3456 *Inorg. Chem.* **1981**, *20*, 3456-3460

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Photochemical Preparation of Transition-Metal Carbonyl Compounds with 1,1,2,2-Tetrafluoro-1,2-disilacyclobutenes as Ligands

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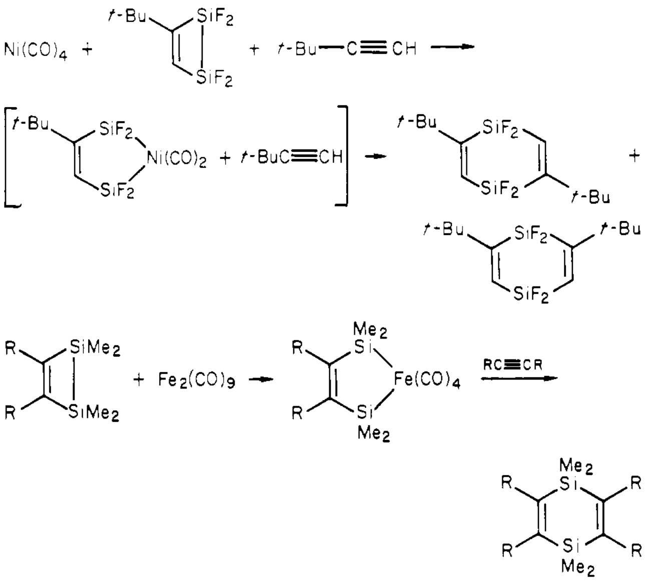
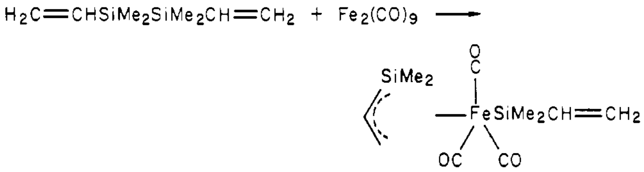
Organometallic compounds involving a five-membered disilametallacyclic structure are conveniently prepared by photochemical reactions between 1,1,2,2-tetrafluoro-1,2-disilacyclobutene and transition-metal carbonyls (M = Mo, Fe, Mn, and Co). The reaction mechanism can be rationalized as an initial dissociation of M–CO followed by oxidative addition of the Si–Si bonds to the coordinatively unsaturated metal carbonyl species. Some intermediates, the olefin complexes, can be isolated and converted to the disilametallacyclic compounds by further irradiation.

Introduction

1,2-Disilacyclobutenes represent a special class of vinyldisilane, which has been a much studied system in connection with the possible involvement of Si=C intermediate species.[1-3] Earlier studies on the stabilization of thermally cleaved 1,2-disilacyclobutenes by transition-metal carbonyls resulted in a number of disilametallacyclic compounds that behaved as intermediates of catalytic cycloaddition reactions forming 1,4-disilacyclohexa-2,5-dienes. For example:[4,5]



Sakurai et al. reported a rather remarkable reaction[6] between divinyltetramethyldisilane and $Fe_2(CO)_9$, which led to a involving a π-bonded η^3 silallyl group:



However, McKennis recently reported that Sakurai had only made a η^2 iron–olefin complex and not the η^3 silallyl structure.[17] It is concluded that the stabilization of a doubly bonded silicon species by a transition metal remains to be conclusively demonstrated.

Under photochemical conditions one might predict that 1,2-disilacyclobutenes would, according to the proposed reaction scheme for vinyldisilanes in general,[7] rearrange to 1,4-disilabutadienes. It is well-known that transition-metal carbonyls $M(CO)_n$ dissociate to $M(CO)_{n-1}$ and carbon monoxide under proper photochemical conditions.[8] If 1,4-disilabutadiene did exist transiently, the coordinatively unsaturated $M(CO)_{n-1}$ is then expected to trap it rapidly and the structure of the product might provide some insight into the nature of such intermediates.

Experimental Section

Preparation of 3-*tert*-Butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobut-3-ene. The four-membered ring compound was prepared from the cocondensation reaction between *tert*-butylacetylene and difluorosilylene, which was described elsewhere.[9]

Reactions of $C_6H_{10}Si_2F_4$ with $Mo(CO)_6$ and $Fe(CO)_5$. A 1.5-g quantity (7 mmol) of the freshly prepared disilacyclobutene and 1.9 g (7 mmol) of $Mo(CO)_6$ were sealed with 15 mL of pentane in a reaction tube under vacuum at −196 °C. The solution was stirred at room temperature under irradiation (medium-pressure Hg lamp) for 12 h. Carbon monoxide, unreacted starting materials, and the solvent were removed by pumping at room temperature. The brown oily liquid left in the reaction tube was then heated to 80 °C under pumping, and compound I was obtained as transparent crystals by sublimation (mp 66–67 °C; yield 65%). Anal. Calcd: C, 29.33; H, 2.22. Found: C, 29.34; H, 2.22.

In the same manner, 0.8 g (3.7 mmol) of the disilacyclobutene and 0.45 mL of $Fe(CO)_5$ were reacted. Compound II was purified by exhaustive vacuum fractionation (mp 21–22 °C; yield 60%).

Reaction of $C_6H_{10}Si_2F_4$ with $(C_6H_7)Mn(CO)_3$. A 1.2-g quantity (5.6 mmol) of the disilacyclobutene and 0.4 mL (2.5 mmol) of $(C_6H_7)Mn(CO)_3$ were reacted in a similar manner under irradiation for 24 h. Compound III was obtained as colorless crystals by vacuum sublimation at 120 °C (mp 73–76 °C; yield 20%).

Reaction of $C_6H_{10}Si_2F_4$ with $(C_7H_8)Mo(CO)_4$. A 1.2-g quantity (5.6 mmol) of the disilacyclobutene and 0.8 g (2.6 mmol) of $(C_7H_8)Mo(CO)_4$ were reacted in 25 mL of pentane for 12 h as described above. Compound IV was obtained as powders by filtration at −78 °C. The filtrate contained mainly compound I. Compound IV was recrystallized in pentane at −78 °C (total yield 35%; relative yield of I/IV about 2:3).

Reaction of $C_6H_{10}Si_2F_4$ with $Co_2(CO)_8$. A 1.5-g quantity of $C_6H_{10}Si_2F_4$ (7 mmol) and equimolar $Co_2(CO)_8$ were reacted as previously described. Compound VI precipitated at −78 °C while

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(1) Barton, T. J.; Wulff, W. D.; Arnold, E. V.; Clardy, J. *J. Am. Chem. Soc.* **1979**, *101*, 2733–2735.
(2) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1976**, *98*, 7424–7425.
(3) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1978**, *149*, 37–48.
(4) Liu, C. S.; Cheng, C. W. *J. Am. Chem. Soc.* **1975**, *97*, 6746–6749.
(5) Sakurai, H.; Kobayashi, T.; Nakadaira, Y. *J. Organomet. Chem.* **1978**, *162*, C43–47.
(6) Nakadaira, Y. N.; Kobayashi, T.; Sakurai, H. *J. Organomet. Chem.* **1979**, *165*, 399–405.
(7) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1976**, *98*, 7424–7425.
(8) Wrighton, M. *Chem. Rev.* **1974**, *74*, 401–430.
(9) Liu, C. S.; Margrave, J. L.; Thompson, J. C. *Can. J. Chem.* **1972**, *50*, 465–473.

0020-1669/81/1320-3456$01.25/0

Table I. Mass Spectral Data of Compounds I–IV and VI–VIII

compd	m/e^a (assignt^b)
I	452 (M^+, $Mo(CO)_5L^+$), 424 ($Mo(CO)_4L^+$), 396 ($Mo(CO)_3L^+$), 368 ($Mo(CO)_2L^+$), 340 ($Mo(CO)L^+$), 312 (MoL^+), 238 ($Mo(CO)_5{}^+$), 210 ($M(CO)_4{}^+$)
II	382 (M^+, $Fe(CO)_4L^+$), 354 ($Fe(CO)_3L^+$), 326 ($Fe(CO)_2L^+$), 298 ($Fe(CO)L^+$), 270 (FeL^+), 168 ($Fe(CO)_4{}^+$), 140 ($Fe(CO)_3{}^+$), 112 ($Fe(CO)_2{}^+$)
III	404 (M^+, $Mn(C_6H_7)(CO)_2L^+$), 376 ($Mn(C_6H_7)(CO)L^+$), 348 ($Mn(C_6H_7)L^+$), 190 ($Mn(C_6H_7)(CO)_2{}^+$), 162 ($Mn(C_6H_7)(CO)^+$)
IV	488 (M^+, $Mo(C_7H_8)(CO)_3L^+$), 460 ($Mo(C_7H_8)(CO)_2L^+$), 432 ($Mo(C_7H_8)(CO)L^+$), 404 ($Mo(C_7H_8)L^+$), 396 ($Mo(CO)_3L^+$), 274 ($Mo(C_7H_8)(CO)_3{}^+$)
VI	500 (M^+, $Co_2(CO)_6L^+$), 472 ($Co_2(CO)_5L^+$), 444 ($Co_2(CO)_4L^+$), 416 ($Co_2(CO)_3L^+$), 388 ($Co_2(CO)_2L^+$), 360 ($Co_2(CO)L^+$), 332 (Co_2L^+), 215 ($C_6H_{11}Si_2F_4{}^+$)
VII	528 (M^+, $Co_2(CO)_7L^+$), 500 ($Co_2(CO)_6L^+$), 472 ($Co_2(CO)_5L^+$), 444 ($Co_2(CO)_4L^+$), 416 ($Co_2(CO)_3L^+$), 388 ($Co_2(CO)_2L^+$), 360 ($Co_2(CO)L^+$), 357 ($Co(CO)_3L^+$), 332 (Co_2L^+), 329 ($Co(CO)_2L^+$), 301 ($Co(CO)L^+$), 273 (CoL^+)
VIII	714 (M^+, $Co_2(CO)_6L_2{}^+$), 686 ($Co_2(CO)_5L_2{}^+$), 658 ($Co_2(CO)_4L_2{}^+$), 630 ($Co_2(CO)_3L^+$), 602 ($Co_2(CO)_2L^+$), 574 ($Co_2(CO)L^+$)

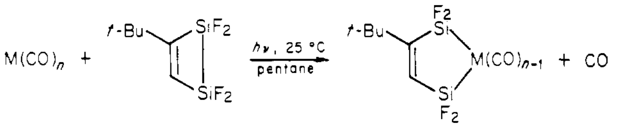
^{a} Mass number of the most abundant isotope is used. ^{b} L = $C_6H_{10}Si_2F_4$.

compound VII remained as an oily liquid in pentane solution. They were separated by repeated washing with pentane at −78 °C and subsequent filtration. Compound VI was purified by recrystallization in pentane at −64 °C, and compound VII was separated from the filtrate solution by vacuum fractionation (VI mp 82–84 °C, yield 23%; VII yield 19%).

Spectra. Mass spectra were obtained from a JMS-100 mass spectrometer. The ^1H and ^{19}F NMR spectra were recorded on a JEOL FX-100 spectrometer operating at 99.6 and 93.6 MHz, respectively. The IR spectra were obtained with use of a Perkin-Elmer 580 spectrometer.

Results and Discussion

When 3-*tert*-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobutene was irradiated together with $Mo(CO)_6$ or $Fe(CO)_5$ in pentane solutions by UV light for 12 h, each reaction gave a crystalline product in moderately high yield. These reactions can be illustrated by the equation



I, II

I: M = Mo, n = 6, yield 65%; II: M = Fe, n = 5, yield 60%

I and II are transparent crystalline compounds with mp 66–67 and 21–22 °C, respectively. Their mass spectra (Table I) show the molecular ions as the highest m/e peaks, fragment ions from the successive loss of (n − 1)CO, and the $M(CO)_{n-1}{}^+$ ions from the loss of the $C_6H_{10}Si_2F_4$ ligand. The formula of I is further confirmed by elemental analysis. The IR spectra of I and II are very similar. They show, in addition to the characteristic absorption bands for ν_{Si-F} (845, 872, 910 cm^{-1}) and $\nu_{C=C}$ (1550 cm^{-1}), the bands of ν_{CO} at 2110 and 1970 cm^{-1}. The ^1H NMR spectra of I and II are quite similar to that of the starting material 3-*tert*-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobutene except the coupling between the olefinic H and the vicinal fluorines is reduced from 19 to ~10 Hz. The ^{19}F NMR spectra of I and II show a drastic change from that of the starting material. Both I and II show large downfield shifts from the chemical shifts of the starting material (Figure 1a,b).[10] Furthermore, the AA′MM′X spectrum typical for the four-membered ring is lost; instead, the spectrum shows a doublet of multiplets and a multiplet for both I and II. The $^3J_{HF}$ values for I and II are 12.2 and 10.6 Hz, respectively (Figure 1a,b). In the proton-decoupled ^{19}F spectra, the vicinal F–F coupling constants are reduced from 16[11] to ≤2 Hz.

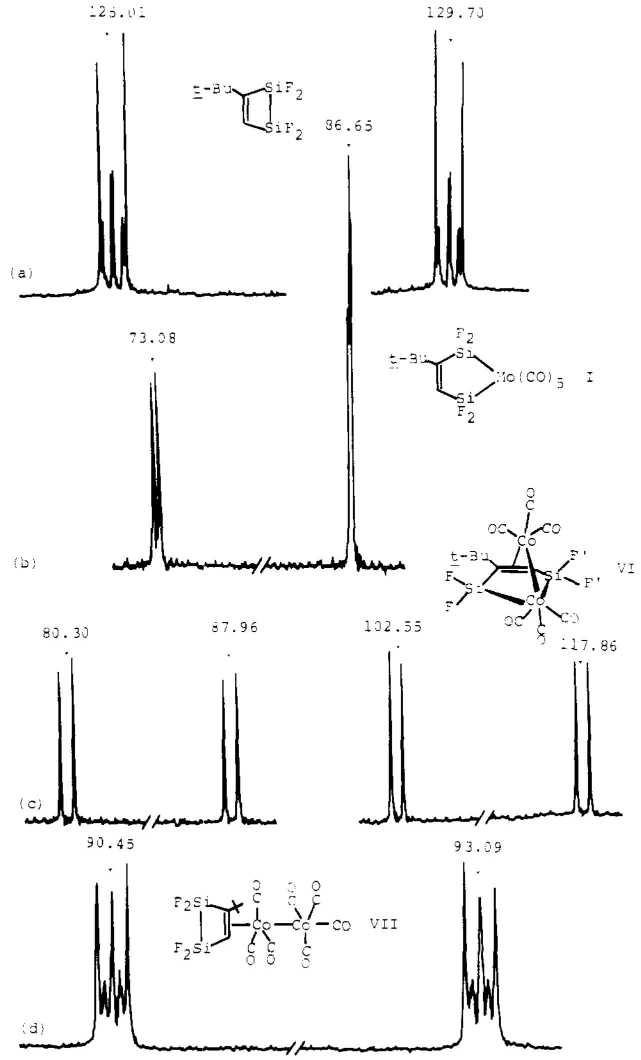


Figure 1. (a) Proton-decoupled ^{19}F NMR spectrum of 3-*tert*-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobutene. (b) ^{19}F NMR spectrum of compound I. (c) Proton-decoupled ^{19}F NMR spectrum of compound VI. (d) Proton-decoupled ^{19}F NMR spectrum of compound VII.

All these spectroscopic data strongly indicate that the Si–Si bond is cleaved in forming I and II. The drastic change of Si–F chemical shifts plus the reduction of all H–F and F–F coupling leads us to conclude the structure of I and II to be as shown. Since the structure of I has now been confirmed by a single-crystal X-ray diffraction study,[12] this kind of spectral change can be used diagnostically for structural assignment. It seems that the original idea of stabilizing the hypothetical 1,4-disilabutadiene by transition-metal carbonyls was not realized.

This type of reaction seems to be quite general; for example, the reaction of the disilacylobutene with (methylcyclopentadienyl)manganese tricarbonyl leads to the formation of compound III (mp 73–76 °C).

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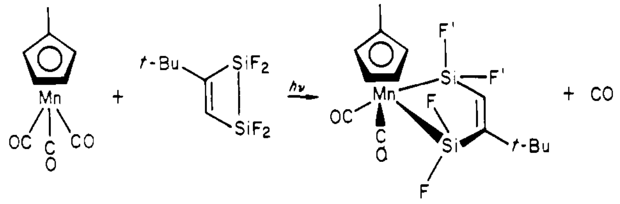
(10) In II, the ^{19}F chemical shift of the SiF_2 adjacent to =CH is 87.14 ppm (doublet of multiplets) and the chemical shift of the other SiF_2 is 97.56 ppm (multiplet).

(11) From a full analysis of the AA′MM′X spectrum of the disilacyclobutene $C_6H_{10}Si_2F_4$.

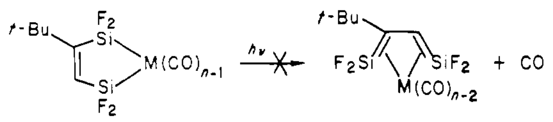
(12) Hseu, T. H.; Chi, Y.; Liu, C. S. *Inorg. Chem.*, **1981**, *20*, 199–204.



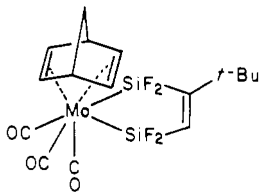
III

Compound III can be identified unequivocally by means of mass spectrometry and IR and NMR spectroscopies. The mass spectrum shows the molecular formula of $(C_6H_7)Mn(C_6H_{10}Si_2F_4)(CO)_2$ (Table I); the IR spectrum shows two strong bands in the ν_{CO} region (2013 and 1966 cm^{-1}), and the ν_{CO} bands of $(C_6H_7)Mn(CO)_3$ are at 2026 and 1949 cm^{-1}, respectively. The ^{1}H NMR spectrum shows resonances at δ 1.18 (s, *t*-Bu), δ 1.95 (s, CH_3), δ 4.47 and 4.65 (br, s, CpH) and δ 7.05 (br, t, vinyl H) with intensity ratio 9:3:4:1. The ^{19}F NMR spectrum is particularly informative. It shows two complex AX systems of equal intensity. On proton-noise decoupling, the spectrum is simplified to four doublets at 83.3, 86.9, 92.2, and 96.4 ppm. In a comparison of the undecoupled and the decoupled spectra, the peaks at 83.3 and 86.9 ppm are assigned to the SiF'_2 group since there are larger HF couplings involved in these peaks. The disappearance of the AA'MM'X pattern in the ^{19}F spectrum characteristic for the disilacyclobutene indicates the cleavage of the Si–Si bond, and the chemical environments of the two F atoms above the five-membered metallacycle become different from the two below because of the influence of the methylcyclopentadiene ring.

Attempts to force these compounds to lose one more carbonyl group in order to induce intramolecular rearrangement were not successful since all these compounds are rather stable toward further irradiation. Heating these compounds merely leads to decomposition:

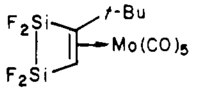


Another example of interest is the reaction of the disilacyclobutene with (bicycloheptadiene)molybdenum tetracarbonyl. The latter is known to be prone to undergo a disubstitution reaction on losing the bicycloheptadiene ligand.[13] One might therefore expect the formation of the disilabutadiene complex by the reaction with the $Mo(CO)_4$ moiety. However, the reaction proceeded in an unexpected way. One of the products is identified by means of mass spectrometry and ^{1}H and ^{19}F NMR spectroscopy to be compound I. The other product shows the highest m/e = 488, which corresponds to a molecular ion $[(C_7H_8)Mo(C_6H_{10}Si_2F_4)(CO)_3]^+$ (Table I). The ^{1}H NMR spectrum shows two sets of signals for the vinyl H (=CHSiF$_2$—, δ 7.59 and 7.44) and *tert*-butyl H (δ 1.55 and 1.61). The resonances of the methylene and methyne protons of the bicycloheptadiene are observed as broadened peaks at δ 1.83 and 4.28, respectively. It is interesting to note that the olefinic protons of the bicycloheptadiene show two broad peaks with equal intensities at δ 4.75 and 5.51. The ^{19}F NMR spectrum shows two sets of doublets (97.26 ppm with J_{HF} = 13.5 Hz and 81.85 ppm with J_{HF} = 10.4 Hz) of multiplets (from F–F couplings) and two sets of multiplets (94.39 ppm and 109.26 ppm). The whole spectrum, therefore, consists of two parts, and each part resembles the spectrum of I and II, which is quite typical for structures with two separate SiF_2 groups. It is quite likely that they represent two geometrical isomers of IV, in the 3:1 ratio of abundance. The difference of the two sets of spectra is caused by the difference in spatial arrangement of the metalladisilacycle with respect to bicycloheptadiene. Thus the reaction can be illustrated by Scheme I.



IV

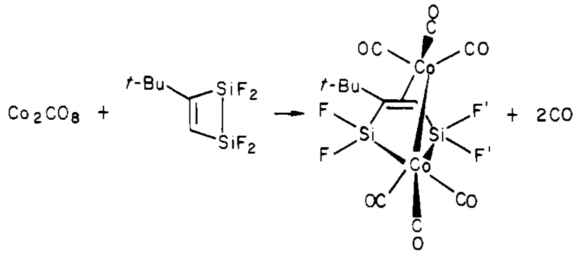
Since McKennis has shown that Sakurai's η^3 silallyl complex is actually an iron–olefin complex, one might expect that similar olefin complexes should also exist in such reactions. Indeed, we found that at the early stage of irradiation another type of compound had been formed in these reactions. In the case of the Mo reaction, for example, a broadened multiplet is observed for the olefinic proton, which shifts 1.07 ppm upfield from the corresponding signals of the starting materials $C_6H_{10}Si_2F_4$ in the ^{1}H NMR spectrum, and two complex resonances of equal intensity are observed in the normal Si–F region in the ^{19}F NMR spectrum (124.1 and 134.3 ppm). The ^{19}F spectrum also resembles an AA'MM'X pattern, but the chemical shifts and coupling constants differ from those of the free ligand. In a comparison of its data to the data of I, it is obvious that this compound involves metal–ligand interaction on the C=C double bond of the ligand instead of the Si—Si single bond. Although this compound has not been isolated, on the basis of the argument given above we propose the structure



V

In view of this result, it is assumed[8] that the reactions start with the dissociation of a CO ligand from the metal carbonyls to form the coordinatively unsaturated $M(CO)_{n-1}$ species, which react with the 1,2-disilacyclobutene forming, in the first step, olefin complexes such as V. The second step can be rationalized as a result of the activation of the Si–Si bond by coordination, and compounds such as I–IV are formed by the oxidative addition reaction of the Si–Si bond. When this reaction occurs, the metal–olefin bond is cleaved to keep 18 electrons around the central metal.

Assuming that the rationalization described above is justified, one would like to obtain a complex in which both Si–M–Si bonds are formed and the metal–olefin bond can be retained. For this reason the reaction between the disilacyclobutene ligand and $Co_2(CO)_8$ was attempted:



VI

Compound VI is an extremely air-sensitive colorless crystalline solid with mp 82–84 °C, formed in about 23% yield. Its mass spectrum exhibits the molecular ion and the fragment ions corresponding to successive losses of the six CO groups.

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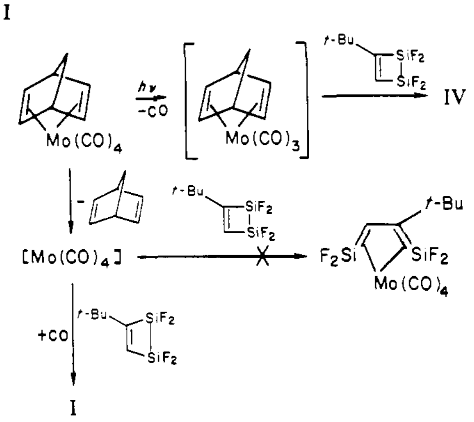
(13) Darensbourg, D. L.; Salzer, A. *J. Am. Chem. Soc.* **1978**, *100*, 4119–4124.

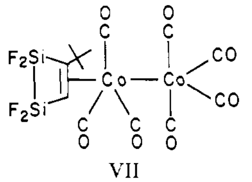
Scheme I



The IR spectrum of VI shows characteristic bands for ν_{CO} (2100 s, 2070 s, 2063 vs, 2030 cm^{-1} s, br), $\nu_{C=C}$ (1550 cm^{-1} w), and ν_{SiF} (800–1000 cm^{-1} s). No bands for bridging CO stretching are observed. An organometallic compound of similar structure with two As donor atoms has been reported by Cullen et al.[14] It shows a very similar IR pattern to that of VI in the CO stretching region.

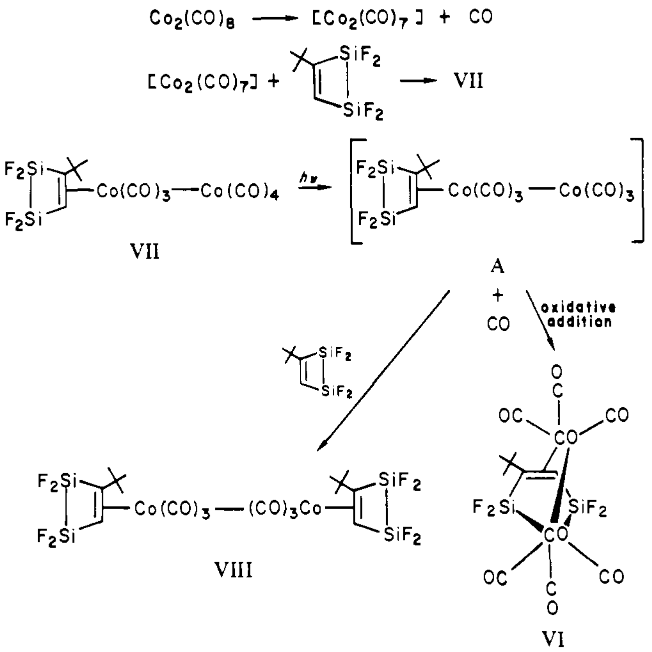
The ^{1}H NMR spectrum of VI shows a multiplet at δ 3.94 for the olefinic H and a singlet at δ 1.24 for the *tert*-butyl H with the intensity ratio 1:9. The proton-decoupled ^{19}F NMR spectrum shows four doublets of equal intensities at 80.30, 102.55 and at 87.96, 117.86 ppm (Figure 1c). The resonances are assigned in pairs to SiF$'_2$ and SiF$_2$, respectively.[15] The geminal F–F coupling constants are 57.7 Hz for each doublet, and the H–F coupling constants for the four fluorines can be obtained from the fine structures of the doublets in the nondecoupled spectrum: 9.6 and 5.9 Hz for $J_{H-F'}$, 2.9 Hz for J_{H-F}. The assignments of the fluorine signals are further confirmed by homonuclear F–F decoupling.

On the basis of our previous knowledge of the spectral features of such disilametallacyclic compounds (I–IV and the compounds in ref 4), the change of the AA′MM′X pattern in the ^{19}F NMR spectrum of the free ligand to a first-order spectrum on complexation is a rather sure indication of the cleavage of the Si–Si bond. Just as in the case of compound III, that the four fluorines show different chemical shifts strongly suggests that the chemical environments above and below the metallacyclic plane have become different. It appears that the structure that fits all these results is the one shown as VI.[16]



VII

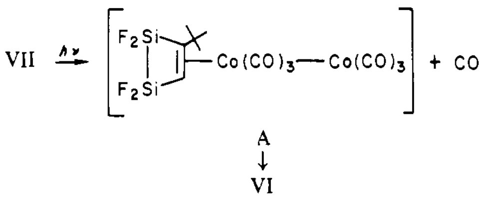
Scheme II



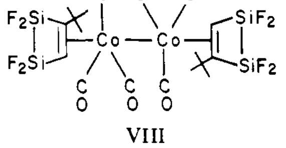
It is interesting to note that, accompanying VI, another compound of the molecular formula $(C_6H_{10}Si_2F_4)Co_2(CO)_7$ (VII) was also obtained. The mass spectrum of this compound is shown in Table I. The IR spectrum of this compound is very similar to that of VI except for some difference in the bands of CO stretching (2108 s, 2055 vs, 2035 cm^{-1} vs, br). No bands for bridging carbonyl stretching are observed. The ^{1}H NMR spectrum shows in addition to the *tert*-butyl proton signal a triplet of triplets, with coupling constants 9.6 and 2.2 Hz for vicinal and long-range H–F couplings, respectively.

The ^{19}F NMR spectrum of this compound shows a typical AA′MM′X pattern at 90.45 and 93.09 ppm. The proton-decoupled ^{19}F spectrum is shown in Figure 1d. These spectral data clearly indicate that the Si–Si bond is retained in this complex and the metal must be bound to the ligand through a metal–olefin bond.

When VII is subjected to further UV irradiation, carbon monoxide is evolved and VI is formed:



As a coordinatively unsaturated species, A is very reactive and cannot be isolated. It may be expected to react with another molecule of disilacyclobutene. Indeed, when the disilacyclobutene is in excess, we do observe in small quantity a species of molecular formula $(C_6H_{10}Si_2F_4)_2Co_2(CO)_6$. The mass spectrum of this compound shows a molecular ion M$^+$ = 714 and the fragment ions involving two $(C_6H_{10}Si_2F_4)$ units resulting from successive losses of the CO groups (Table I). The NMR spectra (^{1}H and ^{19}F) of this compound are almost identical with those of compound VII. The structure seems most likely to be VIII.



VIII

The reactions can be summarized in Scheme II.

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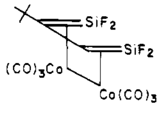
[14] Cullen, W. R.; Harbourne, D. A.; Liengme, B. B.; Sams, J. R. *Inorg. Chem.* **1969**, *8*, 95–100.

[15] The fluorine resonances are assigned according to the H–F coupling constants observed in the nondecoupled ^{19}F NMR spectrum of VI.

[16] Although less likely, the other alternative structure of VI, the 1,4-disilabutadiene complex, cannot definitely be ruled out by the present NMR spectroscopic data:



[17] Radnia, P.; McKennis, J. S. *J. Am. Chem. Soc.* **1980**, *102*, 6349–6351.

Acknowledgment. We are grateful for the financial support of this work by the Chinese National Science Council. Y.C. thanks the Ministry of Education for a postgraduate fellowship.

Registry No. I, 75311-40-9; II, 78514-11-1; III, 78514-10-0; IV, 78514-09-7; V, 78549-86-7; VI, 78514-15-5; VII, 78514-08-6; VIII, 78514-07-5; 3-*tert*-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobut-3-ene, 36091-97-1; $Mo(CO)_6$, 13939-06-5; $Fe(CO)_5$, 13463-40-6; $(C_6H_7)Mn(CO)_3$, 12108-13-3; $(C_7H_8)Mo(CO)_4$, 12146-37-1; $Co_2(CO)_8$, 10210-68-1.

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Synthesis of Tetraphenylstannacyclopentadienes (Stannoles). 2. Derivatives and Adducts of 1,1-Dihalo-2,3,4,5-tetraphenylstannoles[1]

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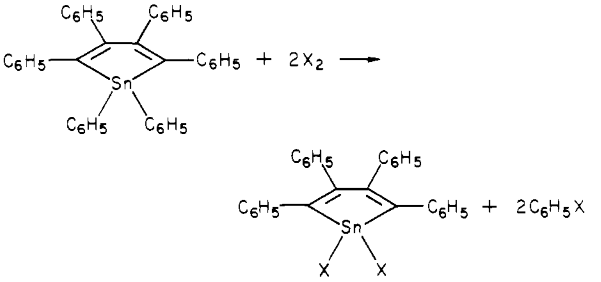
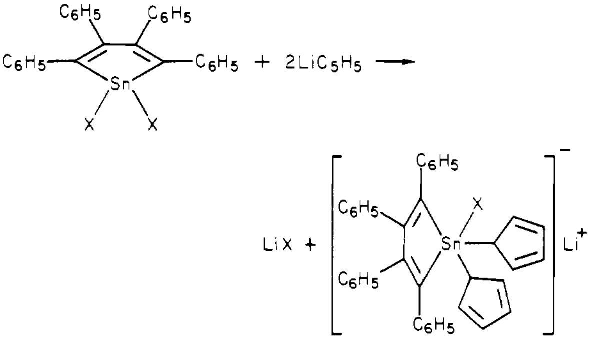
1,1-Dibromo- and 1,1-diiodo-2,3,4,5-tetraphenyl-1-stannacyclopentadiene, dihalotetraphenylstannoles $[XYSnC_4(C_6H_5)_4]$, can be derivatized to form a series of disubstituted products in which X = Y = N_3, *iso*-NCO, *iso*-SCN, $OC(O)CH_3$, $SC(S)N(C_2H_5)_2$, $N(CH_3)_2$, and $P(C_6H_5)_2$. Fluorination by KF in acetone results in the X = F, Y = Br, or Y = I product only, and lithioamination by $LiN[Si(CH_3)_3]_2$ yields the X = $N[Si(CH_3)_3]_2$, Y = Br product only. Attempted synthesis of the dihalostannoles by halogenation of the intermediate tin(II) stannole from 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene and tin(II) chloride yields only the ring-opened products (4-bromo-1,2,3,4-tetraphenylbutadienyl)tin tribromide or (4-iodo-1,2,3,4-tetraphenylbutadienyl)tin triiodide. Even gentle chlorination of hexaphenylstannole by elemental chlorine cleaves the ring tin–carbon bonds to form *cis,cis*-1,4-dichloro-1,2,3,4-tetraphenyl-1,3-butadiene and diphenyltin(IV) dichloride, while the action of a glacial acetic acid–acetic anhydride mixture yields tetraphenylfuran and diphenyltin(IV) diacetate. The dihalostannoles form neutral adducts with pyridine, 2,2′-bipyridyl, and 1,10-phenanthroline and the double salt $[XSnC_4(C_6H_5)_4 \cdot terpy]^+[X_2YSnC_4(C_6H_5)_4]^-$ from 2,2′,2″-terpyridine where X = Y = Br, I = F, and Y = I. The structures of the substituted stannoles and the adducts of the dihalostannoles are discussed on the basis of tin-119m Mössbauer and infrared spectroscopic evidence.

In part 1 of this series we described the synthesis of the 1,1-dihalostannoles by phenyltin bond cleavage of hexaphenylstannole[2–4] by the action of elemental bromine or iodine under controlled conditions[1] (eq 1).



(1)

The availability of 1,1-dihalostannoles by a convenient synthesis in high yield opens up the derivative chemistry of the stannole ring system for exploitation. Comparisons of the 1,1-disubstituted stannoles and their donor–acceptor adducts can be drawn with the analogous diorganotin(IV) derivatives and complexes whose number is vast.[5–7] The stannole ring system is a special case, however, in that the carbon–tin–carbon bond vectors are constrained to the interior angles of the five-membered ring heterocycle, and so adducts of the formula $R_2SnX_2 \cdot 2L$ which adopt *trans*-diorganotin(IV) preferentially will in the stannole series be forced into other structural forms. The unsaturated butadienoid residue of the stannacyclopentadiene will exert an electrical effect of unknown direction and power on the chemistry of the tin atom. In addition, the tetraphenyl substitution pattern and the presumably planar nature of the stannacyclopentadiene stannole ring will have a steric influence on the reactions of the stannoles and the properties of the subsequent products. The formation of the lithium 1,1-bis(η^1-cyclopentadienyl)-1-halo-2,3,4,5-tetraphenylstannole salt (eq 2), a five-coordinated tin(IV) heterocycle with pseudo-rotating axial- and equatorial-fluxional η^1-cyclopentadienyl groups in a unique $[R_4SnX]^-$ anion described in part 1 of this series,[1] is a result of the simultaneous influences.[8]



(2)

In this paper we report the syntheses of the 1,1-disubstituted stannoles and the adducts of the stannole dihalides. For convenience, stannole each time it is used is meant to mean the 1,1-disubstituted-2,3,4,5-tetraphenylstannole derivative.

Experimental Section

Organotin starting materials were of commercial grade and were used without further purification. Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Boiling points were determined at constant pressure with a still-head thermometer and are uncorrected. Gas chromatographic analyses were performed on a Hewlett-Packard Model 5750 laboratory

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(1) For part 1 of this series see: Gustavson, W. A.; Principe, L. M.; Rhee, W.-Z. Min; Zuckerman, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 4126.

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(7) Sawyer, A. K. "Organotin Compounds"; Marcel Dekker: New York, 1972; Vol. 1–3.

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