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Fluorine migration in dimerization of tetrafluorodisilacyclobutene mediated by Group VI transition metal carbonyls

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Abstract

The photochemical dimerization of 1,1,2,2-tetrafluoro-1,2-disilacyclobutene mediated by Group VI transition metal carbonyls generates (fluorosilyl)(trifluorosilyl)alkenes (**5**) by fluorine atom migration. The electronic properties (hardness) of the central metal influence the selection of the reaction pathway: F migration to give the dimer **5** or further oxidative addition to give the tetrasilyl transition metal compound **7** or **9**.

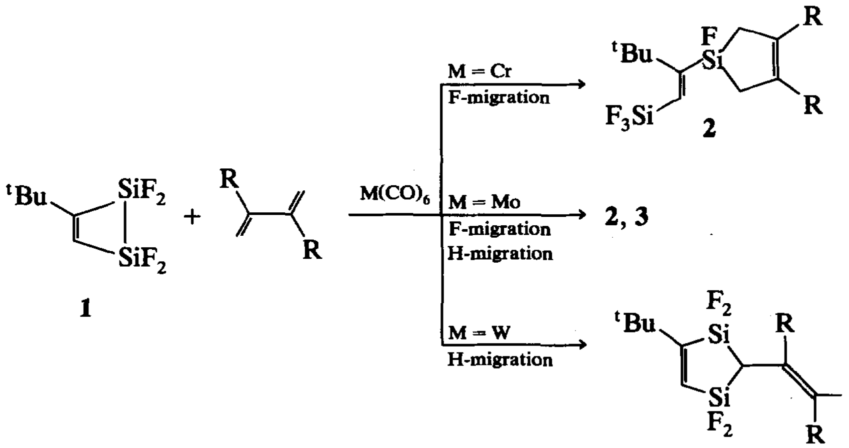
Key words: Silicon; Chromium; Molybdenum; Tungsten

1. Introduction and results

We have reported the cycloaddition reactions between tetrafluorodisilacyclobutenes **1** and conjugated dienes mediated by Group VI metal carbonyls. In these reactions the hardness of the metal appears to be a controlling factor in the determination of the reaction pathway [1]. An example is shown below.

Since F migration is observed together with H migration in the same type of reactions, a common type of intermediate, namely the (η^3-allyl)(η^3-silaallyl) metal complex can be proposed (see **I**).

A similar situation is encountered when Group VI metal carbonyls react photochemically with an excess amount of **1**. The results can be described as shown by the equations on the following page.



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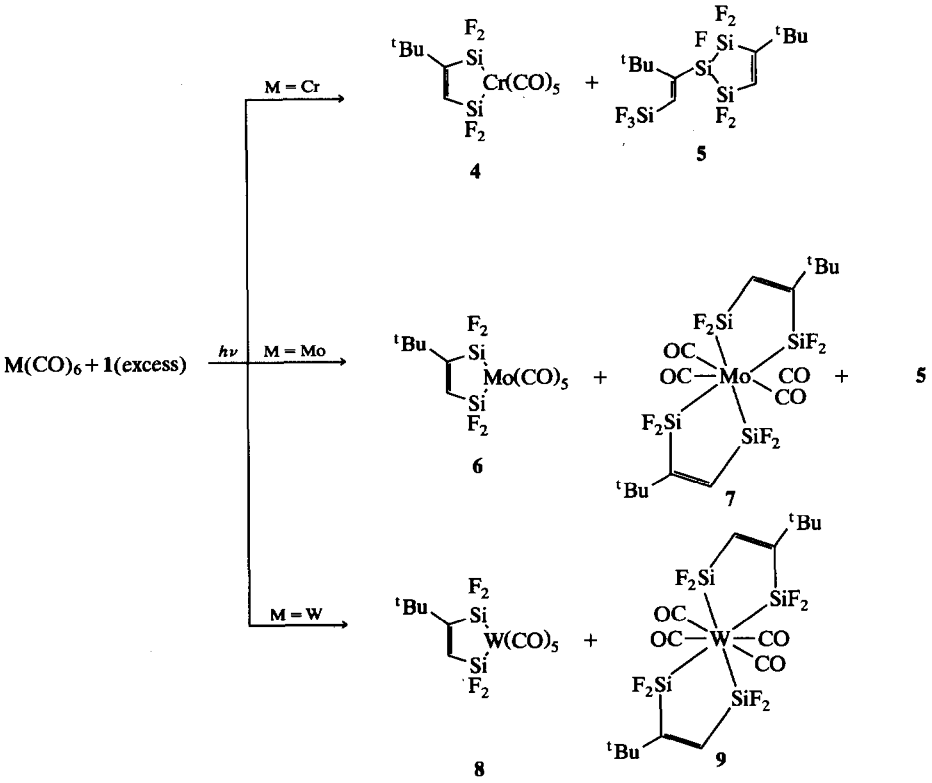
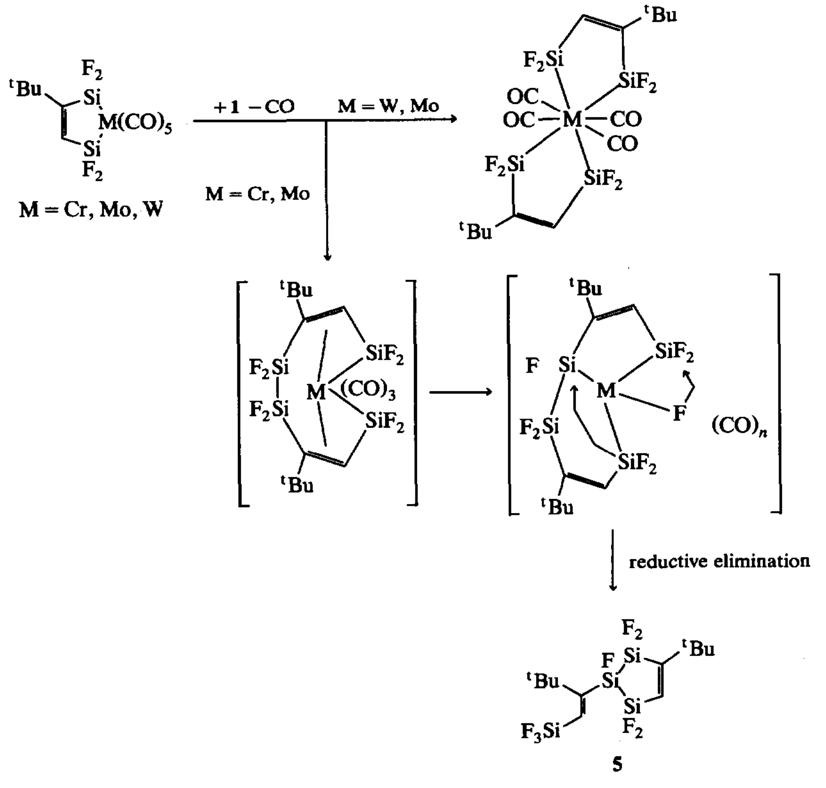
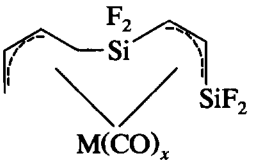
In all cases the disilametallacycle complexes (**4**, **6**, **8** for M = Cr, Mo, W respectively) were the expected products. In addition, two types of new product were obtained. Compound **5** is a product of dimerization of **1** involving F migration. Compounds **7** and **9** are products of double oxidative addition.

Disilametallacycles **4**, **6** and **8** are transparent crystals with melting points of 30, 67 and 93°C respectively.







(I)

The structure of **6** has been determined by single-crystal X-ray diffraction [2]. However, it is reasonably certain that compounds **4**, **6** and **8** all have a very similar slightly distorted pentagonal bipyramid structure.

Compounds **5**, **7** and **9** were characterized by mass spectrometry, elemental analyses and ^1H, ^{19}F and ^{13}C NMR spectroscopies.

The $^{19}F\{^1H\}$ NMR spectrum of **5** shows a doublet at 138.15 ppm and five multiplets at 215.20, 130.80, 131.46, 137.77 and 138.92 ppm with an intensity ratio of 3:1:1:1:1:1. A two-dimensional COSY experiment indicates that the multiplets at 130.80 and 131.46 ppm belong to one SiF_2 group, whereas the multiplets at 137.77 and 138.92 ppm belong to the other SiF_2 group. On the basis of the intensity, the doublet at 138.15 ppm is assigned to the trifluorosilyl group, and the last multiplet at an unusually high field (215.20 ppm) is assigned to the unique SiF group in compound **5**. The position of the ^tBu group is determined by the observation in the $^{13}C\{^1H\}$ NMR spectrum of a quartet at 125.6 ppm for $=CH-SiF_3$ and a doublet at 177.5 ppm for $=C(^tBu)SiF$, with $^{13}C-^{19}F$ coupling constants of 27.5 and 6.4 Hz respectively.

Compounds **7** and **9** are eight-coordinated complexes, and their structures are of great interest. The NMR data show that two sets of signals are observed for almost all of the carbons in **7** and **9**, and therefore the two metallacycles in the molecules of **7** and **9** are not entirely symmetric. Unfortunately the preparation of single crystals of **7** and **9** for X-ray diffraction experiments was not successful.

Since metallacycles **4**, **6** and **8** can be isolated and purified, separate experiments concerning the reaction of **1** with **4**, **6** and **8** were carried out under the same reaction conditions. The results show that compound **5** is the only product in the reaction with **4**, and compound **9** is the only product in the reaction with **8**. In the reaction with **6**, both **5** and **7** were obtained. These results can be rationalized by the reaction scheme shown in the lower section of the previous page.

The results once again show the effect of the hardness of the metal on the choice of reaction pathway. The "harder" Cr assists F migration most effectively so that compound **5** is the only product of reaction. On the other hand, the reaction mediated by the "softer" metal W yields the product of double oxidative addition **9** as the only product. In the case of Mo, however, products from both reaction pathways were obtained (**5** and **7**).

As in the metal-mediated cycloaddition reactions between **1** and conjugated dienes, the intermediacy of a carbon–silicon π-bonding species is proposed [3]. In view of the successful isolation of stable silaethenes [4] and metal-stabilized η^3-silaallyl complexes [5], the proposed reaction scheme seems to be plausible and accounts for all the experimentally observed results.

2. Experimental section

Vacuum distillation and chemical manipulations were carried out on vacuum lines at 10^{-3} Torr. Photochemical preparations employed a 450 W medium-pressure Hg lamp. $M(CO)_6$ (M = Cr, Mo, W) (Sterm) were used as received. The following compounds were prepared according to the literature: **1** [6], $(\overline{F_2Si(^tBu)C=C(H)SiF_2})M(CO)_n$ (M = Cr, Mo, W; $n = 5$) [2,7].

2.1. Spectra

All mass spectra were recorded on a JEOL JMS-100 mass spectrometer operating at 12 eV. The NMR spectra were obtained using 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 as δ values. ^{19}F NMR chemical shifts were measured in parts per million upfield from the internal standard CCl_3F. In the ^{13}C NMR data, the spectral multiplicity following each chemical shift is due to the coupling with heteronuclei, whereas the coupling patterns in $^{13}C\{^1H\}_{cw}$ are given in parentheses.

2.2. Preparation of compound 5

Compound **5** can be prepared photochemically by reaction of **1** with $(\overline{F_2Si(^tBu)C=C(H)SiF_2})Cr(CO)_5$. A typical run can be described as follows: **1** (5.0 mmol) and 10.0 mmol of $(\overline{F_2Si(^tBu)C=C(H)SiF_2})Cr(CO)_5$ were placed in a quartz reaction tube filled with dry nitrogen. Dried and degassed n-pentane (10 ml) was used as the solvent. The reaction was carried out on irradiation at 50°C. The reaction tube was subjected to degassing every 4–5 h. Compound **1** was completely consumed after 30 h. The solution was concentrated to a brown liquid by pumping out the solvent. Distillation under vacuum gave a pale yellow liquid. It was characterized as compound **5**. Anal. Calc. C, 33.64; H, 4.67; F, 35.51. Found: C, 33.78; H, 4.90; F, 35.04. Mass spectrum: *m/e* 428 (M^+, $C_{12}H_{20}Si_4F_8^+$), 413 ($C_{11}H_{17}Si_4F_8^+$), 409 ($C_{12}H_{20}Si_3F_7^+$), 343 ($C_{12}H_{20}Si_3F_5^+$), 214 ($C_6H_{10}Si_2F_4^+$), 195 ($C_6H_{10}Si_2F_3^+$), 129 ($C_6H_{10}SiF^+$), 57 ($C_4H_9^+$). ^{1}H NMR: δ 0.95, 1.2 s, 18H, ^{t}Bu), 6.19 (dq, 1H, $=C\mathit{H}SiF_3$), 6.17 (m, 1H, $=C\mathit{H}SiF_2$). ^{19}F{^{1}H} NMR: 138.15 (d, 3F, $=CHSi\mathit{F}_3$), 215.20 (m, 1F, $=C(^tBu)Si\mathit{F}$), 130.80 (m), 131.46 (m), 137.77 (m), 138.92 (m), four F of five-membered ring of compound **5**, $^5J_{F,F} = 19$ Hz. ^{13}C NMR: δ 29.5, 29.0 (s(q), $(\mathit{C}H_3)_3C$), 38.4, 40.1 (s(s), $(CH_3)_3\mathit{C}$), 125.6 (qd(qdd), $=\mathit{C}HSiF_3$), 144.5 (m(dm), $=\mathit{C}HSiF_2$), 177.5 (dq(dq), $=\mathit{C}(^tBu)SiF$), 184.0 (m(m), $=\mathit{C}(^tBu)SiF_2$). ^{29}SiNMR: -70.2 (dq, $=CH\mathit{Si}F_3$), -10.2 (dm, $=C(^tBu)\mathit{Si}F$), -13.8, -17.0 (tm, SiF_2 of the five-membered ring).

2.3. *Preparation of compounds 7 and 9*

Compounds **7** and **9** can be prepared photochemically by reaction of **1** with compounds **6** and **8**. An *n*-pentane solution containing 4.0 mmol of $(\overline{F_2Si(^tBu)\text{-}C{=}C(H)SiF_2}\rightarrow Mo(CO)_5$ or $(\overline{F_2Si(^tBu)C{=}C(H)SiF_2}\rightarrow W\text{-}(CO)_5$ and 5.0 mmol of compound **1** was degassed and irradiated under a dry nitrogen atmosphere at 30°C for 25 h. After removal of the solvent and volatile compound **5** about 0.75 g of **7** or **9** was precipitated. The yield based on the quantity of **6** or **8** used was about 30%. Compound **7**, a solid. Anal. Calc. C, 30.19; H, 3.14; F, 23.90. Found: C, 30.25; H, 3.20; F, 23.7. Mass spectrum: *m/e* 636 (M^+, $C_{16}H_{20}O_4Si_4F_8Mo^+$), 422 ($C_{10}H_{10}O_4Si_2F_4Mo^+$), 394 ($C_9H_{10}O_3Si_2F_4Mo^+$), 366 ($C_8H_{10}O_2Si_2F_4Mo^+$), 338 ($C_7H_{10}OSi_2F_4Mo^+$), 215 ($C_6H_{11}Si_2F_4^+$), 129 ($C_6H_{10}SiF^+$), 57 ($C_4H_9^+$). ^{1}H NMR: δ 1.10 (s, 18H, ^{t}Bu), 7.04 (m, 2H, $=C\mathit{H}SiF_2$). ^{19}F{^{1}H} NMR: 91.88, 92.26 (m, $=(^tBu)Si\mathit{F}_2$), 78.81, 79.22 (m, $=CHSi\mathit{F}_2$). ^{13}C NMR: δ 29.7 (s(q), $(\mathit{C}H_3)_3C$), 38.18, 38.74 (s(s), $(CH_3)_3\mathit{C}$), 147.9, 148.6 (m(dm), $=\mathit{C}HSiF_2$), 185.5, 185.6 (m(m), $=\mathit{C}(^tBu)SiF_2$), 204.4, 203.7 for $\mathit{C}O$. Compound **9**. Anal. Calc: C, 26.52; H, 2.76; F, 20.99. Found: C, 26.70; H, 2.60; F, 21.05. Mass spectrum: *m/e* 724 (M^+, $C_{16}H_{20}O_4Si_4F_8W^+$), 510 ($C_{10}H_{10}O_4Si_2F_4W^+$), 482 ($C_9H_{10}O_3Si_2F_4W^+$), 454 ($C_8H_{10}O_2Si_2F_4W^+$), 296 ($C_4O_4W^+$), 215 ($C_6H_{11}Si_2F_4^+$), 57 ($C_4H_9^+$). ^{1}H NMR: δ 1.06, 1.02 (s, 18H, ^{t}Bu), 6.90 (m, 2H, $=C\mathit{H}SiF_2$). ^{19}F{^{1}H} NMR: 96.38, 95.92 (m, $=C(^tBu)Si\mathit{F}_2$), 77.11, 77.22 (m(dm), $=CHSi\mathit{F}_2$). ^{13}C NMR: 29.27, 29.40 (s(q), $(\mathit{C}H_3)_3C$), 39.42, 39.78 (s(s), $(CH_3)_3\mathit{C}$), 147.4, 147.6 (tt(dtt), $=\mathit{C}HSiF_2$), 184.2, 184.8 (m(m), $=\mathit{C}(^tBu)SiF_2$), 194.4, 195.3 for $\mathit{C}O$.

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