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Cycloaddition reactions of tetrafluorodisilacyclobutene with 1,3-butadienes mediated by $Ru_3(CO)_{12}$.

VI *. Control by steric effects of the substituents

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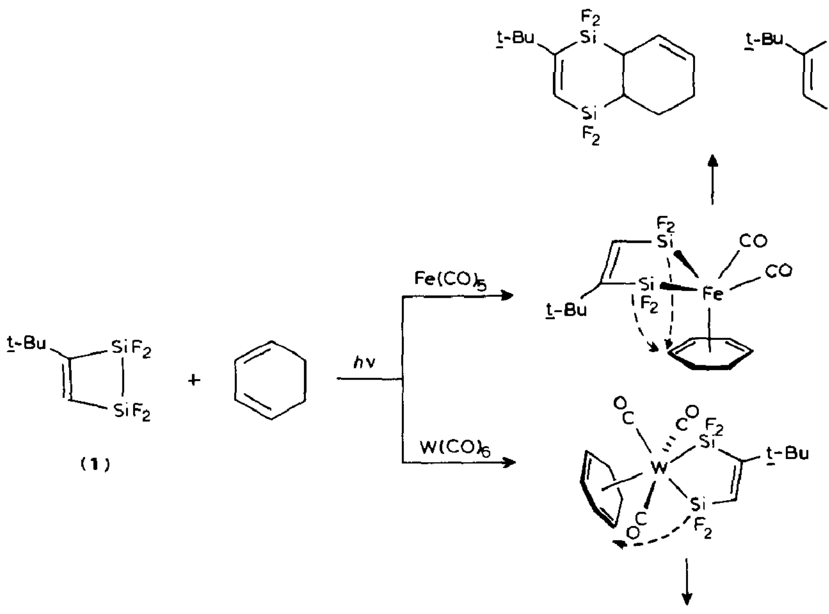
Abstract

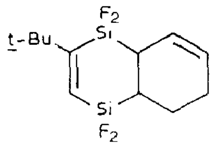
Cycloaddition reactions of 3-t-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobutene (**1**) with various 1,3-butadienes mediated by $Ru_3(CO)_{12}$ are described. The reactions proceed distinctly via 1,1-, 1,2-, and 1,4-additions, and are controlled entirely by the steric effects of the substituents. In the initial stages of the reactions compound **1** and $Ru_3(CO)_{12}$ form the intermediates $F_2\overline{SiC(t\text{-}Bu)=CHSiF_2-Ru}(CO)_4$ (I) and $(F_2\overline{SiC(t\text{-}Bu)=CHSiF_2)_2Ru}(CO)_3$ (II). Compound II with two disilametallacycles is the first such intermediate observed in this series of studies.

In our study of a fine-tuning system of the metal-mediated cycloaddition reactions between the 1,2-disilacyclobutene (**1**) and conjugated dienes [1–7], we have

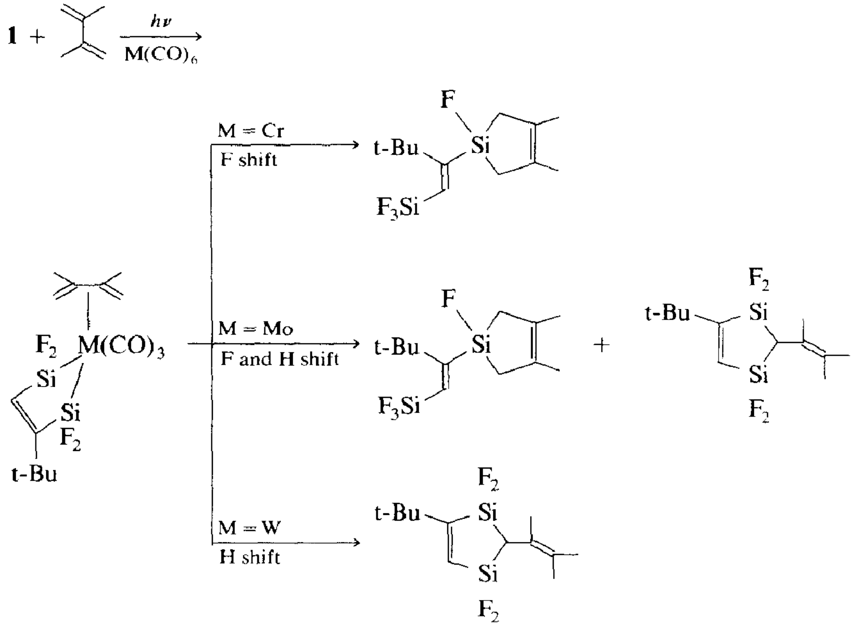


(1)

0022-328X/89/$03.50



found that there is a correlation between the reaction pathways and the geometry and electronic properties of the common intermediate $(\eta^4\text{-diene})(F_2SiC(t\text{-}Bu)=CHSiF_2)M(CO)_x$ has been established. The effects of the geometry and electronic properties of the central metal are best illustrated by eqs. 1 and 2.



(2)

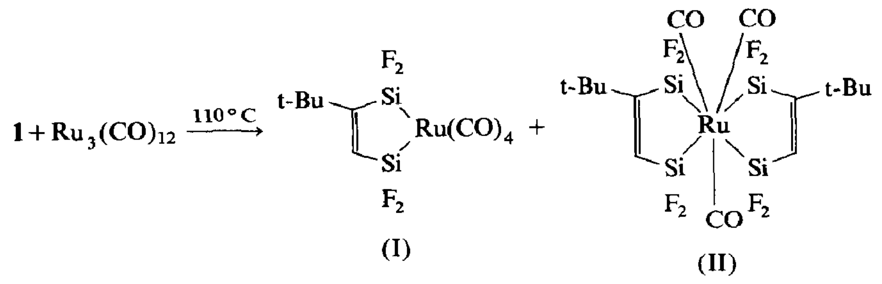
Fine-tuning by the substituents of the diene has also been studied with M = Fe [2,3]. However, the effects are less clear-cut because substitution at different positions of the diene causes jumbling of the reaction pathways. For example, in the reaction between 1 and *trans,trans*-hexadiene 1,2-, 1,4- and 1,0-addition products are obtained [2].

In this paper we report the results of Ru-mediated cycloadditions of **1** to variously substituted dienes, and show conclusively the fine-tuning effect by substitutents on the direction followed by the reaction.

Results and discussion

In general, the cycloaddition reactions mediated by Ru are much slower than those mediated by Fe. We chose to use the reaction of **1** with $Ru_3(CO)_{12}$ to form the disilametallcycle I followed by reaction with the diene, since cleaner results were obtained than with the mixture of **1**, the diene, and $Ru_3(CO)_{12}$.

The reaction between **1** and $Ru_3(CO)_{12}$ at 110 °C initially gave a mixture of I and II. After **1** was exhausted, prolonged heating converted all the II into I.

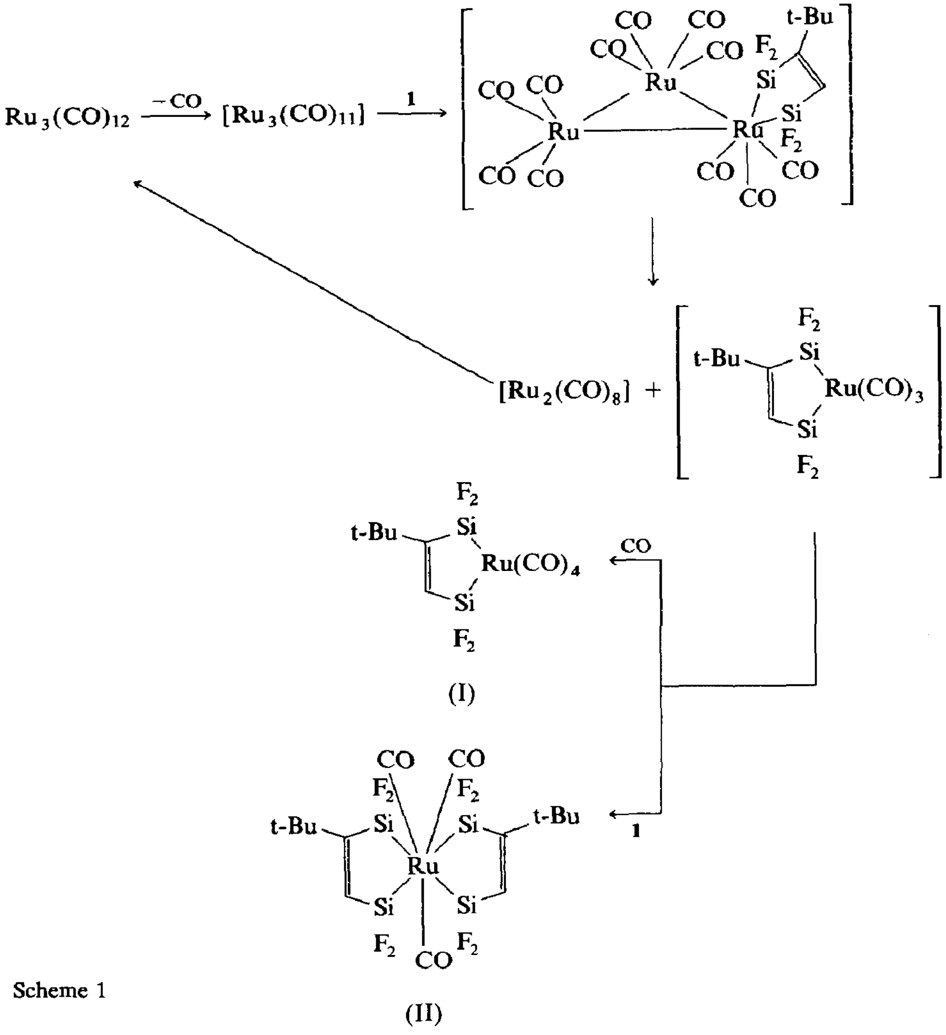


(I) (II)

(3)

$$\mathrm{II}\ \xrightarrow[120\,^\circ\mathrm{C}]{\mathrm{Ru_3(CO)_{12}}}\ \mathrm{I}$$

This is the first time that the formation of bis(1,4-disila-2-butene-1,4-diyl)metal carbonyl compound has been observed. The reaction probably involves the oxidative addition of the disilacyclobutene to one Ru accompanied by the cleavage of the cluster to form the intermediate $[F_2\overline{SiC(t\text{-}Bu)=CHSiF_2\text{-}Ru}(CO)_3$. This 16-electron species then adds one CO to form I, or reacts with another molecule of **1** to form II. The mechanism proposed is shown in Scheme 1. A kinetic study of this reaction is in progress.



Scheme 1

Table 1

Products from the reactions of I with various dienes mediated by ruthenium carbonyl [a]

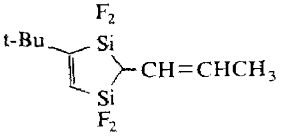
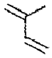
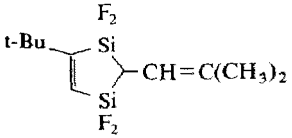
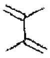
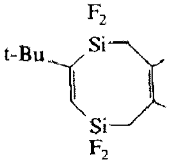
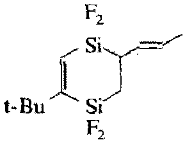
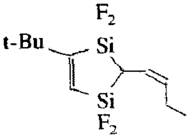
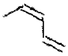
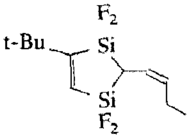
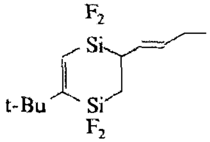
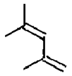
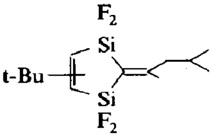
Dienes	Products
	 *cis* and *trans* **8a/8b** (60%)
	 **3** (88%)
	 **5** (35%)
	 **6** (38%)  (trace)
	**6** (30%)  (trace)
	 **7** (25%)
	**7** (22%)

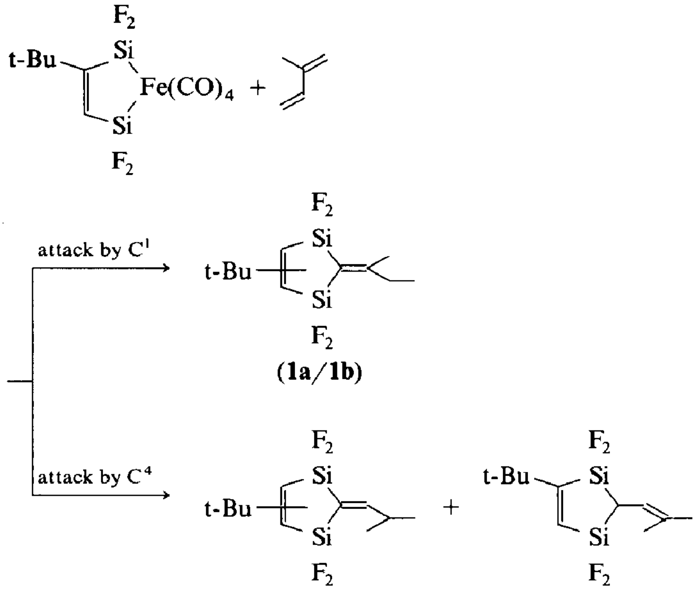
Table 1 (continued)

Dienes	Products
	 **9a/9b** (75%)

[a] Typical conditions. A 1 ml n-hexane solution containing 0.28 mmol of compound I and 0.3 ml of the respective diene was degassed, sealed in a Pyrex tube, and heated at 110–160 °C for 20 min. The solution was concentrated, and the products were isolated by distillation under vacuum.

The reactions between I and various dienes (buta-1,3-diene, 2-methyl-buta-1,3-diene, 2,3-dimethyl-buta-1,3-diene, *cis*- and *trans*-penta-1,3-diene, *trans,trans*-hexadiene, *cis,trans*-hexadiene) are very slow under photochemical conditions, so they were carried out thermally at ~ 120 °C. The results are listed in Table 1.

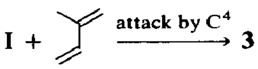
Compared with the same reactions mediated by Fe, these reactions are more sensitive to the effect of the substituents in respect of the reaction pathway followed. The steric effects not only affect the attack by silyl groups but also affect the migration of a hydrogen atom. For example, in the reaction with 2-methyl-buta-1,3-diene, the Fe-mediated reaction allows the initial silyl migration to occur at both terminal carbons (C^1 and C^4), whereas the Ru-mediated reaction takes place only at C^4:



(1a/1b)

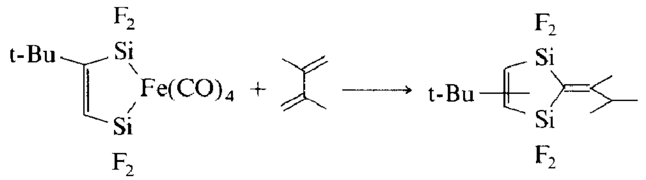
(2a/2b) (3)

(5)



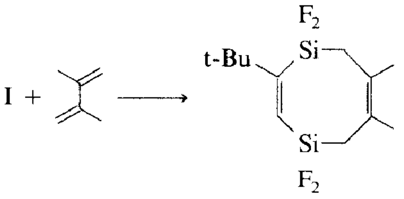
(6)

In the reaction with 2,3-dimethyl-buta-1,3-diene, the Fe-mediated reaction proceeds by a 1,1-addition, whereas the Ru-mediated reaction gives the 1,4-addition product:



(4a/4b)

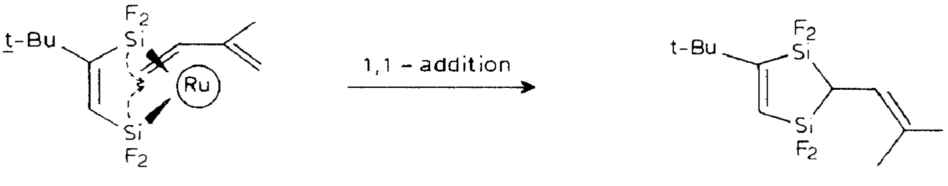
(7)



(5)

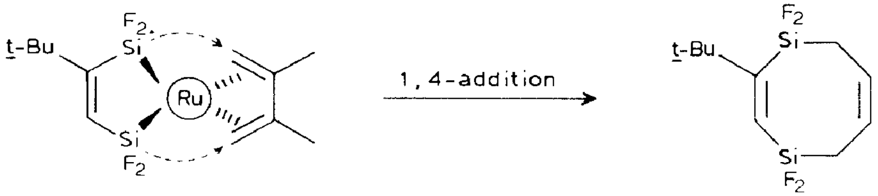
(8)

The energy barrier to rotation in the η^2-olefin complexes is in the range of 2–6 kcal/mol. [8,9]. The barrier to rotation in the η^4-diene complexes is expected to be somewhat higher because of their more extended π-bonding to the metal. When coupled with the fact that the silyl migration is much slower in the Ru complexes than in the Fe complexes, it is conceivable that in the case of Ru the steric effects brought about by the substituents on the diene may cause the (η^4-diene)disilametallacycle to assume a more favored orientation during the silyl migration. For example, if the steric interaction between the methyl substituent and CO is smaller than that between the methyl and the silyl groups, then the more favorable orientations for isoprene and 2,3-dimethylbuta-1,3-diene disilametallacycles are as shown, and these would lead to the 1,1- and 1,4-addition products, respectively.



(3)

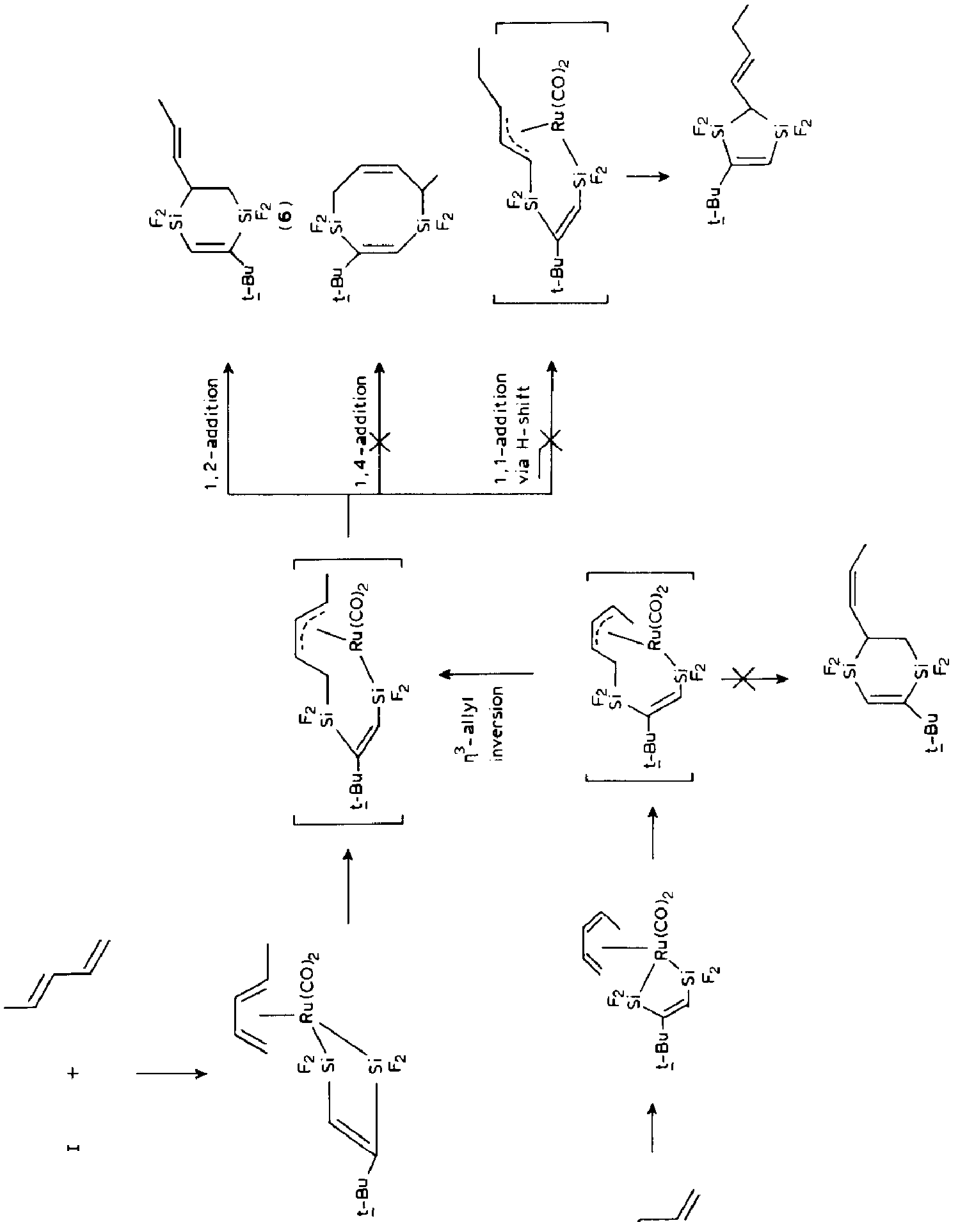
(9)



(5)

(10)

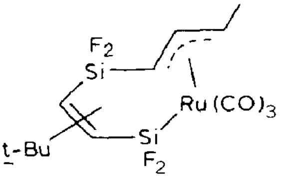
In the reactions with *trans*- and *cis*-penta-1,3-diene, the Fe-mediated reactions give different and complicated products [3], whereas the Ru-mediated reactions yield the same, simple 1,2-addition product (compound **6**, see Scheme 2).


I
+
t-Bu
F2
Si
Ru(CO)2
η3-allyl inversion
1,2-addition
1,4-addition
1,1-addition via H-shift
(6)

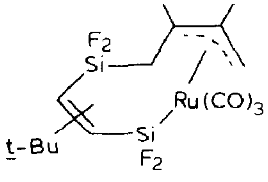
Scheme 2

This observation suggests that (i) the steric effect by one methyl group on the terminal carbon of the diene not only affects the second silyl migration but also the 1,4-hydrogen migration, and (ii) the reaction at 120 °C results in the inversion of the η^3-allyl intermediate after the first silyl attack. While the former effect rules out all other reaction pathways except 1,2-addition, the latter results in the same isomeric form of the final product from both reactions. These mechanistic details are illustrated in Scheme 2.

Although we did not observe the η^3-allyl intermediate in these particular reactions, analogous η^3-allyl intermediates were observed during the reactions with buta-1,3-diene and 2,3-dimethylbuta-1,3-diene.

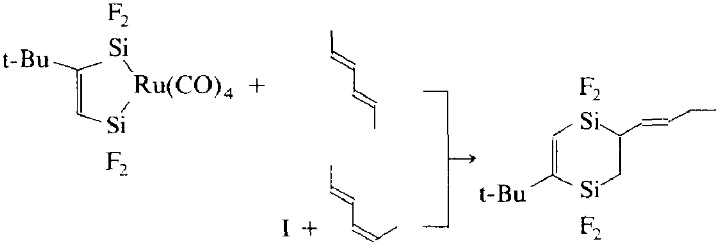


(IIIa / IIIb)



(IVa / IVb)

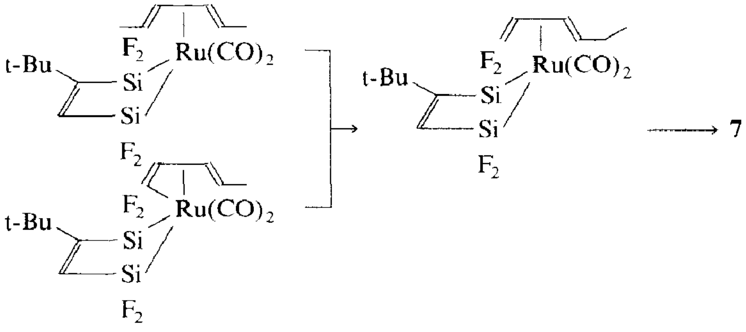
Such pronounced steric effects by a single methyl substitutent on the terminal carbon of the diene is also manifested in the reactions with *trans,trans-* and *trans,cis*-hexadiene. In both cases, the sole product, 7, is the result of a "0,1"-addition by way of a H-shift.



(7)

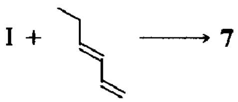
(11)

It is obvious that when both terminal carbons of the diene are replaced by a methyl group, direct silyl migrations are prevented and the (η^4-diene)disilametallacycle intermediates isomerize to the terminal diene complex, (η^4-hexa-1,3-diene)disilametallacycle, before silyl migration takes place:



(12)

Such a "0,1"-addition was observed in the Fe-mediated cycloaddition with 2,5-dimethylhexa-2,4-diene, in which each terminal carbon of the diene skeleton had been replaced by two methyl groups [3]. Further evidence is provided by the reaction of I with hexa-1,3-diene. The reaction of compound I with hexa-1,3-diene under the same reaction conditions gives **7** as the sole product.

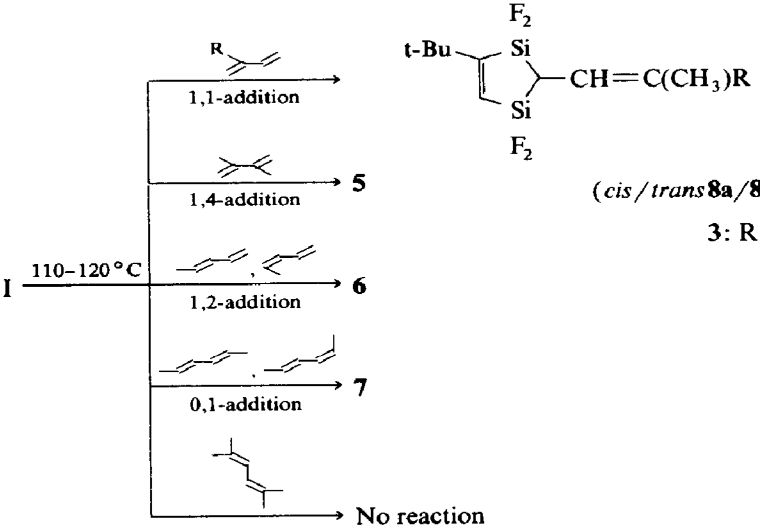


(13)

No cycloaddition products are observed in the reaction of I with 2,5-dimethylhexa-2,4-diene under the same conditions.

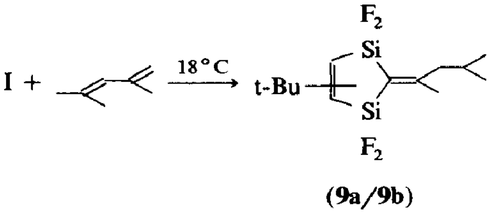
It is obvious that the steric effects by two terminal methyl groups (on C^1 and C^4) in the case of Ru is as effective as that by four terminal methyl groups in the case of Fe. It seems reasonable to assume that the larger size of Ru (relative to Fe) provides room for the π-bonded diene which may thermodynamically choose a favored orientation, whereas the kinetically more inert Ru–Si bond (compared with the Fe–Si bond) retards silyl migration. These combined effects result in the more selective reaction pathways expected from steric effects by the substituents on coordinated dienes.

The results can be summarized as follows:



(*cis*/*trans* **8a**/**8b**: R = H;
3: R = CH_3)

It is noteworthy that no products containing the $\overline{F_2Si{-}C(t\text{-}Bu){=}CH{-}SiF_2{-}C}{=}$ moiety (such as **1a** and **1b**) can be obtained from the reactions listed above. In general, the formation of such compounds requires a 1,4- and 1,3-hydrogen shift from the same target terminal carbon of the diene, a process which is greatly facilitated by an alkyl group on the carbon adjacent to the target terminal carbon. 2,3-Dimethylbuta-1,3-diene fits this criterion but it reacts by 1,4-addition under the mediation of Ru. 2,4-Dimethylpenta-1,3-diene seems to be the best choice for preparing the compound. The combined steric effects by the methyl on C^2 and the two methyl groups on C^4 would force the reaction ro proceed as a 1,1-addition with two H shifts. Indeed, the reaction of I with 2,4-dimethylpenta-1,3-diene gives the desired products in high yields (75%).



(**9a**/**9b**)

Experimental

Vacuum distillations and manipulations were carried out by use of vacuum lines at 10^{-3} Torr. Solvents were dried and distilled over calcium hydride. The dienes (Aldrich) and $Ru_3(CO)_{12}$(Strem) were used as received. Compound **1** was prepared by a published procedure [10].

Spectra. All mass spectra were recorded on a JEOL JMS-100 mass spectrometer operating at 12 eV. The NMR spectra were recorded on a JEOL JMX FX-100 instrument operating at 99.55, 93.65, and 25.0 MHz for the ^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 signals are 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 that resulted after each chemical shift is attributable to coupling with heteronuclei. The coupling patterns in $^{13}C\{^1H\}_{CW}$ are included in the parentheses. Preparation of I and II. A mixture of 462 mg (0.72 mmol) of $Ru_3(CO)_{12}$ and 0.6 g (2.9 mmol) of compound 1 in 10 ml of dried n-hexane was degassed, then frozen at −196 °C, and the reaction tube was sealed under vacuum. The reaction tube was then heated at 110 °C for 30 min. After removal of the solvent and unchanged **1**, freshly dried and degassed n-hexane (10 ml) was distilled in and the solution was kept at −18 °C for crystallization. After recrystallization from n-hexane solution, the crystals were filtered at 0 °C and washed twice with n-hexane at −10 °C. About 400 mg of compound II in the form of colorless crystals was isolated. The yield of II based on the quantity of **1** used was about 47%.

If the mixture was heated at 100 ~ 120 °C for a longer period of time, compound II slowly converted to I at the further expense of $Ru_3(CO)_{12}$. The reaction monitored by ^{19}F NMR spectroscopy; readings were taken every 30 min until all of II had been consumed. After removal of solvent, the residuel was subjected to vacuum sublimation at 100 °C. Compound I was collected as colorless crystals by a cold finger kept at 0 °C. The yield based on the quantity of **1** used was 65%.

For I. Anal. Found. C, 27.89; H, 2.71; F, 17.58. $C_{10}H_{10}F_4O_4RuSi_2$ calcd.: C, 28.04; H, 2.34; F, 17.76%. Mass spectrum: *m/e* 428(M^+, $C_{10}H_{10}O_4Si_2F_4Ru^+$), 400($C_9H_{10}O_3Si_2F_4Ru^+$), 372($C_8H_{10}O_2Si_2F_4Ru^+$), 214($C_6H_{10}Si_2F_4^+$), 57($C_4H_9^+$). ^1H NMR: δ 1.09(s), 9H, t-Bu; 7.13(t), 1H, $=CHSiF_2$. ^{19}F NMR: 89.31(d). $=CHSiF_2$; 99.99(s), $=C(t\text{-}Bu)SiF_2$. ^{13}C NMR: δ 189.39 s(s), $(CO)_{ax}$; 188.35 m(m), $(CO)_{eq}$; 187.78 m(m), $=C(t\text{-}Bu)SiF_2$; 151.27 m(d, m), $=CHSiF_2$; 38.79 s(s), $-C(CH_3)_3$; 30.08 s(q), $-C(CH_3)_3$.

For II. Anal. Found. C, 29.04; H, 3.52; F, 24.77%. $C_{15}H_{20}F_8O_3RuSi_4$ calcd.: C, 29.32; H, 3.26; F, 24.76%. Mass spectrum: *m/e* 614(M^+, $C_{15}H_{20}O_3Si_4F_8Ru^+$), 586($C_{14}H_{20}O_2Si_4F_8Ru^+$), 558($C_{13}H_{20}OSi_4F_8Ru^+$), 530($C_{12}H_{20}Si_4F_8Ru^+$), 400($C_9H_{10}O_3Si_2F_4Ru^+$), 372($C_8H_{10}O_2Si_2F_4Ru^+$), 344($C_7H_{10}OSi_2F_4Ru^+$), 215($C_6H_{11}Si_2F_4^+$), 57($C_4H_9^+$). ^1H NMR: δ 1.27 (s), 18H, t-Bu; 7.33(t), 2H, $=CHSiF_2$. ^{19}F NMR: 76.09 (d), $=CHSiF_2$; 89.44 (s), $=C(t\text{-}Bu)SiF_2$. ^{13}C NMR of II: 197.76 m(m), $(CO)_{eq}$; 185.70 s(s), $(CO)_{ax}$; 183.70 m(m), $=C(t\text{-}Bu)SiF_2$; 150.29 m(d, m), $=CHSiF_2$; 38.60 s(s), $-C(CH_3)_3$; 29.65 s(q), $-C(CH_3)_3$.

Preparation of IIIa/IIIb. A solution of 120 mg (0.28 mmol) of I and a slight excess of buta-1,3-diene in 10 ml of n-hexane was degassed and sealed under vacuum at −196 °C. The solution was heated at 110 °C for 15 min, then cooled at

0 °C to stop the reaction. After removal of the solvent and the unchanged reactants, the residue liquid contained mainly IIIa, IIIb and a small amount of (η^4-C_4H_6)Ru(CO)$_3$ (^{19}F NMR showed in ratio of 7:2:1). The yield was estimated to be 25%.

IIIa/IIIb Mass spectrum: *m/e* 454(*M*$^+$, $C_{13}H_{16}O_3Si_2F_4Ru^+$), 426 ($C_{12}H_{16}O_2Si_2F_4Ru^+$), 398($C_{11}H_{16}OSi_2F_4Ru^+$), 370($C_{10}H_{16}Si_2F_4Ru^+$), 214($C_6H_{10}Si_2F_4^+$), 57($C_4H_9^+$). ^{19}F{^{1}H} NMR of IIIa: 83.09 (d, d) and 85.46 (d), 2F in Ru–Si*F*$_2$–CH=; 126.97 (d) and 147.65 (d,d), 2F in =C(t-Bu)–Si*F*$_2$. ^{19}F{^{1}H} NMR of IIIb: 94.85 (d, d) and 96.11 (d), two fluorines in Ru–Si*F*$_2$–C(t-Bu)=; 128.11 (d) and 139.66 (d, d), two fluorines in =CH–Si*F*$_2$. (The above chemical shifts are assigned by selective ^{1}H-decoupled spectra irradiating at the resonance of =C*H*–SiF$_2$.)

The η^3-allyl intermediates IVa and IVb in the reaction with 2,3-dimethylbuta-1,3-diene were not isolated; however, their existence was shown by the ^{19}F spectra.

IVa/IVb. ^{19}F{^{1}H} NMR: 81.43 (d) and 90.85 (d), Ru–SiF$_2$–CH= of IVa; 126.02 (d) and 133.01 (d), =C(t-Bu)SiF$_2$ of IVa. 95.23 (d) and 100.80 (d), Ru–SiF$_2$–C(t-Bu)= of IVb; 128.24 (d) and 142.36 (d), =CH–SiF$_2$ of IVb.

Of the compounds **1**–**10**, only **6** and **7** are novel. The experimental procedures are described below.

Preparation of **6**. A solution containing 240 mg (0.56 mmol) of I and an equimolar amount of *trans*-penta-1,3-diene (or *cis*-penta-1,3-diene) in 10 ml n-hexane was degassed and sealed under vacuum at −196 °C. The reaction tube was heated at 110 °C for 40 min. About 200 mg of triphenylphosphine was added under Ar and the tube was re-sealed under vacuum. After heating at 80 °C for 30 min, the solvent and excess reactant were pumped out. The residual liquid was subjected to vacuum distillation at 90 °C. A colorless liquid was obtained which contained 95% of **6** and 5% of **10**, a known compound from the 1,1-addition reaction. The total yield was about 40%. (The purpose of adding triphenylphosphine was to remove the by-product (η^4-C_5H_8)Ru(CO)$_3$).

Preparation of **7**. Similar procedures were used for the reaction with *trans,trans*-hexadiene (or *trans,cis*-hexadiene). The yield of **7** was 25%.

For **6**. Anal. Found. C, 46.48; H, 6.09; F, 27.14. $C_{11}H_{18}Si_2F_4$ calcd.: C, 46.81; H, 6.38; F, 26.95%. Mass spectrum: *m/e* 282 (*M*$^+$, $C_{11}H_{18}Si_2F_4^+$), 267($C_{10}H_{15}Si_2F_4^+$), 82($C_6H_{10}^+$), 69($C_5H_9^+$), 57($C_4H_9^+$). ^{1}H NMR of **6**: δ 1.12 (s), 9H, t-Bu; 1.32 (m), 2H, CH$_2$; 1.69 (d, c), 3H, =CH–C*H*$_3$; 2.15 (br), 1H, allylic H; 5.46 (d, d) and 5.53 (d, q), 2H, AB spectrum for *trans* -HC=CH–; 6.55 (m), 1H, =CH–SiF$_2$. ^{19}F{^{1}H} NMR: 138.01 (d) and 139.21 (d, d), =C(t-BuSiF$_2$; 138.50 (d) and 141.31 (d, d), =CHSiF$_2$. (Assigned with the help of selective ^{19}F{^{1}H} decoupling technique irradiating at the resonances of =CHSiF$_2$, =CH–C*H*<, and –C*H*$_2$–SiF$_2$, respectively.) ^{13}C NMR: δ 173.49 m(m), =C(t-Bu)SiF$_2$; 134.56 c(d, c), =*C*H–SiF$_2$; 127.26 s(d) and 126.49 s(d), -H*C*=*C*H–; 39.45 s(s), –*C*(CH$_3$)$_3$; 29.23 s(q), –C(*C*H$_3$)$_3$; 22.90 t(d, t), =CH–*C*HSiF$_2$; 11.49 t(t, t), CH$_2$.

For **7**. Anal. Found. C, 48.90; H, 6.38; F, 25.54. $C_{12}H_{20}Si_2F_4$. Calcd.: C, 48.65; H, 6.76; F, 25.68%. Mass spectrum: *m/e* 296(*M*$^+$, $C_{12}H_{20}Si_2F_4^+$), 267($C_{10}H_{15}Si_2F_4^+$), 57($C_4H_9^+$). ^{1}H NMR: δ 0.83 (t), H, –CH$_2$C*H*$_3$; 0.96 (s), 9H, t-Bu; 1.03 (m), 2H, –SiF$_2$–CH$_2$; 1.23 (m), 2H, –C*H*$_2$CH$_3$; 1.85 (m), 1H, allylic H; 5.30 (d, d) and 5.31 (d, t), 2H, AB spectrum for trans –C*H*=C*H*–C$_2$H$_5$; 6.39(m), 1H, =CHSiF$_2$. ^{19}F{^{1}H} NMR: 138.10 (d) and 139.52 (d, d), =C(t-Bu)SiF$_2$; 138.56 (d) and 141.44 (d, d), =CHSiF$_2$. (^{19}F chemical shifts are assigned on the basis of selective $^{19}F\{^1H\}$ decoupling, irradiating at the resonances of =CHSiF$_2$, =CH–CH<, and –CH$_2$–SiF$_2$, respectively). ^{13}C NMR: δ 173.65 m(m), =*C*(t-Bu)SiF$_2$; 135.11 m(d, m), =*C*HSiF$_2$; 127.98 s(d) and 125.54 s(d), –*C*H=*C*H–; 39.44 s(s), –*C*(CH$_3$)$_3$; 29.15 s(q), –C(*C*H$_3$)$_3$; 25.91 s(t), –*C*H$_2$CH$_3$; 23.14 t(d, d), =CH–*C*HSiF$_2$–; 13.87 s(q), –CH$_2$*C*H$_3$; 11.13 t(t, t), –SiF$_2$–*C*H$_2$–.

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