

Cycloaddition Reactions of Tetrafluorodisilacyclobutenes with Conjugated Dienes Mediated by Metal Carbonyls. 5.

1,4-Addition versus 1,2-Hydrogen Migration

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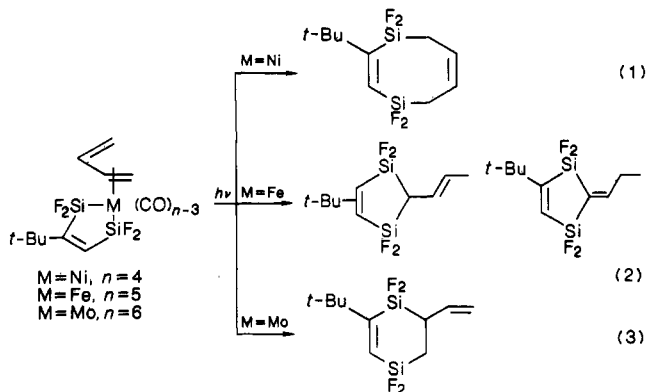
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($\eta^5\text{-C}_5\text{H}_5$)Co(CO)₂-mediated cycloaddition reactions of 3-*tert*-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobutene (1) with various dienes have been studied. The reactions show the competition between 1,4-addition and 1,1-addition via 1,2-hydrogen migration. Correlation between the detailed structure of the (η^2 -diene)disilametallacycle intermediate and the reaction pathways is established.

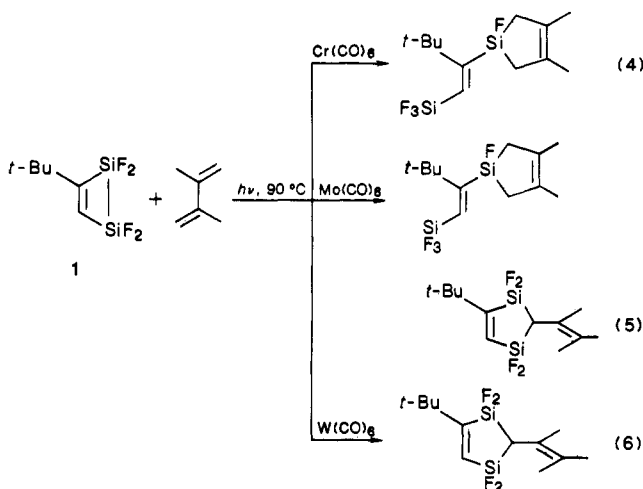
We recently reported a number of unusual cycloaddition reactions between 3-*tert*-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobutene (1) and conjugated dienes mediated by transition metal carbonyls.¹⁻⁶ All these reactions proceed

via an intermediate $\text{F}_2\text{Si}(t\text{-Bu})\text{C}=\text{CHSiF}_2\text{M}(\eta^4\text{-diene})(\text{CO})_x$. These reactions represent a remarkable system in which a close correlation between the detailed structures of the intermediate and the different reaction pathways can be established. In other words, one is able to fine-tune the structures of the intermediate, such as the geometry of the coordination sphere, the electronic properties of the metal, the steric effects of the substituents of the diene, etc., to control the reaction pathways.

For example, when Ni(CO)₄ is used, the intermediate has a less crowded geometry of the coordination sphere, which leads to the products of the usual 1,4-addition (eq 1).⁶ When Fe(CO)₅ is used, a more crowded intermediate¹ would slow down the attack of the second silyl group at C₄ of the coordinated diene and the strong hydrogen affinity of Fe (referred to the softness of Fe) would result in the products of 1,1-addition via hydrogen migration (eq 2).² In the case of Mo(CO)₆, the crowdedness of the coordination sphere of the intermediate would rule out the pathway of 1,4-addition; also the poorer hydrogen affinity of Mo (relative hardness of Mo) would not favor the process involving H-migration. So the reaction yields the products of direct 1,2-addition (eq 3).³



The control of the reaction pathways by fine-tuning the electronic properties of the metal can be illustrated by another example. Under strictly controlled conditions the reaction with 2,3-dimethyl-1,3-butadiene proceeds via F (a hard base) migration when harder Cr(CO)₆ is used (eq 4). On the other hand, the softer W(CO)₆ would lead the reaction to the product via H (a soft base) migration (eq 6). In the middle case of Mo(CO)₆, both products are obtained (eq 5).⁴



Between group 6 and group 8 lies Mn. ($\eta^5\text{-C}_5\text{H}_5$)Mn(CO)₃ as a mediator has been demonstrated to show characteristic properties of a hard metal carbonyl species (forms products via F-migration).⁴

Between Fe and Ni, there is Co. Although there is no simple mononuclear zerovalent metal carbonyl species of Co, ($\eta^5\text{-C}_5\text{H}_5$)Co(CO)₂ is expected to show characteristics of a soft metal carbonyl species because the ligand $\eta^5\text{-C}_5\text{H}_5$ is a soft base. The coordination sphere of the intermediate is not crowded because $\eta^5\text{-C}_5\text{H}_5$ can be considered as a planar ligand. These considerations may result in the competition of 1,4-addition versus H-migration. Besides, the expected intermediate $\text{F}_2\text{Si}(t\text{-Bu})\text{C}=\text{CHSiF}_2\text{Co}(\eta^2\text{-diene})(\text{CO})$ would involve only one Co-olefin bond. All these special features make this system a very interesting one for investigation.

Results and Discussion

In principle the reactions can be carried out by either one of the following ways: (i) 1 and ($\eta^5\text{-C}_5\text{H}_5$)Co(CO)₂ react first to give ($\eta^5\text{-C}_5\text{H}_5$)(F₂Si(*t*-Bu)C=CHSiF₂CoCO) (I), which is then reacted with the dienes, or (ii) 1, ($\eta^5\text{-C}_5\text{H}_5$)Co(CO)₂, and the dienes react all together. In practice, the first method was adapted in the study. The

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

(2) Part 1: Lin, C. H.; Lee, C. Y.; Liu, C. S. *Organometallics* 1987, 6, 1861.

(3) Part 2: Lee, C. Y.; Lin, C. H.; Liu, C. S. *Organometallics* 1987, 6, 1870.

(4) Part 3: Lin, C. H.; Lee, C. Y.; Liu, C. S. *Organometallics* 1987, 6, 1878.

(5) Chen, Y. C.; Lin, C. H.; Lee, C. Y.; Liu, C. S. *Organometallics* 1987, 6, 1882.

(6) Part 4: Jzang, T. T.; Lee, C. Y.; Liu, C. S. *Organometallics*, preceding paper in this issue.

Table I. Co-Mediated Cycloaddition Reactions between 1 and Various Conjugate Dienes

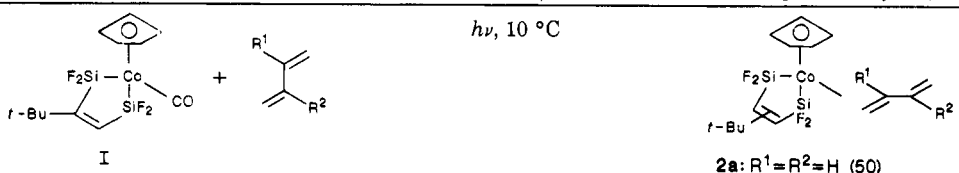
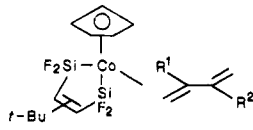
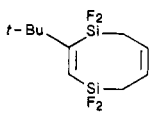
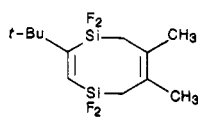
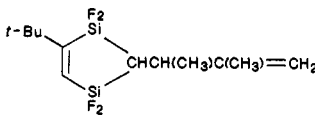
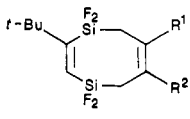
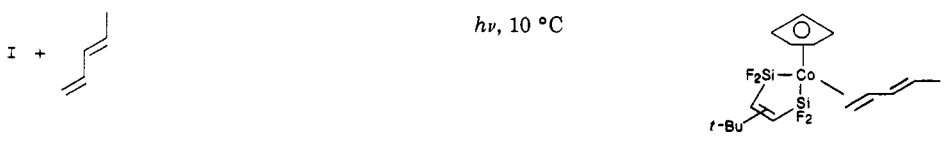
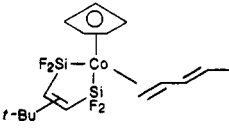
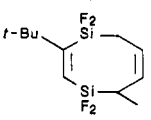
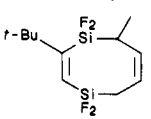
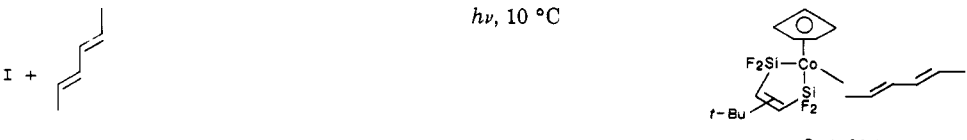
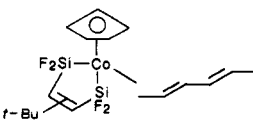
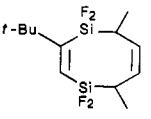

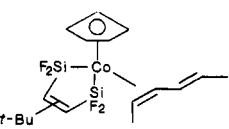
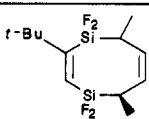

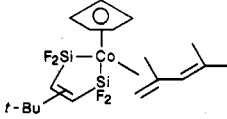
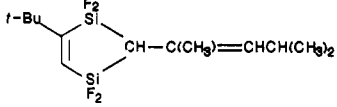
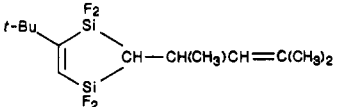
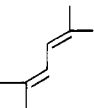

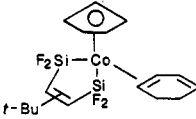
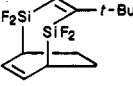
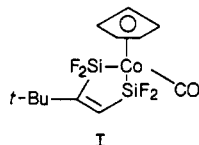
reactants	conditns	products (yield, %)
 <p>I</p>	$h\nu, 10\text{ }^\circ\text{C}$	 <p>2a: $R^1 = R^2 = \text{H}$ (50) b: $R^1 = R^2 = \text{CH}_3$ (50) c: $R^1 = \text{H}, R^2 = \text{CH}_3$ (50)</p>
2a decomposition	$h\nu, 60\text{ }^\circ\text{C}$	 <p>3a (100)</p>
2b decomposition	$h\nu, 60\text{ }^\circ\text{C}$	 <p>3b (20%)</p>  <p>4a (80%)</p>
2c decomposition	$h\nu, 60\text{ }^\circ\text{C}$	 <p>3c: $R^1 = \text{H}, R^2 = \text{CH}_3$ (50%) d: $R^1 = \text{CH}_3, R^2 = \text{H}$ (50%)</p>
	$h\nu, 10\text{ }^\circ\text{C}$	 <p>2d (50%)</p>
2d decomposition	$h\nu, 60\text{ }^\circ\text{C}$	 <p>3e (50%)</p>  <p>3f (50%)</p>
	$h\nu, 10\text{ }^\circ\text{C}$	 <p>2e (40%)</p>
2e decomposition	$h\nu, 60\text{ }^\circ\text{C}$	 <p>3g (85%)</p>
	$h\nu, 60\text{ }^\circ\text{C}$	 <p>2f (40%)</p>

Table I (Continued)

reactants	conditns	products (yield, %)
2f decomposition	$h\nu$, 60 °C	 3h (80%)
I + 	$h\nu$, 10 °C	 2g (50%)
2g decomposition	$h\nu$, 60 °C	 5a (30%)
		 4b (50%)
I + 	$h\nu$, 10 °C	no reaction
I + 	$h\nu$, 10 °C	 2h (40%)
2h decomposition	$h\nu$, 60 °C	 3i (100%)

structure of I was identified by spectroscopies and confirmed by a single-crystal X-ray experiment.⁷



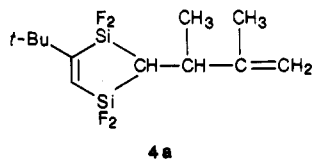
The results of the cycloadditions reactions of 1 with 1,3-butadiene, 2-methyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, trans-penta-1,3-diene, trans,trans-hexa-2,4-diene, cis,trans-hexa-2,4-diene, 2,4-dimethylpenta-1,3-diene, 2,5-dimethylhexa-2,4-diene, and cyclohexa-1,3-diene are summarized in Table I.

There are mainly two types of products in these reactions. The most common type is that of 1,4-addition, namely, disilacyclobutenes (3 family). The identification of these compounds have been discussed previously.⁶ These products may suggest that the less crowded intermediates of Co allow 1,4-addition to compete favorably, just as is in the case of Ni.⁶

The second type is that of 1,1-addition (4 family). Unlike the products of 1,1-addition in the Fe-mediated reactions, which are formed via 1,4- and/or 1,3-H-migra-

tion,² these products of the 4 family presumably are formed via an unprecedented 1,2-H-migration.

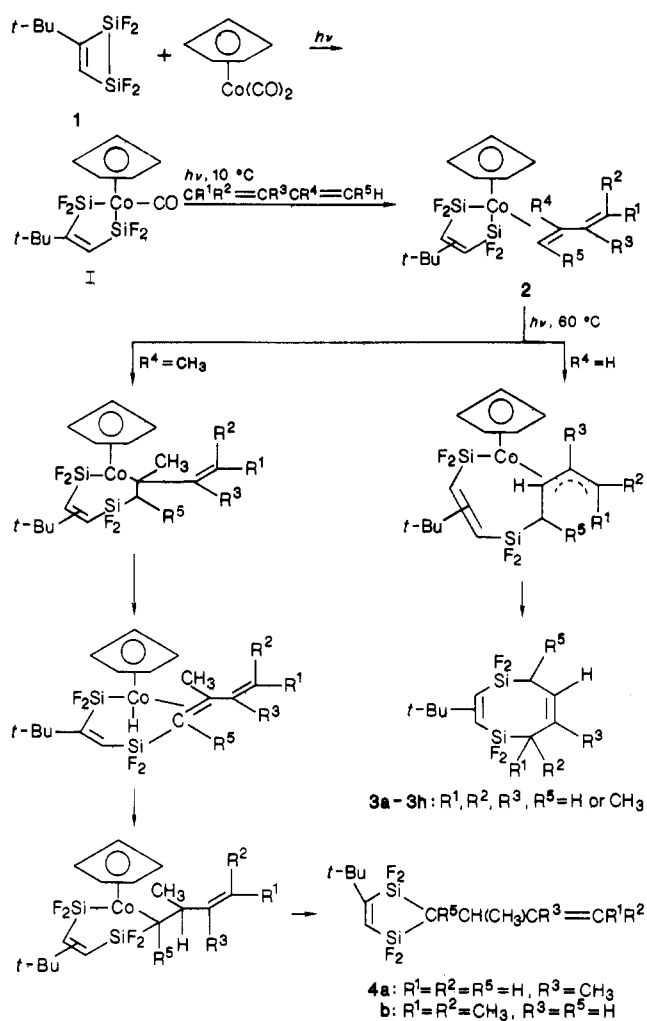
All compounds in the 4 family were characterized by mass spectra, elemental analyses, and ¹H, ¹⁹F, and ¹³C NMR spectra. For example, the reaction with 2,3-dimethylbuta-1,3-diene results in compound 4a in 80% yield. Compound 4a shows the molecular formula of C₁₂H₂₀Si₂F₄ (*m/e* 296 (M⁺)). The ¹⁹F NMR spectrum shows four doublets (²J_{F,F} = 34.2 Hz, typical for geminal couplings) with fine structures (due to H and long-range F couplings) at 131.63, 136.24, 136.60, and 141.65 ppm. These are typical features for the four fluorines in the 1,3-disilacyclopentenyl moiety of 4a.²



The ¹H NMR spectrum of 4a shows in addition to the resonances of *tert*-butyl protons (δ 1.13 (s)), two methyl groups (δ 1.16 (d), 1.68 (s)), two methine protons (δ 2.11 (m), 2.67 (m)), =CHSiF₂ (δ 6.65 (m)), and an AB spectrum at δ 4.81 typical for the resonance of =CH₂.

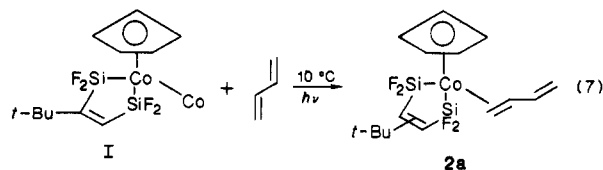
The ¹³C NMR spectrum of 4a is most informative. Beside the typical resonances of the *tert*-butyl group (δ 29.58 and 38.26), F₂Si(*t*-Bu)C= (δ 180.78 (m)), =CHSiF₂

Scheme I



(δ 139.93 (t)), $-\text{CH}(\text{CH}_3)-$ (δ 37.09, 20.97), and $=\text{C}(\text{CH}_3)-$ (δ 112.79, 23.55), the spectrum shows two resonances most characteristic for the structure of **4a**: the singlet at δ 109.80 for $=\text{CH}_2$, which splits to a triplet in the $^{13}\text{C}\{^1\text{H}\}_{\text{CW}}$ spectrum; and the multiplet at δ 14.64 (due to fluorine couplings) for $(\text{F}_2\text{Si})_2\text{CH}-$, which splits to a doublet of multiplets in the $^{13}\text{C}\{^1\text{H}\}_{\text{CW}}$ spectrum.

When the reactions between **I** and the dienes were carried out photochemically at 10°C , η^2 -diene intermediates were isolated before the final products appeared. For example, in the reaction with 1,3-butadiene one obtained intermediate **2a**.



Intermediate **2a** is a mixture of two isomers (roughly in 1:1 ratio). The structural difference of these two isomers lies in the position of the *tert*-butyl group relative to the η^2 -diene moiety.

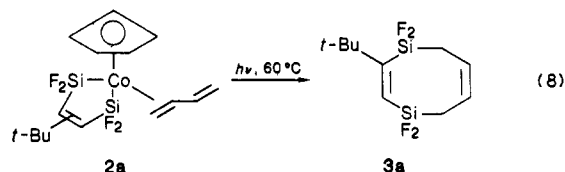
The $^{19}\text{F}\{^1\text{H}\}$ spectrum of **2a** consists of eight doublets. Homonuclear F-F decoupling shows the four resonances at 95.41, 92.54 and 90.59, 87.63 ppm belonging to one isomer and the rest belonging to the other (110.88, 111.52 and 99.13, 99.67 ppm).

The ^1H NMR spectrum of **2a** shows two sets of spectrum fitting the structure of **2a** well. The most significant

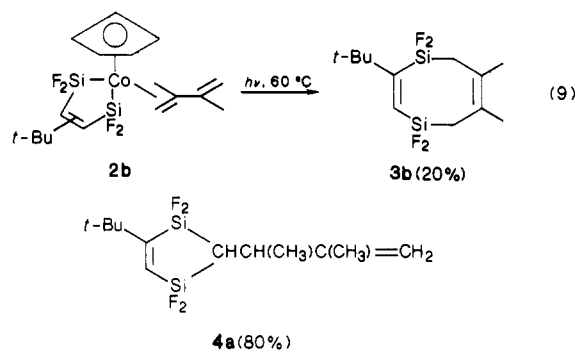
spectral feature is the observation of the upfield shifts of the metal-bonded olefin protons at δ 2.65 and 2.68^{8,9} while the free olefin protons show normal chemical shifts at δ 4.81-5.46.

The ^{13}C NMR spectrum is most informative. The spectrum consists of two sets of resonances fitting the proposed structures perfectly. The $^{13}\text{C}\{^1\text{H}\}_{\text{CW}}$ spectrum shows upfield shifted triplets for metal-bonded $\text{CH}_2=$ of the two isomers at δ 35.00 and 35.44 respectively, and doublets for the metal-bonded $=\text{CH}-$ at δ 60.12 and 60.73, respectively.^{8,9} The free olefin carbons show in the $^{13}\text{C}\{^1\text{H}\}_{\text{CW}}$ spectrum the doublets at δ 141.87 and 141.91 (for free $-\text{CH}=\text{C}$) and triplets at δ 114.56 and 114.63 (for free $=\text{CH}_2$) of the two isomers. These chemical shifts are within the range of normal sp^2 carbons.

When **2a** was further irradiated at 60°C , it converted to product **3a** quantitatively (eq 8).



In the reaction with 2,3-dimethyl-1,3-butadiene under the same experimental conditions, two types of products, **3b** and **4a**, were obtained with relative yields 20% and 80%, respectively (eq 9).



The reaction with 2-methyl-1,3-butadiene gave the intermediate **2c**. Compound **2c** showed in its $^{13}\text{C}\{^1\text{H}\}_{\text{CW}}$ spectrum a triplet at δ 37.44, a doublet at δ 59.41, a singlet at δ 146.13, and a triplet at δ 110.39. They are assigned to C_4 , C_3 , C_2 , and C_1 of the butadiene, respectively. It is clear that the metal-bonded olefin in **2c** is the unsubstituted double bond of the butadiene, namely, C_3 and C_4 .

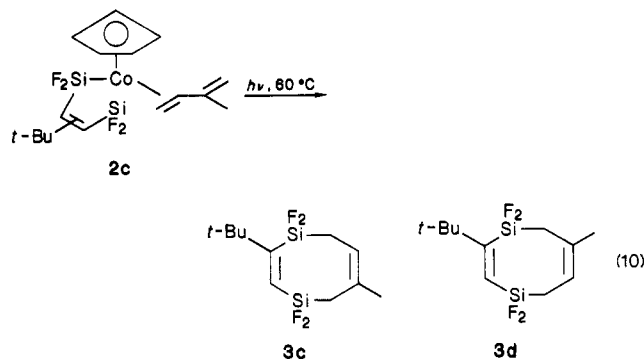
When **2c** was further irradiated at 60°C , it converted to **3c** and **3d** quantitatively.

On the basis of the results described above and in Table I, a plausible reaction mechanism can be proposed as shown in Scheme I.

According to Scheme I, further irradiation on the η^2 -diene intermediate **2** at 60°C results in two different reaction pathways: (i) 1,4-addition leading to products of the **3** family via a η^3 -allyl intermediate and (ii) 1,1-addition via 1,2-H-migration leading to the formation of **4**. The choice of reaction pathway seems to be determined by the conformation of the metal-bonded η^2 -diene. If the η^2 -bu-

(8) (a) Lee, T. W.; Liu, R. S. *J. Organomet. Chem.* 1987, 320, 211. (b) Faller, J. W.; Chodosh, D. F.; Katahira, D. *J. Organomet. Chem.* 1980, 187, 227.

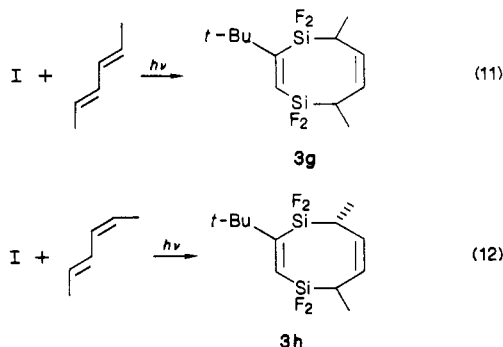
(9) (a) Lee, G. H.; Peng, S. M.; Lee, T. W.; Liu, R. S. *Organometallics* 1986, 5, 2378. (b) Tolman, C. A.; Ittle, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* 1978, 101, 585.



tadiene converts from the *E* form to the *Z* form during the reaction, path i predominates and compound 3 is formed. On the other hand, if the η^2 -butadiene keeps its *E* form during the reaction, path ii becomes important and compound 4 is formed. It seems that the key point is the nature of R^4 . In cases where $R^4 = H$, the *E* \rightarrow *Z* conversion of the η^2 -butadiene is easier. With $R^4 = CH_3$, the steric hindrance seems to slow down the *E* \rightarrow *Z* conversion and path ii becomes more favored.

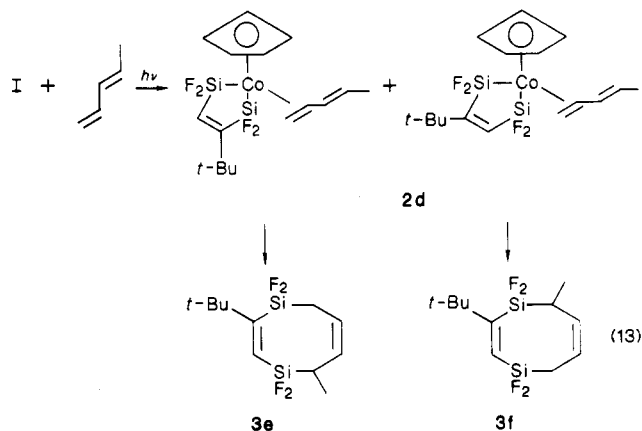
As a result of the above argument, the only two dienes leading to formation of products of 4 family are 2,3-dimethyl-1,3-butadiene and 2,4-dimethyl-1,3-pentadiene (both dienes with $R^4 = CH_3$). Notably, no products of type 4 were observed in the reaction with isoprene ($R^3 = CH_3$, $R^4 = H$). Also, when cyclohexadiene (intrinsic *Z* form) was used, the only product found was 3i.

It is interesting to note that in the reactions with *trans*-2,*trans*-4-hexadiene and *cis*-2,*trans*-4-hexadiene, the cycloaddition seems to be stereospecific (3g and 3h, respectively). We have discussed that the specificity was mainly due to the regioselectivity of the first silyl attack and the complete configuration retention of the η^3 -allyl moiety during the second silyl attack.⁶

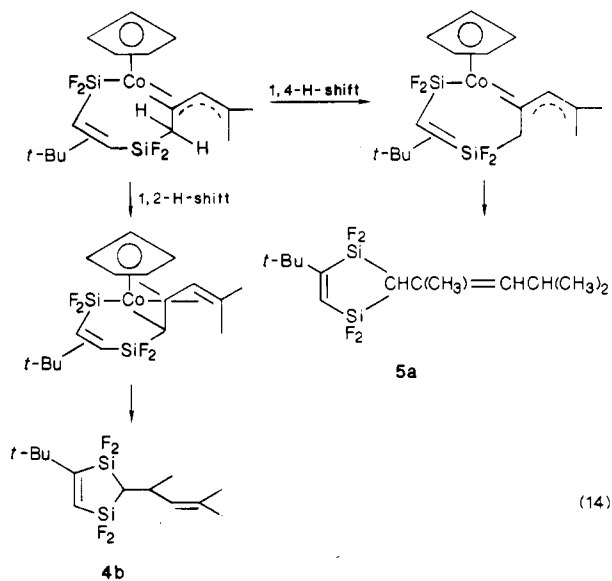


However, the reaction with *trans*-penta-1,3-diene gave two isomers, 3e and 3f, in equal abundance. From the structures of 3e and 3f, it is obvious that they have resulted from initial attack of two different silyl groups. Since the intermediate species 2d also consists of two isomers (in almost 1:1 ratio) differing only in the position of the *tert*-butyl group in relation to the η^2 -diene moiety, it is very likely that the initial silyl attack was controlled by the geometry of the intermediate. The two structural isomers of the intermediate result in the isomeric mixture of 3e and 3f. The same arguments apply to the reaction with isoprene.

It seems that the cycloaddition reactions mediated by $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ do show the expected nature of 1,4-addition versus 1,2-hydrogen migration. The only exception is the case of 2,4-dimethylpenta-1,3-diene, in which 1,4-addition was not observed. Instead, 1,1-additions via 1,4-hydrogen shift (product 5a) and 1,2-hydrogen shift (product 4b) were obtained in 30% and 50% yields, re-



spectively. The same reaction mediated by $\text{Ni}(\text{CO})_4$ yielded the product of 1,4-addition only. Since these Co-mediated cycloaddition reactions proceed much slower than Ni-mediated reactions,¹⁰ it is possible that the second silyl attack was further slowed down by the steric hindrance of the two methyl groups on C_4 of the diene, which allowed 1,4-hydrogen shift to occur in the η^3 -allyl intermediacy.



Compound 4 cannot be converted to 5a by irradiation in the presence of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$. The fact that only one isomer of 5a was obtained in the reaction also agrees with the proposed mechanism, for if 5a were formed via isomerization of 4b, one would expect to obtain a pair of isomers of *Z* and *E* configurations, respectively.

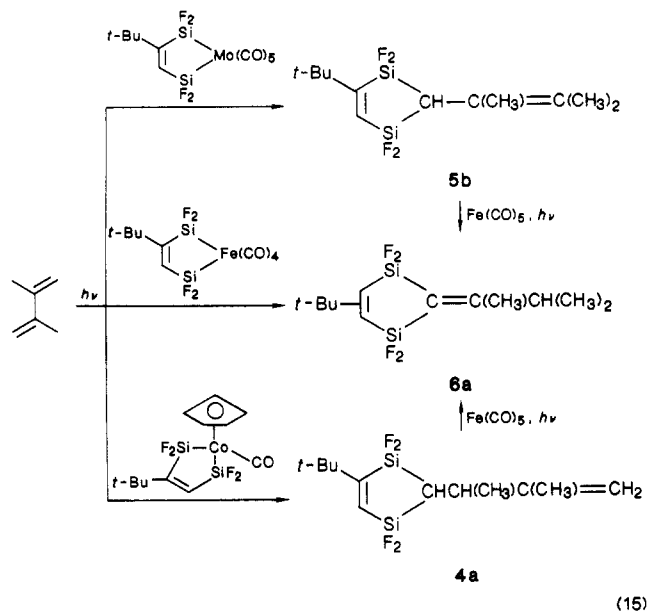
Although 1,1-addition via 1,4-hydrogen shift is common in the cycloaddition reactions mediated by $\text{Fe}(\text{CO})_5$ and $\text{W}(\text{CO})_6$,²⁻⁴ it is the first time we observe compound 5a with this particular diene.

It is interesting to note that for 1,1-addition reactions, all three types of products with respect to the different positions of the double bond can be obtained under control, for example, in the reaction of 2,3-dimethylbuta-1,3-diene (eq 15).

Identification of 5b and 6a have been reported previously.² When irradiated in the presence of $\text{Fe}(\text{CO})_5$, both 4a and 5b isomerize to 6a quantitatively.

(10) Jzang, T. T. Ph.D. Thesis, National Tsing Hua University, 1987.

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



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 NMR 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 NMR spectra, respectively. Chemical shifts of ^1H and ^{13}C NMR spectra were measured in δ values, ^{19}F chemical shifts were measured in parts per million upfield from internal standard CCl_3F . For the ^{13}C NMR data listed below, the spectra multiplicity following each chemical shift is due to the coupling with heteronuclei, whereas the coupling patterns in $^{13}\text{C}\{^1\text{H}\}_{\text{CW}}$ are included in the parentheses.

Preparation of 3-tert-Butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobutene (1) and $(\eta^5\text{-C}_5\text{H}_5)(\text{F}_2\text{Si}(t\text{-Bu})\text{C}=\text{CHSiF}_2)\text{CoCO}$ (I). Compound 1 was prepared by the cocondensation reaction between 3,3-dimethylbut-1-yne and difluorosilylene. Compound I was prepared by photochemical reaction between 1 and $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$. The preparation procedures and structure identifications were reported previously.^{7,11}

Preparation of Intermediates 2. Compounds of the 2 family, intermediates involving η^2 -diene moieties, were prepared by reacting $(\eta^5\text{-C}_5\text{H}_5)(\text{F}_2\text{Si}(t\text{-Bu})\text{C}=\text{CHSiF}_2)\text{CoCO}$ (I) and the corresponding diene under UV irradiation at 10 °C.

A typical run can be described as follows. A 10-mL benzene solution containing 1.8 mmol of I (0.66 g) and 4.0 mmol of a diene was transferred into an evacuated quartz tube and irradiated by a medium-pressure Hg lamp. The reaction tube was subjected to degassing every 3 h for two times. The reaction was stopped after I was consumed (checked by ^{19}F NMR). After removal of the solvent, a reddish solution was then subjected to molecular distillation at 80 °C under vacuum. Compounds 2 were obtained as yellow liquids. On the basis of the quantity of I used, the yields for various diene reactions are reported below (all samples designated by 2 contain two isomers in approximate 1:1 ratio).

(i) **2a** from the reaction with 1,3-butadiene; yield 50%. Anal. Calcd for **2a**: C, 45.92; H, 5.36; F, 19.39. Found: C, 46.34; H, 5.80; F, 19.12. Mass spectrum of **2a**: m/e , 392 (M^+ , $\text{C}_{15}\text{H}_{21}\text{Si}_2\text{F}_4\text{Co}^+$); 338 ($\text{C}_{11}\text{H}_{15}\text{Si}_2\text{F}_4\text{Co}^+$), 215 ($\text{C}_6\text{H}_{11}\text{Si}_2\text{F}_4^+$), 124 ($\text{C}_5\text{H}_5\text{Co}^+$), 57 (C_4H_9^+). ^1H NMR of **2a**: δ 1.04 (s) and 1.06 (s) (18 H, two *t*-Bu), 2.65 (m, 4 H, two Co-bonded $\text{CH}_2=\text{CH}$), 2.68 (m, 4 H, two Co-bonded $=\text{CH}$), 4.81 (m) and 4.83 (m) (2 H, two free $-\text{CH}=\text{CH}$), 5.42 (m) and 5.46 (m) (4 H, two free $-\text{CH}_2$), 4.48 (m, 10 H, two $\eta^5\text{-C}_5\text{H}_5$), 6.51 (t, t, 2 H, two $\text{F}_2\text{SiCH}=\text{CH}$). $^{19}\text{F}\{^1\text{H}\}$ NMR of **2a**: 95.41 (d) and 92.54 (d) ($=\text{C}(t\text{-Bu})\text{SiF}_2$), 90.59 (d) and 87.63 (d) ($=\text{CHSiF}_2$), 111.52 (d) and 110.85 (d) ($=\text{C}(t\text{-Bu})\text{SiF}_2$), 99.67 (d) and 99.13 (d) ($=\text{CHSiF}_2$). ^{13}C NMR of **2a**: δ 184.0 (m (m), two $=\text{C}(t\text{-Bu})$), 143.38 (t (d, t), two $=\text{CHSiF}_2$), 141.87 (s (d) and 141.91 (s (d), two free $-\text{CH}=\text{CH}_2$), 114.56 (s (t)) and 114.63 (s (t))

(two free $-\text{CH}=\text{CH}_2$), 88.03 (s (d) and 88.08 (s (d)) (two $\eta^5\text{-C}_5\text{H}_5$), 60.12 (s (d) and 60.73 (s (d)) (two Co-bonded $\text{CH}_2=\text{CH}$), 37.78 (s (s) and 37.83 (s (s) (two $-\text{C}(\text{CH}_3)_3$), 35.0 (s (t)) and 35.44 (s (t)) (two Co-bonded $\text{CH}_2=\text{CH}$), 29.32 (s (q)) and 29.37 (s (q)) (two $-\text{C}(\text{CH}_3)_3$).

(ii) **2b** from the reaction with 2,3-dimethylbuta-1,3-diene: yield 50%. Mass spectrum of **2b**: m/e 420 (M^+ , $\text{C}_{17}\text{H}_{25}\text{Si}_2\text{F}_4\text{Co}^+$), 338 ($\text{C}_{11}\text{H}_{15}\text{Si}_2\text{F}_4\text{Co}^+$), 215 ($\text{C}_6\text{H}_{11}\text{Si}_2\text{F}_4^+$), 124 ($\text{C}_5\text{H}_5\text{Co}^+$), 82 ($\text{C}_6\text{H}_{10}^+$), 57 (C_4H_9^+). ^1H NMR of **2b**: δ 1.05 (s) and 1.07 (s) (18 H, two *t*-Bu), 1.62 (s) and 1.65 (s) (6 H, two Co-bonded $=\text{C}(\text{CH}_3)-$), 1.92 (s, 6 H, two free $=\text{C}(\text{CH}_3)-$), 2.65 (s (br), 4 H, two Co-bonded $\text{CH}_2=\text{CH}$), 4.68 (s, 10 H, two $\eta^5\text{-C}_5\text{H}_5$), 5.12 (s (br), 4 H, two free $=\text{CH}_2$), 6.58 (t, t, 2 H, two $\text{F}_2\text{SiCH}=\text{CH}$). $^{19}\text{F}\{^1\text{H}\}$ NMR of **2b**: 94.27 (d) and 90.95 (d) ($=\text{C}(t\text{-Bu})\text{SiF}_2$), 88.48 (d) and 85.76 (d) ($=\text{CHSiF}_2$), 110.10 (d) and 109.68 (d) ($=\text{C}(t\text{-Bu})\text{SiF}_2$), 98.80 (d) and 96.81 (d) ($=\text{CHSiF}_2$). Compound **2b** was too unstable for elemental analysis and ^{13}C NMR spectroscopy.

(iii) **2c** from the reaction of 2-methylbuta-1,3-diene: yield 50%. Anal. Calcd for **2c**: C, 47.29; H, 5.67; F, 18.72. Found: C, 46.98; H, 6.04; F, 18.94. Mass spectrum of **2c**: m/e 406 (M^+ , $\text{C}_{16}\text{H}_{23}\text{Si}_2\text{F}_4\text{Co}^+$), 338 ($\text{C}_{11}\text{H}_{15}\text{Si}_2\text{F}_4\text{Co}^+$), 215 ($\text{C}_6\text{H}_{11}\text{Si}_2\text{F}_4^+$), 124 ($\text{C}_5\text{H}_5\text{Co}^+$), 68 (C_5H_9^+), 57 (C_4H_9^+). ^1H NMR of **2c**: δ 1.06 (s, 18 H, two *t*-Bu), 2.68 (c, 4 H, two Co-bonded $\text{CH}_2=\text{CH}$); 3.21 (m, 2 H, two Co-bonded $\text{CH}_2=\text{CH}$), 1.92 (s, 6 H, two $\text{CH}_2=\text{CCH}_3$), 5.0 (d, 4 H, $\text{CH}_2=\text{CCH}_3$), 4.92 (s, 10 H, two $\eta^5\text{-C}_5\text{H}_5$), 6.45 (m, 2 H, two $=\text{CH}-\text{SiF}_2$). $^{19}\text{F}\{^1\text{H}\}$ NMR of **2c**: 95.56 (d) and 91.14 (d) ($=\text{C}(t\text{-Bu})\text{SiF}_2$), 90.92 (d) and 86.29 (d) ($=\text{CHSiF}_2$), 105.85 (d) and 111.85 (d) ($=\text{C}(t\text{-Bu})\text{SiF}_2$), 93.33 (d) and 100.03 (d) ($=\text{CHSiF}_2$). ^{13}C NMR of **2c**: δ 184.0 (m (m), two $=\text{C}(t\text{-Bu})$), 142.26 (t (d, t), two $=\text{CHSiF}_2$), 146.13 (s (s), two $\text{CH}_2=\text{CCH}_3$), 110.39 (s (t), two $\text{CH}_2=\text{C}-\text{CH}_3$), 88.30 (s (d), two $\eta^5\text{-C}_5\text{H}_5$), 59.41 (s (d), two Co-bonded $\text{CH}_2=\text{CH}$); 37.44 (s (t), two Co-bonded $\text{CH}_2=\text{CH}$), 38.48 (s (s), two $-\text{C}(\text{CH}_3)_3$), 28.95 (s (q), two $-\text{C}(\text{CH}_3)_3$), 26.37 (s (q), two $\text{CH}_2=\text{CCH}_3$).

(iv) **2d** from the reaction with *trans*-penta-1,3-diene; yield 50%. Anal. Calcd for **2d**: C, 47.29; H, 5.66; F, 18.72. Found: C, 47.06; H, 5.94; F, 18.78. Mass spectrum of **2d**: m/e 406 (M^+ , $\text{C}_{16}\text{H}_{23}\text{Si}_2\text{F}_4\text{Co}^+$), 338 ($\text{C}_{11}\text{H}_{15}\text{Si}_2\text{F}_4\text{Co}^+$), 215 ($\text{C}_6\text{H}_{11}\text{Si}_2\text{F}_4^+$), 124 ($\text{C}_5\text{H}_5\text{Co}^+$), 68 (C_5H_9^+), 57 (C_4H_9^+). ^1H NMR of **2d**: δ 1.07 (s) and 1.09 (s) (18 H, two *t*-Bu), 1.45 (d, 6 H, two CH_3), 2.65 (c, 4 H, two Co-bonded $\text{CH}_2=\text{CH}$), 2.68 (c, 2 H, two Co-bonded $\text{CH}_2=\text{CH}$), 4.78 (c, 2 H, two $-\text{CH}=\text{CHCH}_3$), 5.92 (m, 2 H, two $-\text{CH}=\text{CHCH}_3$), 4.52 (s, 10 H, two $\eta^5\text{-C}_5\text{H}_5$), 6.55 (m, 2 H, two $=\text{CHSiF}_2$). $^{19}\text{F}\{^1\text{H}\}$ NMR of **2d**: 94.73 (d) and 92.05 (d) ($=\text{C}(t\text{-Bu})\text{SiF}_2$), 90.01 (d) and 87.24 (d) ($=\text{CHSiF}_2$), 110.20 (d) and 109.99 (d) ($=\text{C}(t\text{-Bu})\text{SiF}_2$), 98.58 (d) and 99.54 (d) ($=\text{CHSiF}_2$). ^{13}C NMR of **2d**: δ 183.90 (m (m), two $=\text{C}(t\text{-Bu})$), 142.20 (t (d, t), two $=\text{CHSiF}_2$), 135.70 (s (d)) and 135.72 (s (d)), (two $-\text{CH}=\text{CHCH}_3$), 127.48 (s (d)) and 127.50 (s (d)) (two $-\text{CH}=\text{CHCH}_3$), 87.75 (s (d), two $\eta^5\text{-C}_5\text{H}_5$), 62.29 (s (d)) and 62.35 (s (d)) (two Co-bonded $\text{CH}_2=\text{CH}$), 37.70 (s (s), two $-\text{C}(\text{CH}_3)_3$), 34.56 (s (t)) and 34.62 (s (t)) (two Co-bonded $\text{CH}_2=\text{CH}$), 29.39 (s (q), two $-\text{C}(\text{CH}_3)_3$), 18.08 (s (q), two $=\text{CHCH}_3$).

(v) **2e** from the reaction with *trans*-2,trans-4-hexadiene; yield 50%. Anal. Calcd for **2e**: C, 48.57; H, 5.95; F, 18.09. Found: C, 48.05; H, 6.28; F, 19.18. Mass spectrum of **2e**: m/e , 420 (M^+ , $\text{C}_{17}\text{H}_{25}\text{Si}_2\text{F}_4\text{Co}^+$), 338 ($\text{C}_{11}\text{H}_{15}\text{Si}_2\text{F}_4\text{Co}^+$), 215 ($\text{C}_6\text{H}_{11}\text{Si}_2\text{F}_4^+$), 124 ($\text{C}_5\text{H}_5\text{Co}^+$), 82 ($\text{C}_6\text{H}_{10}^+$), 57 (C_4H_9^+). ^1H NMR of **2e**: δ 1.04 (s, 18 H, two *t*-Bu), 1.50 (d) and 1.59 (d) (6 H, two Co-bonded $\text{CH}_2\text{CH}=\text{CH}$), 1.76 (d), 6 H, two free $-\text{CH}=\text{CHCH}_3$), 2.82-2.84 (c, 4 H, two Co-bonded $\text{CH}_2\text{CH}=\text{CH}$), 5.40 (t) and 5.42 (t) (2 H, free $-\text{CH}=\text{CHCH}_3$), 5.69 (m) and 5.71 (m) (2 H, two free $-\text{CH}=\text{CHCH}_3$), 5.04 (d), 10 H, two $\eta^5\text{-C}_5\text{H}_5$), 6.84 (m, 2 H, two $=\text{CHSiF}_2$). $^{19}\text{F}\{^1\text{H}\}$ NMR of **2e**: 93.26 (d) and 89.68 (d) ($=\text{C}(t\text{-Bu})\text{SiF}_2$), 89.24 (d) and 83.94 (d) ($=\text{CHSiF}_2$), 111.71 (d) and 112.88 (d) ($=\text{C}(t\text{-Bu})\text{SiF}_2$), 98.41 (d) and 101.30 (d) ($=\text{CHSiF}_2$). ^{13}C NMR of **2e**: δ 184.27 (m (m), two $=\text{C}(t\text{-Bu})$), 144.43 (t (d, t), two $=\text{CHSiF}_2$), 131.01 (s (d), two free $-\text{CH}=\text{CHCH}_3$), 125.74 (s (d), two free $-\text{CH}=\text{CHCH}_3$), 87.19 (s (d), two $\eta^5\text{-C}_5\text{H}_5$), 63.57 (s (d) and 64.45 (s (d)) (two Co-bonded $-\text{CH}=\text{CHCH}_3$), 55.48 (s (d) and 55.24 (s (d), two Co-bonded $-\text{CH}=\text{CHCH}_3$), 37.50 (s (s), two $-\text{C}(\text{CH}_3)_3$), 29.30 (s (q), two $-\text{C}(\text{CH}_3)_3$), 19.17 (s (q), two free $-\text{CH}=\text{CHCH}_3$), 17.75 (s (q), two Co-bonded $-\text{CH}=\text{CHCH}_3$).

(vi) **2f** from the reaction with *cis*-2,trans-4-hexadiene: yield 40%. Mass spectrum of **2f**: m/e 420 (M^+ , $\text{C}_{17}\text{H}_{25}\text{Si}_2\text{F}_4\text{Co}^+$), 338 ($\text{C}_{11}\text{H}_{15}\text{Si}_2\text{F}_4\text{Co}^+$), 215 ($\text{C}_6\text{H}_{11}\text{Si}_2\text{F}_4^+$), 124 ($\text{C}_5\text{H}_5\text{Co}^+$), 82 ($\text{C}_6\text{H}_{10}^+$),

57 ($C_4H_9^+$). 1H NMR of **2f**: δ 1.09 (s, 18 H, two *t*-Bu), 1.53 (d) and 1.61 (d) (6 H, two Co-bonded $CH_3CH=CH-$), 1.77 (d, 6 H, two free $-CH=CHCH_3$), 2.80 (c) and 2.82 (c) (4 H, two Co-bonded $CH_3CH=CH-$), 5.55 (t) and 5.58 (t) (2 H, two free $-CH=CHCH_3$), 5.96 (m) and 6.0 (m) (2 H, two free $-CH=CHCH_3$), 4.94 (s, 10 H, two $\eta^5-C_5H_5$), 6.49 (m, 2 H, two $=CHSiF_2$). $^{19}F\{^1H\}$ NMR of **2f**: 94.99 (d) and 91.75 (d) ($=C(t-Bu)SiF_2$), 90.29 (d) and 86.63 (d) ($=CHSiF_2$), 114.21 (d) and 118.11 (d) ($=C(t-Bu)SiF_2$), 102.61 (d) and 105.81 (d) ($=CHSiF_2$). ^{13}C NMR of **2f**: δ 182.58 (m (m), two $=C(t-Bu)$), 142.32 (t (d, t), two $=CHSiF_2$), 130.84 (s (d) and 128.90 (s (d), two free $-CH=CHCH_3$), 87.83 (s (d), two $\eta^5-C_5H_5$), 62.40 (s (d)) and 62.05 (s (d) (two Co-bonded $CH_3CH=CH-$), 54.90 (s (d)) and 54.67 (s (d)) (two Co-bonded $CH_3CH=CH-$), 37.67 (s (s), two $-C(CH_3)_3$), 29.24 (s (q), two $-C(CH_3)_3$), 19.28 (s (q), two free $-CH=CHCH_3$), 18.51 (s (q), two Co-bonded $CH_3CH=CH-$).

(vii) **2g** from the reaction with 2,4-dimethylpenta-1,3-diene, yield: 50%. Mass spectrum of **2g**: m/e , 434 (M^+ , $C_{18}H_{27}Si_2F_4Co^+$), 338 ($C_{11}H_{15}Si_2F_4Co^+$), 215 ($C_6H_{11}Si_2F_4^+$), 124 ($C_5H_5Co^+$), 96 ($C_7H_{12}^+$), 57 ($C_4H_9^+$). 1H NMR of **2g**: δ 1.04 (s) and 1.06 (s) (18 H, two *t*-Bu), 1.58 (s) and 1.60 (s) (6 H, two Co-bonded $=C(CH_3)-$), 1.70 (s) and 1.76 (s) (12 H, two $=C(CH_3)_2$), 2.65 (br, 4 H, two Co-bonded $CH_2=$), 5.40 (br, 2 H, two free $-CH=$), 6.65 (t, t, 2 H, two $F_2SiCH=$). $^{19}F\{^1H\}$ NMR of **2g**: 93.93 (d) and 91.54 (d) ($=C(t-Bu)SiF_2$), 88.02 (d) and 86.04 (d) ($=CHSiF_2$), 110.27 (d) and 112.71 (d) ($=C(t-Bu)SiF_2$), 99.52 (d) and 97.83 (d) ($=CHSiF_2$). Compound **2g** was too unstable for elemental analysis and ^{13}C NMR spectroscopy.

(viii) **2h** from the reaction with cyclohexa-1,3-diene, yield 40%. Anal. Calcd for **2h**: C, 48.80; H, 5.50; F, 18.18. Found: C, 48.22; H, 5.91; F, 18.10. Mass spectrum of **2h**: m/e , 418 (M^+ , $C_{17}H_{23}Si_2F_4Co^+$), 338 ($C_{11}H_{15}Si_2F_4Co^+$), 215 ($C_6H_{11}Si_2F_4^+$), 124 ($C_5H_5Co^+$), 80 ($C_5H_5^+$), 57 ($C_4H_9^+$). 1H NMR of **2h**: δ 1.08 (s, 18 H, two *t*-Bu), 1.74 (c, 8 H, two $-CH_2CH_2-$), 2.80 (c, 4 H, two Co-bonded $-HC=CH-$), 4.93 (s, 10 H, two $\eta^5-C_5H_5$), 5.68 (m, 4 H, two free $-HC=CH-$), 6.49 (m, 2 H, two $=CH-SiF_2$). $^{19}F\{^1H\}$ NMR of **2h**: 94.86 (d) and 92.88 (d) ($=C(t-Bu)SiF_2$), 87.85 (d) and 89.68 (d) ($=CHSiF_2$), 112.51 (d) and 114.22 (d) ($=C(t-Bu)SiF_2$), 100.57 (d) and 101.85 (d) ($=CHSiF_2$). ^{13}C NMR of **2h**: δ 184.0 (m (m), two $=C(t-Bu)$), 142.15 (t (d, t), two $=CHSiF_2$), 127.85 (s (d)) and 130.48 (s (d)) (two free $-HC=CH-$), 88.24 (s (d), two $\eta^5-C_5H_5$), 51.21 (s (d)) and 53.55 (s (d)) (two Co-bonded $-CH=CH-$), 37.32 (s (s), two $-C(CH_3)_3$), 29.06 (s (q), two $-C(CH_3)_3$), 24.36 (s (t)) and 21.15 (s (t), two $-CH_2CH_2-$).

Preparation and Identification of Compounds of the 3 Family. All products of the 3 family were prepared by prolonged irradiation of the benzene solution of the corresponding intermediate **2** at 60 °C. Characterization of **3a-i** were reported previously.⁶

Preparations of 4a and 4b/5a. A benzene solution (10 mL) containing 0.38 g (0.9 mmol) of **2b** was degassed and subjected to irradiation at 60 °C for 2 days. After removal of solvent, the reddish brown liquid was subjected to molecular distillation under vacuum at 80 °C. A colorless liquid (0.24 g, 0.9 mmol) was obtained which contained 80% of **4a** and 20% of **3b** (determined by ^{19}F NMR). Total yield based on the quantity of **2b** used was 100%. All attempts to further purify **4a** failed.

Similar procedures were carried out with **2g**. The products were **4b** and **5a** in 5:3 ratio. The total yield was 80%. Anal. Calcd for the sample containing 80% **4a** and 20% **3b**: C, 48.64; H, 6.75; F, 25.67. Found: C, 48.18; H, 6.14; F, 25.55. Mass spectrum of **4a** (mixture with 20% **3b**): m/e 296 (M^+ , $C_{12}H_{20}Si_2F_4^+$), 281 ($C_{11}H_{17}Si_2F_4^+$), 255 ($C_9H_{15}Si_2F_4^+$), 215 ($C_6H_{11}Si_2F_4^+$), 57 ($C_4H_9^+$). NMR spectra of **4a** were obtained by subtracting the spectra of

the minor component **3b**, a known compound.^{1,2} 1H NMR of **4a**: δ 1.13 (s, 9 H, *t*-Bu); 1.16 (d, 3 H, $-CH(CH_3)-$), 1.68, (s, 3 H, $-(CH_3)C=$), 2.11 (m, 1 H, $-CH(SiF_2)_2$), 2.67 (m, 1 H, $-CH(CH_3)-$), 4.81 (AB, br, 2 H, $=CH_2$), 6.65 (m, 1 H, $-F_2SiCH=$). $^{19}F\{^1H\}$ NMR of **4a**: δ 141.65 (d, d, d) and 136.60 (d, d, d) ($=C(t-Bu)SiF_2-$), 136.24 (d, d, d) and 131.63 (d, d, d) ($=CHSiF_2-$). ^{13}C NMR of **4a**: δ 180.78 (m (m), $=C(t-Bu)$), 139.93 (t (d, t), $=CHSiF_2$), 112.70 (s (s), $-C(CH_3)=$), 109.80 (s (t), $=CH_2$), 38.26 (s (s), $-C(CH_3)_3$), 37.09 (s (d), $-CH(CH_3)-$), 29.58 (s (q), $-C(CH_3)_3$), 23.55 (s (q), $-C(CH_3)=$), 20.97 (s (q), $-CH(CH_3)-$), 14.64 (m (d, m), $-CH(SiF_2)_2$). Anal. Calcd for the sample containing **4b** and **5a** in 5:3 ratio: C, 50.32; H, 7.09; F, 24.52. Found: C, 51.04; H, 6.81; F, 24.41. Mass spectrum of the sample containing **4b** and **5a** in 5:3 ratio: m/e 310 (M^+ , $C_{13}H_{22}Si_2F_4^+$), 295 ($C_{12}H_{19}Si_2F_4^+$), 255 ($C_9H_{15}Si_2F_4^+$), 215 ($C_6H_{11}Si_2F_4^+$), 57 ($C_4H_9^+$). Since **4b** and **5a** were not obtained in pure form, their NMR spectra were tentatively assigned by comparing with the chemical shifts of known compounds of analogous structures. 1H NMR of **4b** and **5a**: δ 1.0 (s, $-CH(CH_3)-$ of **4b**), 1.13 (s, *t*-Bu of **4b** and **5a**), 1.2 (d, $-CH(CH_3)_2$ of **5a**), 1.66 (s, $-C(CH_3)=$ of **5a**), 1.69 (s, $=C(CH_3)_2$ of **4b**), 2.18 (m, $-CH(SiF_2)_2$ of **5a** and $-CH(CH_3)-$ of **4b**), 2.89 (m, $-CH(CH_3)_2$ of **5a** and **4b**), 4.70 (d, $=C(H)(i-Pr)$ of **5a**), 4.98 (d, $-CH=C(CH_3)_2$ of **4b**), 6.70 (m, $=CHSiF_2-$ of **4b** and **5a**). $^{19}F\{^1H\}$ NMR of **4b** and **5a**: 141.82 (d, d, d), 136.92 (d, d, d), 136.48 (d, d, d), 132.21 (d, d, d) (two SiF_2 groups of **5a**), 139.52 (d, d, d), 135.61 (d, d, d), 135.98 (d, d, d), 130.42 (d, d, d) (two SiF_2 groups of **4b**). ^{13}C NMR of **4b** and **5a**: δ 185.30 (m (m), *t*-Bu of **4b** and **5a**), 140.40 (t (d, t), $=CHSiF_2-$ of **4b**), 140.25 (t (d, t), $=CHSiF_2-$ of **5a**), 142.91 (s (s), $=C(CH_3)_2$ of **4b**), 139.57 (s (s), $-C(CH_3)=$ of **5a**), 130.08 (s (d), $-CH=C(CH_3)_2$ of **4b** and $=CH(i-Pr)$ of **5a**), 48.90 (s (d), $-CH(CH_3)_2$ of **5a**), 38.08 (s (s), $-C(CH_3)_3$ of **4b** and **5a**), 29.35 (s (q), $-C(CH_3)_3$ of **4b** and **5a**), 26.90 (s (d), $-CH(CH_3)-$ of **4b**), 25.48 (s (q), $-C(CH_3)=$ of **5a** and $=C(CH_3)_2$ of **4b**), 17.63 (s (q), $-CH(CH_3)-$ of **4b**), 15.58 (m (d, m), $-CH(SiF_2)_2$ of **4b** and **5a**), 13.94 (s (q), $-CH(CH_3)_2$ of **5a**).

Isomerization of 4a and 5b to 6a. A sample containing 0.12 g (0.4 mmol) of **4a** and 0.03 g (0.1 mmol) of **3b** was added to 10 mL of a degassed *n*-pentane solution which contained 0.1 g (0.5 mmol) of $Fe(CO)_5$. The solution was irradiated at 0 °C for 20 h. After removal of the solvent, the solution was subjected to molecular distillation at 90 °C under vacuum. Approximately 0.14 g (0.47 mmol) of **6a** was obtained. Obviously both **4a** and **3b** were converted to **6a** quantitatively. The $Fe(CO)_5$ -catalyzed isomerization of **3b** to **6a** has been reported previously.⁵

Isomerization of **5b** to **6a** has also been reported previously.²

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Registry No. 1, 36091-97-1; **2a**, 113794-87-9; **2b**, 113794-88-0; **2c**, 113794-89-1; **2d**, 113794-90-4; **2e**, 113794-91-5; **2f**, 113889-76-2; **2g**, 113794-92-6; **2h**, 113794-93-7; **3a**, 109034-51-7; **3b**, 109034-52-8; **3c**, 113794-96-0; **3e**, 113794-97-1; **3f**, 113810-76-7; **3g**, 113794-98-2; **3h**, 113794-99-3; **3i**, 100513-61-9; **4a**, 113794-94-8; **4b**, 113795-01-0; **5a**, 113795-00-9; **6a** (isomer 1), 109034-57-3; **6a** (isomer 2), 109034-56-2; I, 105992-51-6; ($\eta^5-C_5H_5$)Co(CO)₂, 12078-25-0; Fe(CO)₅, 13463-40-6; $CH_2=CHCH=CH_2$, 106-99-0; $CH_2=C(C-H_3)C(CH_3)=CH_2$, 513-81-5; $CH_2=C(CH_3)_cH=CH_2$, 78-79-5; *trans*- $CH_2=CHCH=CHCH_3$, 2004-70-8; *trans,trans*- $CH_3CH=CHCH=CHCH_3$, 5194-51-4; *cis,trans*- $CH_3CH=CHCH=CHCH_3$, 5194-50-3; $CH_2=C(CH_3)CH=C(CH_3)_2$, 1000-86-8; 3,3-dimethylbut-1-yne, 917-92-0; difluorosilylene, 13966-66-0; cyclohexa-1,3-diene, 592-57-4.