up to 70 °C, it converted to **2a**, **2b**, **3a**, and **3b** (eq 7).

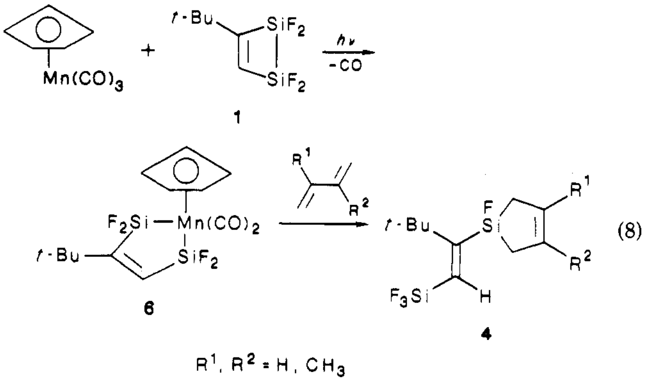
The isolation of **5** is strong evidence that the postulated types of common intermediates, such as X, which allow both hydride migration and fluoride migration to take place, do exist in the cycloaddition reaction between butadiene and disilacyclobutene. The fact that two fluorosila groups are trans to each other in compounds **4** is strong evidence for the existence of η^3-silaallyl species such as X_2.



Since hydride and fluoride can be considered, respectively, as soft and hard bases, the effect of the hardness (or softness) of the metal on the reaction pathways was also investigated.

The results of the reactions using $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ as catalyst are listed in Table II. These reactions were carried out under controlled experimental conditions. It is generally true that the softer tungsten tends to assist hydride migration to form **3**, whereas the harder chromium tends to facilitate fluoride migration to form **4**. In the middle case of molybdenum, products due to both H migration and F migration are obtained. This trend is particularly obvious in the cases of isoprene (*hν*, 30 °C) and 2,3-dimethylbuta-1,3-diene (*hν*, 0 and 30 °C).

When "softer" $Fe(CO)_5$ and $Ni(CO)_4$ were used, no products involving F migration were observed even at elevated temperatures (≥100 °C). In the case of $Ni(CO)_4$, 1,4-addition leading to disilacyclooctadienes was found to be the only reaction pathway.[14] In the first transition-metal period, another "hard" metal carbonyl, $(\eta^5\text{-}C_5H_5)Mn(CO)_3$, was tried to test the trend observed above. It was found that only **4**, the product of F migration, was obtained (eq 8).



Because of the relative rigidity of the disilabutene moiety in the disilametallacycle intermediate, the migration of the silyl groups is expected to move with some constraint. As a consequence, after the insertion of the first silyl group, the attack of the second silyl group may proceed via four competitive reaction pathways: (i) 1,4-addition to form 1,4-disilacyclooctadienes,[14] (ii) 1,2-addition to form 1,4-disilacyclohexenes,[13] (iii) H migration leading to the 1,1-addition to form alkylidenedisilacyclopentenes and disilacyclopentenylalkenes,[12] and (iv) F migration to form (fluorosilyl)(trifluorosilyl)alkenes.

We have shown that both the geometry of the disilametallacycle intermediate[11,14] and the electronic properties (such as hardness) of the central metal play controlling roles in selecting the reaction pathway. The steric effects of the substituents on various carbons of the 1,3-dienes can also be controlling factors.[12,13] The excellent correlation between the structures of the intermediates and the reaction pathways makes it possible to fine tune the reaction pathways of this particular reaction system.

Experimental Section

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 is due to couplings with heteronuclei, whereas the coupling patterns in $^{13}C\{^1H\}_{CW}$ are included in the parentheses.

Preparation and identification of compounds of families **2**, **3**, and **5** have been described previously.[12]

Preparation of Family 4. A 10-mL *n*-pentane solution containing 0.4 mmol of **1**, 0.4 mmol of $CH_2{=}CR^1CR^2{=}CH_2$ ($R^1 = R^2 = H$; $R^1 = R^2 = CH_3$; $R^1 = H$, $R^2 = CH_3$), and 0.4 mmol $Cr(CO)_6$ was irradiated under dry nitrogen at 90 °C for 3 h. After removal of solvent, about 80–90 mg of **4a** ($R^1 = R^2 = H$), **4b** ($R^1 = R^2 = CH_3$), and **4c** ($R^1 = H$, $R^2 = CH_3$) was obtained, respectively, by vacuum distillation at 100 °C. The yields based on the quantity of **1** used were 75–80%.

Anal. Calcd for **4a**: C, 44.78; H, 6.00; F, 28.36. Found: C, 44.66; H, 6.08; F, 28.79. Mass spectrum of **4a**: *m/e* 268 (M^+, $C_{10}H_{16}Si_2F_4^+$), 253 ($C_9H_{13}Si_2F_4^+$), 167 ($C_6H_{10}SiF_3^+$), 101 ($C_4H_6SiF^+$), 57 ($C_4H_9^+$). ^1H NMR of **4a**: δ 1.18 (s), 9 H, *t*-Bu; 1.8–1.9 (br), 4 H, CH_2; 5.70 (c), 2 H, $-CH{=}CH-$; 6.27 (qd), 1 H, $=CHSiF_3$; $^3J_{CHSiF} = 4.0$, $^4J_{CH=CSiF} = 2.0$ Hz. $^{19}F\{^1H\}$ NMR of **4a**: 137.37 (d), SiF_3; 159.97 ppm (q) SiF; $^5J_{F,F} = 20$ Hz. ^{13}C NMR of **4a**: δ 181.52 m (m), $=C(t\text{-}Bu)SiF_2$; 130.34 s (d), $-CH{=}CH-$; 121.62 q (dq), $=CHSiF_3$; 39.60 s (s), $(CH_3)_3C$; 29.76 s (q), $(CH_3)_3C$; 23.72 d (dt), CH_2.

Anal. Calcd for **4b**: C, 48.64; H, 6.76; F, 25.68. Found: C, 48.35; H, 6.92; F, 25.85. Mass spectrum of **4b**: *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 **4b**: δ 1.1 (s), 9 H, *t*-Bu; 1.5–1.8 (br), 10 H, CH_2CCH_3; 6.2 (qd), 1 H, $=CHSiF_3$. ^{19}F NMR of **4b**: 137.53 (d), SiF_3; 161.54 ppm (q), SiF. ^{13}C NMR of **4b**: δ 19.28 s (q), $=CCH_3$; 26.48 d (dt), CH_2; 30.18 s (q), $(CH_3)_3C$; 40.14 s (s), $(CH_3)_3C$; 122.02 q (dq), F_3SiCH; 130.20 s (s) $=CCH_3$; 182.58 c (dc), $=C(t\text{-}Bu)SiF$.

Mass spectrum of **4c**: 282 (M^+, $C_{11}H_{18}Si_2F_4^+$), 267 ($C_{10}H_{15}Si_2F_4^+$), 215 ($C_6H_{11}Si_2F_4^+$), 57 ($C_4H_9^+$). ^1H NMR of **4c**: δ 1.18 (s), 9 H, *t*-Bu; 1.3 (s), 3 H, $=CCH_3$; 1.8–1.9 (br), 4 H, CH_2; 5.7 (br), 1 H, $=CHCH_2$; 6.3 (qd), 1 H, $F_3SiCH{=}$. ^{19}F NMR of **4c**: 137.37 (d), SiF_3; 159.97 ppm (q), SiF. ^{13}C NMR of **4c**: δ 19.72 and 23.35 d (dt), CH_2; 22.56 s (q), $=CCH_3$; 29.8 s (q), $(CH_3)_3C$; 39.6 s (s), $(CH_3)_3C$; 121.62 q (dq), $F_3SiCH{=}$; 123.22 s (d), H_2CCH; 138.67 s (s), $H_2CC(CH_3){=}$; 181.52 m (m), $=C(t\text{-}Bu)SiF$.

Preparation of Compound 6. *n*-Pentane solution (10 mL) containing 5.0 mmol of **1** and 5.0 mmol of $(\eta^4\text{-}C_5H_5)Mn(CO)_3$ was irradiated under nitrogen atmosphere at 0 °C for 12 h. After removal of solvent and prolonged pumping to remove unreaction reactants, about 1.0 g of **6** was obtained as a brown liquid. The yield based on the quantity of **1** was about 50%.

Mass spectrum of **6**: *m/e* 390 (M^+, $C_{11}H_{15}Si_2F_4Mn(CO)_2^+$), 362 ($C_{11}H_{15}Si_2F_4Mn(CO)^+$), 325 ($C_6H_{10}Si_2F_4Mn(CO)_2^+$), 297 ($C_6H_{10}Si_2F_4Mn(CO)^+$), 215 ($C_6H_{11}Si_2F_4^+$). ^1H NMR of **6**: δ 1.19 (s), 9 H, *t*-Bu; 4.75 (s), 5 H, C_5H_5; 7.15 (m), 1 H, $=CH$. $^{19}F\{^1H\}$ NMR of **6**: 82.57 (d), 87.30 (d), $=CHSiF_2$; 92.19 (d), 95.10 ppm (d), $=C(t\text{-}Bu)SiF_2$. ^{13}C NMR of **6**: δ 220.7, 220.5 s (s), CO; 189.9 m (m), $=C(t\text{-}Bu)$; 148.7 m (d), $=CHSiF_2$; 85.3 s (d), C_5H_5; 38.2 s (s), $C(CH_3)_3$; 29.3 s (q), $C(CH_3)_3$.

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

[14] Reactions mediated by $Ni(CO)_4$ proceed via an intermediate of less crowded geometry that leads to products of 1,4-addition; details will be published elsewhere.

thanks the Nuclear Energy Research Institute for a research fellowship.

Registry No. 1, 36091-97-1; **3a**, 109064-32-6; **3c**, 109283-40-1; **3d**, 109283-39-8; **4a**, 109283-36-5; **4b**, 109283-37-6; **4c**, 109283-38-7; **6**, 109283-42-3; (η^5-C_5H_5)Mo(CO)$_3$, 12079-65-1; Cr(CO)$_6$, 13007-92-6; Mo(CO)$_6$, 13939-06-5; W(CO)$_6$, 14040-11-0; (SiF$_2$(Bu-*t*)C=CHSiF$_2$)Mo(CO)5, 75311-40-9; (SiF$_2$(Bu-*t*)C=CHSiF$_2$)W(CO)$_5$, 109283-41-2; 1,3-butadiene, 106-99-0; 2,3-dimethyl-1,3-butadiene, 513-81-5; 2-methyl-1,3-butadiene, 78-79-5.

Metal Carbonyl Mediated Isomerization of 1,4-Disilacyclohexa-2,5-dienes Involving Cleavage of C–Si Bonds

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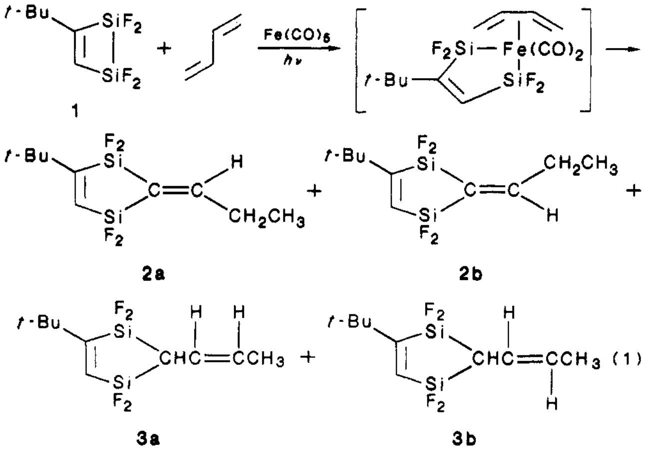
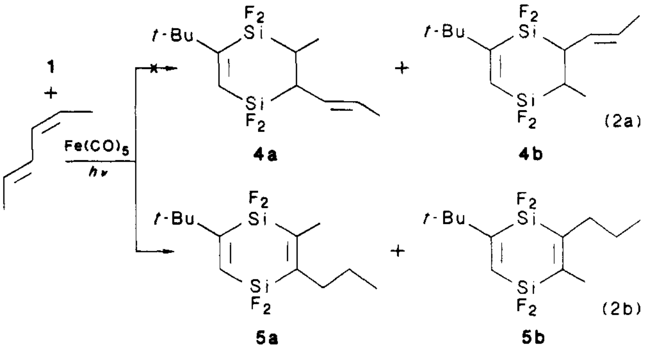
The isomerization between 2,5- and 2,6-disubstituted 1,4-disilacyclohexa-2,5-diene derivatives is studied under photochemical conditions in the presence of Fe(CO)$_5$. Strong evidence is given for the process involving two metal-assisted Si–C bond cleavages to form an alkyne complex as the intermediate. Other possible mechanisms are discussed for comparison.

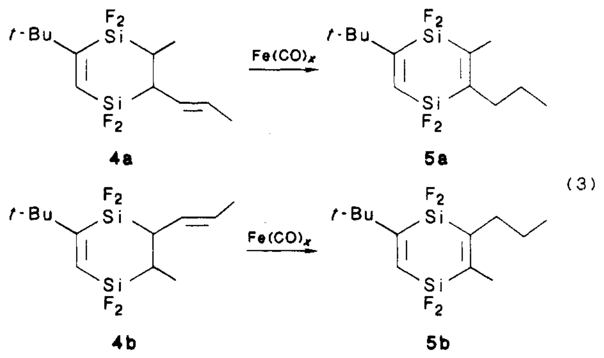
Recently we reported the novel cycloaddition reactions between 1,1,2,2-tetrafluoro-1,2-disilacyclobutene (1) and conjugated dienes mediated by metal carbonyls.[1-4] All these reactions involved the disilametallacycle intermediates which facilitated the migration of silyl groups to the dienes via various routes, for example, in the case of butadiene,[2,4] eq 1.



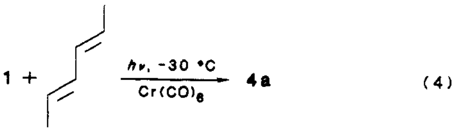
During the course of our study of the iron-mediated cycloaddition reaction of 1 with *cis,trans*-2,4-hexadiene,[3] products from direct 1,2-addition reaction, namely, 1,4-disilacyclohexa-2-enes **4a,b**, were not obtained. Instead, 1,4-disilacyclohexa-2,5-dienes **5a,b** were found to be the major products (eq 2).

It is believed that 1,4-disilacyclohexa-2-enes **4a,b** were formed first but converted to **5a** and **5b**, respectively, by the iron carbonyl species that existed in the reacting system (eq 3).





Fortunately, it was possible to obtaine **4a** from the reaction of *trans,trans*-2,4-hexadiene,[3] which provided an opportunity to verify the idea described above (eq 4).



However, when **4a** was treated with Fe(CO)$_5$ photochemically, not only **5a** but also a mixture of **5a** and **5b** (in a ratio of 2:3) were obtained (eq 5).[3]

$$\mathbf{4a} \xrightarrow[h\nu]{Fe(CO)_5} \mathbf{5a}/\mathbf{5b} \qquad (5)$$

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

[2] Lin, C. H.; Lee, C. Y.; Liu, C. S. *Organometallics*, first four papers in this issue.

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

[4] Lee, C. Y.; Lin, C. H.; Liu, C. S. *Organometallics*, third of four papers in this issue.

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