atmosphere. After the solution was stirred for 5 h, the solvent was removed in vacuo to give a white solid.

Reaction with PtOOH. (diphoe)Pt(CF_3)($CO^{18}OH$) (0.050 g, 0.071 mmol) and (diphoe)Pt(CF_3)(OOH) (0.049 g, 0.071 mmol) were placed as the solids in a Schlenk tube bearing a screw-capped silicone septum. The system was evacuated and filled with N_2. Dry, N_2-saturated, chilled THF (10 mL) was added and the reaction mixture stirred for 2 h. The gas phase was then sampled with a gastight syringe and the sample injected into a GC-MS system.

Reactions with H_2O_2. Reactions of (diphoe)Pt(Me)(COOH), (dppe)Pt(Ph)(COOH), (diphoe)Pt(CF_3)(COOH), (dppe)Pt(CF_3)(COOH), (dppp)Pt(CF_3)(COOH), *trans*-$(PPh_3)_2$Pt(CF_3)(COOH), *trans*-$(PPh_2Me)_2$Pt(CF_3)(COOH), (diphoe)Pt(CF_3)(COOMe), (dppe)Pt(CF_3)(COOMe), (dppp)Pt(CF_3)(COOMe), $(diphoe)_2Pt_2(CF_3)_2(\mu\text{-}CO_2)$, and $(dppe)_2Pt_2(CF_3)_2(\mu\text{-}CO_2)$ with H_2O_2 were carried out, according to the general procedure described here, in a round-bottomed flask equipped with two stopcocks for gas inlet and outlet, a side arm fitted with a screw-capped silicone septum to allow sampling, and an external jacket connected to the external circulation of a thermostat; stirring was performed with a Teflon-coated bar driven externally by a magnetic stirrer.

In the reactor 0.1 mmol of complex was suspended in 15 mL of dry THF. The system was degassed, N_2-saturated, and thermostated at 0 °C. To the stirred mixture was added 100 μL of H_2O_2 (34% or 72%), and the reaction was carried out for 20 h. The presence of CO_2 in the gas phase was determined by flushing the reaction vessel with N_2 and bubbling the gas through a water solution containing $Ba(OH)_2$. The weight of $BaCO_3$, which can be recovered by filtration, gave a semiquantitative estimate of the CO_2 evolved. The reaction mixture was then concentrated, and addition of Et_2O yielded a solid, which was filtered and analyzed.

Catalytic Reactions. The catalytic reactions were carried out in the same reactors described above according to the following procedure with either (diphoe)Pt(CF_3)(OH) or (dppe)Pt(CF_3)(OH) as catalyst and either 1-octene or cyclohexene as substrate.

A 0.05-mmol amount of the complex was dissolved in 3 mL of dry THF. The system was degassed by several freeze and thaw cycles, saturated with CO admitted from a gas reservoir (~1 L) connected to the system, and thermostated at the required temperature (either −25 or −10 °C). Through the septum was added 50 μL of 72% H_2O_2 and 1 mL of olefin. The mixture was stirred for up to 5 days and sampled periodically. The liquid phase was analyzed with a 30-m HP-5 capillary column, while the gas phase was analyzed with a 3-m Porapak Q packed column. At the end of the reaction the solution was concentrated and addition of Et_2O yielded a solid, which was filtered and analyzed.

Acknowledgment. This work was supported jointly by the European Economic Community (Brussels, Belgium) and Degussa AG (Frankfurt, Germany) through the special program BRITE. Degussa AG also provided a free sample of 72% H_2O_2. Special thanks are expressed to Drs. G. Goor and M. Schmidt (Degussa AG), to Professor W. Drenth (University of Utrecht), and to Professor J. W. Buchler (University of Darmstadt) for stimulating discussions. Dr. R. Bertani (CNR, Padua, Italy) is gratefully acknowledged for running the ^{13}C NMR spectra.

Direct Evidence for the Formation of a Disiladiferracyclic Compound through Dimerization of an Iron–Silylene Intermediate

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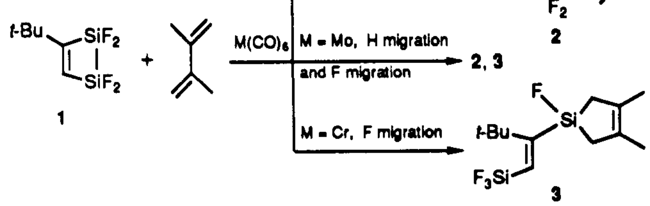
Received May 3, 1990

In the reaction between tetrafluorodisilacyclobutene (1) and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, a metal-mediated intramolecular fluorine migration results in an Fe–silylene intermediate that rapidly dimerizes to a disiladiferracyclic compound (6). The structure of 6 is determined by spectroscopies in solution and X-ray diffraction of a single crystal. The Fe–silylene intermediate can be stabilized (in the form of 7) by weak donor solvents such as tetrahydrofuran (THF), acetonitrile, and hexamethylphosphoric triamide (HMPT).

Recently we proposed that during cycloaddition reactions between tetrafluorodisilacyclobutene (1) and conjugated dienes mediated by metal carbonyls,[1-3] a η^3-allyl–η^3-silaallyl complex intermediate might facilitate either hydride or fluorine migration depending on the hardness of the central metal. For example, the cycloaddition between 1 and 2,3-dimethylbuta-1,3-diene mediated by group 6 metal carbonyls resulted in the product from H migration (2) or F migration (3) according to the hardness of the metal (Cr > Mo > W) (eq 1).



(1)

If one tunes the hardness of the metal horizontally across the periodic table, the harder Mn would facilitate F mi-

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(1) Lee, C. Y.; Lin, C. H.; Liu, C. S. *Organometallics* **1987**, *6*, 1878.
(2) Lin, C. H.; Lee, C. Y.; Liu, C. S. *Organometallics* **1987**, *6*, 1861.
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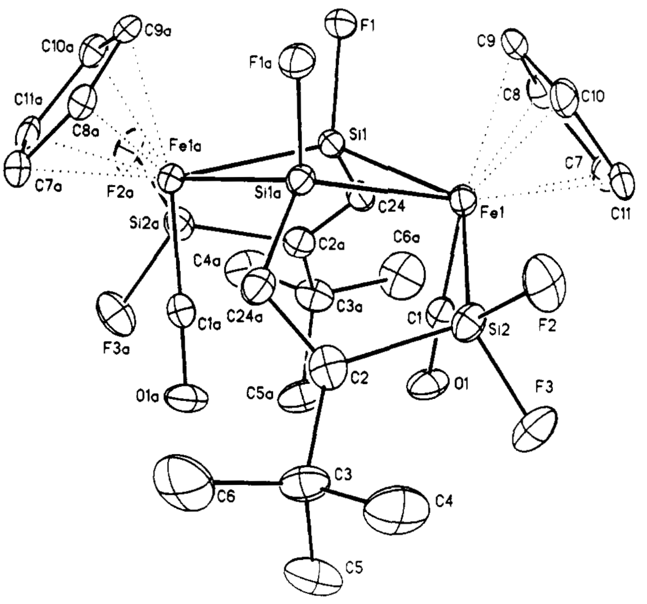
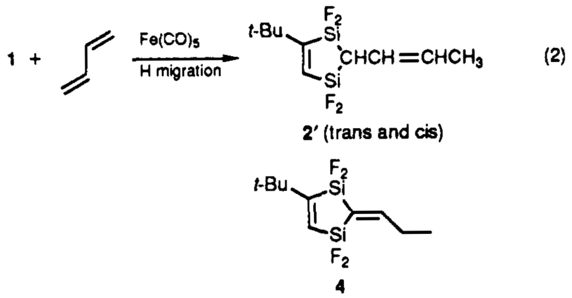


Figure 1. ORTEP drawing of the molecule of compound **6**. The molecule has a 2-fold rotational symmetry in its center.

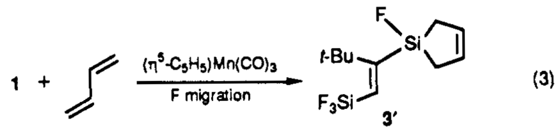
gration whereas the softer Fe would assist H migration only[1,2] (eqs 2 and 3).



(2)

2' (trans and cis)

4



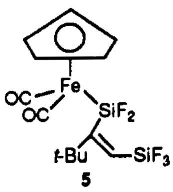
3'

(3)

In this paper, we report another way to fine-tune the hardness of the metal by changing the formal oxidation state of the metal. For example, the use of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ instead of $Fe(CO)_5$ would change the formal oxidation state of iron from Fe(0) to Fe(I).

Results and Discussion

When $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ is reacted with **1**, F migration does occur, as is evident from the observation of product **5**.



5

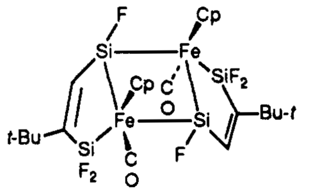
Compound **5** shows in its $^{19}F\{^1H\}$ NMR spectrum the typical triplet (137.47 ppm) and quartet (89.49 ppm), and its structure is confirmed by elemental analysis and its mass and ^1H, ^{29}Si, and ^{13}C NMR spectra. The position of the *tert*-butyl group is shown by the $^{13}C\{^1H\}_{cw}$ NMR spectrum, which shows that $=CSiF_3$ has a hydrogen atom attached to the carbon. This is also supported by a comparison of the H–F coupling constants between J_{H,SiF_3} (4.4 Hz) and J_{H,SiF_2} (1.5 Hz).

Table I. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³)

	x	y	z	U(eq)[a]
Fe(1)	−279 (1)	908 (1)	3796 (1)	36 (1)
Fe(2)	1331 (1)	2582 (1)	7753 (1)	33 (1)
Si(1)	840 (1)	1049 (1)	2624 (1)	35 (1)
Si(2)	−1669 (1)	511 (1)	3807 (1)	47 (1)
Si(3)	1371 (1)	2955 (1)	9137 (1)	42 (1)
Si(4)	110 (1)	2450 (1)	6675 (1)	34 (1)
F(1)	1159 (3)	1627 (1)	2674 (2)	49 (1)
F(2)	−2439 (3)	810 (2)	4336 (3)	76 (2)
F(3)	−1617 (3)	19 (2)	4405 (3)	76 (2)
F(4)	1874 (3)	2623 (2)	9893 (3)	69 (2)
F(5)	161 (3)	1880 (1)	6352 (2)	49 (1)
F(6)	2038 (3)	3422 (2)	9131 (3)	71 (2)
O(1)	328 (4)	−105 (2)	3583 (3)	63 (2)
O(2)	1149 (4)	3600 (2)	7196 (4)	73 (2)
C(1)	97 (5)	299 (3)	3659 (4)	41 (3)
C(2)	−2179 (5)	369 (3)	2690 (5)	43 (3)
C(3)	−2914 (6)	−29 (3)	2515 (6)	59 (3)
C(4)	−3668 (7)	11 (4)	3220 (9)	91 (5)
C(5)	−2459 (8)	−537 (3)	2592 (9)	88 (4)
C(6)	−3342 (7)	36 (5)	1594 (9)	105 (6)
C(7)	302 (6)	998 (3)	5092 (5)	51 (3)
C(8)	643 (6)	1355 (3)	4498 (5)	48 (3)
C(9)	−94 (7)	1650 (3)	4187 (5)	51 (3)
C(10)	−883 (6)	1470 (3)	4569 (5)	50 (3)
C(11)	−638 (6)	1062 (3)	5131 (5)	48 (3)
C(12)	1205 (5)	3192 (3)	7407 (5)	44 (3)
C(13)	−386 (5)	2842 (3)	9319 (5)	44 (3)
C(14)	257 (5)	3130 (2)	9651 (4)	39 (2)
C(15)	115 (5)	3521 (3)	10380 (4)	46 (3)
C(16)	828 (9)	3470 (5)	11104 (7)	97 (5)
C(17)	236 (8)	4027 (4)	9931 (8)	90 (5)
C(18)	−836 (8)	3497 (4)	10783 (8)	92 (5)
C(19)	2002 (5)	2130 (3)	6812 (5)	46 (3)
C(20)	1685 (5)	1837 (3)	7533 (6)	48 (3)
C(21)	2117 (5)	2009 (3)	8319 (5)	49 (3)
C(22)	2695 (5)	2412 (3)	8079 (6)	53 (3)
C(23)	2625 (5)	2484 (3)	7143 (5)	48 (3)
C(24)	1849 (5)	671 (3)	2926 (5)	46 (3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

It is interesting to note that there is another product (**6**) formed in addition to **5**. The mass spectrum of **6** suggests a molecular formula of $C_{24}H_{30}O_2Si_4F_6Fe_2$. The $^{19}F\{^1H\}$ NMR spectrum shows two resonances in the typical region of fluorosilyl attached to metals at 86.10/81.23 ppm (AX pattern, $^2J_{F,F}$=36Hz) and 114.09 ppm (singlet), respectively, with an intensity ratio of 2:1. The ^1H and ^{13}C NMR spectra also fit the structure of **6**.



6

Since compound **6** can be recrystallized in methylcyclohexane solution, a single-crystal X-ray diffraction experiment also confirms the structure (Figure 1).

The main feature of the structure of **6** is a four-membered diferradisilacycle fused with two five-membered disilametallacycles. The two Fe and two Si atoms involved in the four-membered ring are approximately coplanar. These three rings are fused in a "boat" conformation so the molecule has a 2-fold rotational symmetry in its center. The vertical planes along the diagonals of the four-membered ring cut the molecules into two symmetric parts.

Table II. Summary of Crystal Data and Intensity Collection

empirical formula	$C_{24}H_{30}O_2F_6Si_4Fe_2$
color; habit	yellow; chunk
cryst size, mm	0.50 × 0.50 × 0.46
cryst system	orthorhombic
space group	*Pbcn*
unit cell dimens	a = 14.624 (4) Å b = 27.028 (6) Å c = 14.868 (5) Å
vol, $Å^3$	5877 (5)
Z	8
formula wt	688.5
density (calcd), mg/m^3	1.556
abs coeff, mm^{-1}	1.205
$F(000)$	2816
diffractometer used	Nicolet R3m/V
radiation	Mo Kα (λ = 0.71073 Å)
temp, K	297
monochromator	highly oriented graphite crystal
2θ range, deg	2.0–50.0
scan type	$\theta/2\theta$
scan speed, deg/min	variable; 4.19–14.65 in ω
scan range (ω), deg	0.90 plus Kα separation
background measurement	stationary crystal and stationary counter at beginning and end of scan, each for 50.0% of total scan time
std reflns	3 measd every 50 reflns
index ranges	$0 \le h \le 16$, $0 \le k \le 30$, $-17 \le l \le 0$
independent reflns	4457 (2268 > $3.0\sigma(I)$)
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0002F^2$
final R indices (obsd data)	R = 3.85%, wR = 3.40%
goodness of fit	1.21
largest and mean Δ/σ	0.483, 0.006
data-to-param ratio	5.2:1
largest diff peak, e $Å^{-3}$	0.36
largest diff hole, e $Å^{-3}$	−0.33

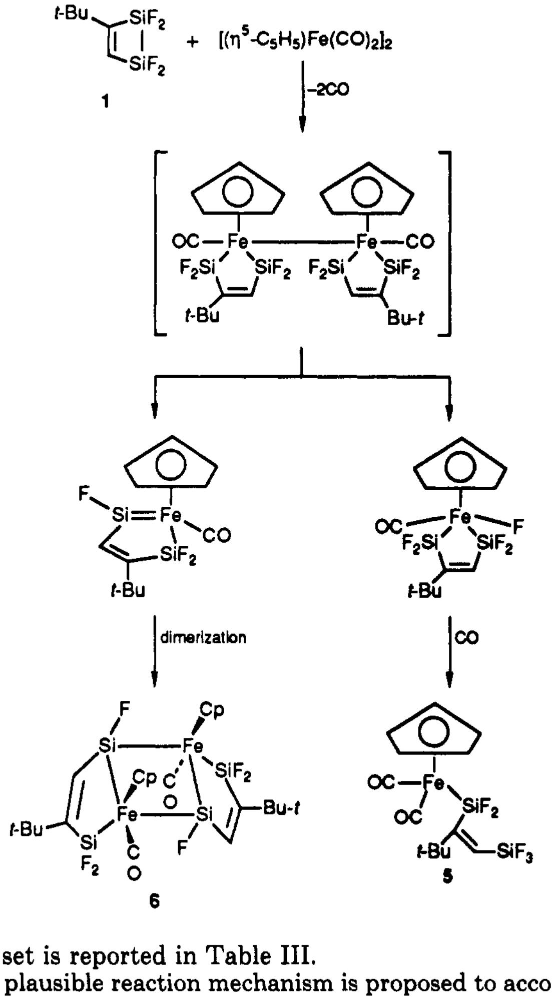
Each Fe atom can be considered to be in a distorted tetragonal-pyramidal geometry, with an apical cyclopentadienyl ring, and three Si and one carbonyl form the tetragonal base. It is interesting to note that the bond distances of all four Fe–Si bonds involved in the five-membered disilametallacycles are normal (2.296 Å) as compared with the reported values for the iron–fluorosilane compounds, i.e., 2.29–2.32 Å.[4,5] However, the two Fe–Si bonds linking the two symmetric parts of the molecule are substantially longer (2.420 Å).

Structural studies of a number of compounds $M_2L_nL'_m(SiR_2)_2$ containing the M_2Si_2 four-membered ring[6,7] (M = Pt, Ru, Mn, Re, W, Ti; L, L′ = phosphines, carbonyls, hydrides) indicate that $(PEt_3)_4Pt_2(SiPhCl)_2$ has the shortest Si–Si distance of 2.602 Å, only 0.25 Å longer than the single bond value of 2.35 Å. An analysis based on molecular orbital theory indicates considerable bonding interaction between the two silicon atoms.[7] It has also been predicted that a compound containing the Fe_2Si_2 unit would have a long Fe–Fe distance and a short Si–Si distance.[7] Indeed, the present case of 6 shows a very long Fe–Fe distance (3.939 Å) and a very short Si–Si distance (2.483 Å, only 0.13 Å longer than the Si–Si bond length).

Table III. Selected Bond Lengths and Bond Angles

Fe(1)–Si(1)	2.421 (3)	Fe(1)–Si(2)	2.297 (3)
Fe(1)–C(1)	1.749 (7)	Fe(1)–C(7)	2.120 (7)
Fe(1)–C(8)	2.090 (8)	Fe(1)–C(9)	2.105 (7)
Fe(1)–C(10)	2.099 (8)	Fe(1)–C(11)	2.095 (7)
Fe(1)–Si(1A)	2.296 (2)	Si(1)–C(24)	1.852 (8)
Si(1)–F(1)	1.631 (4)	Si(1)–Si(1A)	2.483 (4)
Si(1)–Fe(1A)	2.296 (2)	Si(2)–F(3)	1.603 (5)
Si(2)–F(2)	1.594 (5)	C(2)–C(24A)	1.317 (10)
Si(2)–C(2)	1.861 (7)	C(3)–C(5)	1.530 (12)
O(1)–C(1)	1.147 (8)	C(7)–C(8)	1.401 (11)
C(2)–C(3)	1.541 (10)	C(8)–C(9)	1.417 (12)
C(3)–C(4)	1.526 (14)	C(10)–C(11)	1.429 (11)
C(3)–C(6)	1.516 (16)	C(9)–C(10)	1.374 (12)
C(7)–C(11)	1.389 (12)		
Si(1)–Fe(1)–Si(2)	132.6 (1)	Si(1)–Fe(1)–C(1)	81.6 (2)
Si(2)–Fe(1)–C(1)	80.8 (2)	Si(2)–Fe(1)–Si(1a)	76.6 (1)
Si(1)–Fe(1)–Si(1A)	63.5 (1)	Fe(1)–Si(1)–C(24)	106.1 (3)
C(1)–Fe(1)–Si(1A)	99.3 (2)	Fe(1)–Si(1)–Fe(1A)	113.2 (1)
Fe(1)–Si(1)–F(1)	108.1 (2)	C(24)–Si(1)–Fe(1A)	114.5 (3)
F(1)–Si(1)–C(24)	106.8 (3)	Fe(1)–Si(2)–C(2)	116.4 (2)
F(2)–Si(2)–F(3)	100.4 (3)	Fe(1)–C(1)–O(1)	178.3 (6)
Si(1)–C(24)–C(2A)	117.8 (6)	Si(2)–C(2)–C(24A)	110.2 (5)
C(3)–C(2)–C(24A)	124.7 (7)	F(1)–Si(1)–Fe(1A)	107.7 (2)
		Si(2)–C(2)–C(3)	125.1 (5)

Scheme I



Detailed structural parameters of compound 6 are listed in Tables I–III. It should be noted that there are two independent half molecules in the unit cell of 6 that give rise to two independent molecules. The bond lengths and angles in these two molecules are slightly different. Only one set is reported in Table III.

A plausible reaction mechanism is proposed to account for the formation of compounds 5 and 6 (Scheme I). After the oxidative addition of 1, F migration accompanied by the cleavage of the Fe–Fe bond would lead to 5 and a Fe-silylene complex, which rapidly dimerizes to form compound 6.

When the reaction is followed by ^{19}F NMR spectroscopy, it is found that compounds 5 and 6 keep a constant ratio of 2:1 throughout the reaction. The observations seems

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(4) Hseu, T. H.; Lin, C. H.; Lee, C. Y.; Liu, C. S. *J. Chin. Chem. Soc.* **1989**, *36*, 91.

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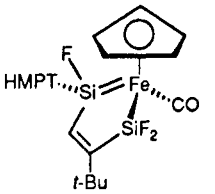
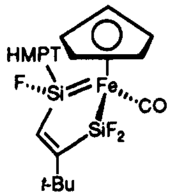
to agree with the reaction mechanism proposed in Scheme I.

Compared with the well-established chemistry of germylene and stannylene complexes, the chemistry of silylene complexes is rare.[8] Nonetheless, transition-metal–silylene complexes have been proposed as reaction intermediates to account for a number of chemical transformations of organosilicon compounds mediated by metals.[9-12] Recently there have been several reports on the stabilization of such metal–silylene complexes by weak donor solvents.[13-16]

When the reaction was carried out in 10% HMPT (hexamethylphosphoric triamide)/benzene solution, the $^{19}F\{^1H\}$ NMR spectrum showed that the resonance of **5** remained the same, whereas the spectrum of **6** disappeared completely. Instead, two sets of new resonances for SiF_2 (87.49 and 87.65 ppm, in the ratio ~5:1) and SiF (98.94 and 95.23 ppm, in the ratio ~5:1) showed up. The former two are of AB pattern with long-range F–F couplings, whereas the latter two are doublets of doublets of doublets, which involved two long-range F–F couplings and a P–F coupling. It is quite certain that HMPT was involved in the stabilization of an Fe-silylene complex in the form of **7a** and **7b**, two isomers differing in the relative orientation of the coordinated HMPT. Considering the relative steric interactions, **7a** is tentatively assigned to the more abundant isomer.



7a



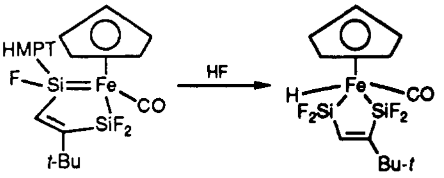
7b

The possibility that these spectral changes from **6** to **7a**/**7b** were due to solvent effects was ruled out because the chemical shifts (in both ^{19}F and ^{29}Si NMR) of **5** change very little even in 20% $HMPT/C_6D_6$ solution.

A doublet at δ 116.32 and triplet at δ 68.96 were shown in the ^{29}Si NMR spectrum of **7a**/**7b**. They are assigned to the SiF and SiF_2 groups, respectively. ^{29}Si NMR data for (fluorosilyl)iron compounds are rare in the literature. The reported chemical shifts are in an approximate range of δ 45–70.[17] Since no significant solvent effect is found in the present system, the downfield shift to δ 116.32 for the SiF group may reflect the change from a normal silyl ligand to a silylene group. However, chemical shifts reported so far for donor-stabilized silylene complexes are found to be quite dependent on the nature of the substituents.[16b] Unfortunately, no literature data of iron–fluorosilylene compounds are available for comparison.

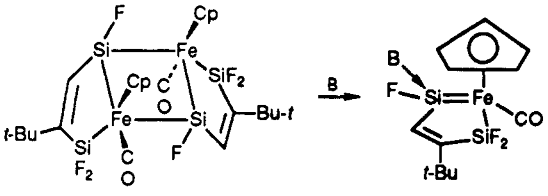
The ^1H NMR spectrum also showed two sets of spectra (in intensity ratio ~5:1) for all proton signals. In addition to the resonance of bulk HMPT (δ 2.72), we observed the resonances for coordinated HMPT at δ 2.23 (for **7a**) and 2.17 (for **7b**), respectively. This observation is also in agreement with the existence of two HMPT-stabilized Fe-silylene isomers, in the ratio approximately 5:1.

When a trace amount of HF was added to the solution of **7a**/**7b**, iron hydride **8** was obtained, which could be considered to be the result of the addition of HF to the Fe=Si double bond.



7a/7b **8**

It is interesting to note that **7a**/**7b** and their analogues with different donors can be prepared by adding donor solvents such as tetrahydrofuran (THF), acetonitrile, and HMPT to the benzene solution of **6**. For example, when a small amount of HMPT was added to the benzene solution of **6**, we observed in the ^{19}F NMR a gradual decrease of the resonances of **6** accompanied by an increase of the resonances of **7a**/**7b**, until the conversion of **6** to **7a**/**7b** was complete.

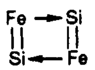


6

B = THF, HMPT, CH_3CN

Although the equilibria between the dimeric complexes $[(CO)_4FeMY_2]_2$ containing a symmetrical four-membered ring system (with M = Ge, Sn, Pb and Y = halogens) and the base-stabilized ylide complexes are known,[8] the conversion of the disiladiferracycle to a monomeric Fe–silylene complex by a donor solvent is unprecedented in the literature. The present case may be due to the fact that in the disiladiferracycle **6**, the two Fe–Si bonds that link the symmetric parts of the dimer (2.420 Å) are longer than the other two Fe–Si bonds (2.296 Å) by more than 0.1 Å.

The very short cross-ring Si–Si distance of **6** may have some influence on the orbital hybridization of the silicon atoms, which facilitates the addition of a base molecule that then helps to cleave compound **6** into two molecules of **7**. Also, the long–short alternating Fe–Si bonds in the Fe_2Si_2 core may reflect the contribution of the resonance structure



The contribution of such a resonance structure would also explain the ready cleavage of **6** by base molecules. However, such an idea should not be overemphasized because the shorter Fe–Si bonds in this Fe_2Si_2 unit have the

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normal value of the Fe–Si bond length (2.296 Å).

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 the JEOL JMX-100 spectrometer operating at 99.55, 93.65, 25.0, and 19.0 MHz for ^{1}H, ^{19}F, ^{13}C, and ^{29}Si spectra, respectively, and a Bruker AM 400 spectrometer operating at 400.0, 376.5, and 100.0 MHz for ^{1}H, ^{19}F, and ^{13}C spectra, respectively. Chemical shifts of ^{1}H, ^{29}Si, and ^{13}C were measured in δ values; ^{19}F chemical shifts were measured in parts per million upfield from internal standard CCl_3F (C_6D_6 was the solvent for all NMR data). For the ^{13}C data listed below, the spectral multiplicity following each chemical shift is due to the coupling with heteronuclei, whereas the coupling patterns in $^{13}C\{^{1}H\}_{cw}$ are included in parentheses.

Preparation of 3-*tert*-Butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobutene (1). Compound **1** was prepared by the cocondensation reaction between 3,3-dimethylbut-1-yne and difluorosilylene. The preparation procedures and structure identification were reported previously.[18]

Preparation of (η^5-C_5H_5)(CO)$_2$FeSiF$_2$C(*t*-Bu)=CHSiF$_3$ (5) and [(η^5-C_5H_5)(CO)FeSiF$_2$C(*t*-Bu)=CHSiF]$_2$ (6). **1** (0.4 g, 1.82 mmol) and 0.5 g (1.41 mmol) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ were added to 12 mL of dried and degassed *n*-heptane in a reaction tube under vacuum. The reaction mixture was heated at 85 °C for 24 h. The deep-red solution turned to pale yellow and crystals appeared. Compound **6**, formed as yellowish crystals, was obtained by filtration under Ar atmosphere at 0 °C. The filtered solution was subjected to removal of solvent and vacuum distillation at 90 °C. Compound **5** was obtained as a colorless liquid. Based on the quantity of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ used, the yields of **5** and **6** were 60% and 30%, respectively. Anal. Calcd for **5**: C, 38.05; H, 3.66; F, 23.17. Found: C, 38.65; H, 3.90; F, 23.04. MS of **5**: *m/e* 410 (M^+, $C_{13}H_{15}O_2Si_2F_5Fe^+$), 382 ($C_{12}H_{15}OSi_2F_5Fe^+$), 354 ($C_{11}H_{15}Si_2F_5Fe^+$), 299 ($C_{11}H_{16}Si_2F_5^+$), 57 ($C_4H_9^+$). ^{1}H NMR of **5**: δ 1.23 (s, 9 H, *t*-Bu), 4.15 (s, 5 H, C_5H_5), 7.18 (q, t, 1 H, =CHSiF$_3$). $^{19}F\{^{1}H\}$ NMR of **5**: 89.49 (q, SiF$_2$, $^{5}J_{F,F}$ = 1 Hz), 137.47 (t, SiF$_3$). ^{13}C NMR of **5**: δ 30.60 (s(q), C(*C*H$_3$)$_3$), 39.23 (s(s), *C*(CH$_3$)$_3$), 84.17 (s(d), *C*$_5$H$_5$), 118.59 (q,(d,q), =*C*HSiF$_3$), 187.56 (t(t), =*C*(*t*-Bu)SiF$_2$), 212.53 (s(s), *C*O). ^{29}Si NMR of **5**: δ 54.27 (t, SiF$_2$, $J_{Si,F}$ = 376 Hz), −75.37 (q, SiF$_3$, $J_{Si,F}$ = 260 Hz). Anal. Calcd for **6**: C, 41.86; H, 4.36; F, 16.57. Found: C, 41.55; H, 4.70; F, 16.50. MS of **6**: *m/e* 688 (M^+, $C_{24}H_{30}O_2Si_4F_6Fe_2^+$), 660 ($C_{23}H_{30}OSi_4F_6Fe_2^+$), 632 ($C_{22}H_{30}Si_4F_6Fe_2^+$). ^{1}H NMR of **6**: δ 1.37 (s, 9 H, *t*-Bu), 4.49 (s, 5 H, C_5H_5), 7.61 (m, 1 H, =CHSiF). $^{19}F\{^{1}H\}$ NMR of **6**: 86.10 and 81.23 (AX, =C(*t*-Bu)SiF$_2$, $^{2}J_{F,F}$ = 36 Hz), 114.09 (s, =CHSiF). ^{13}C NMR of **6**: δ 29.62 (s(q), C(*C*H$_3$)$_3$), 37.84 (s(s), *C*(CH$_3$)$_3$), 85.2 (s(d), C$_5$H$_5$), 153.85 (d(d,d), =CHSiF), 179.41 (t(t), =C(*t*-Bu)SiF$_2$), 208.20 (s(s), CO). $^{29}Si\{^{1}H\}$ NMR of **6**: δ 89.74 (d, SiF, $J_{Si,F}$ = 390.6 Hz), 49.44 (t, SiF$_2$, $J_{Si,F}$ = 376.0 Hz).

Preparation of (η^5-C_5H_5)(CO)Fe=SiF(HMPT)—CH=C(*t*-Bu)SiF$_2$ (7a/7b). Compounds **7a/7b** were prepared by reacting 100 mg (0.15 mmol) of **6** and 30 mg of HMPT in 3 mL of benzene solution at room temperature. The reaction was quantitative, but **7a** and **7b** could not be isolated. On removal of solvent, **7a/7b** were converted to unidentified compounds. ^{1}H NMR of **7a**: δ 1.50 (s, 9 H, *t*-Bu), 2.23 (d, 18H, N(CH$_3$)$_2$ of HMPT, $J_{H,P}$ = 10 Hz), 4.63 (s, 5 H, C_5H_5), 7.05 (t, d, 1 H, =CHSiF). $^{19}F\{^{1}H\}$ NMR of **7a**: 87.49 (AB, with long-range F–F couplings, =C(*t*-Bu)SiF$_2$), 98.94 (d, d, d, =CHSiF, $^{4}J_{F,F}$ = 2.9 Hz, 1.2 Hz, $^{3}J_{F,P}$ = 1.3 Hz). ^{13}C NMR of **7a**: δ 30.81 (s(q), C(*C*H$_3$)$_3$), 36.28 (d(d,q), N(*C*H$_3$)$_2$, $^{2}J_{C,P}$ = 5 Hz), 38.10 (s(s), *C*(CH$_3$)$_3$), 78.01 (s(d), C$_5$H$_5$), 151.09 (d(d,d), =*C*HSiF), 192.76 (t(t), =*C*(*t*-Bu)SiF$_2$), 216.77 (s(s), CO). ^{1}H NMR of **7b**: δ 1.46 (s, 9 H, *t*-Bu), 2.17 (d, 18 H, N(CH$_3$)$_2$ of HMPT, $J_{H,P}$ = 10 Hz), 4.56 (s, 5 H, C_5H_5), 6.95 (t, d, 1 H, =CHSiF). $^{19}F\{^{1}H\}$ NMR of **7b**: 87.65 (AB with long-range F–F couplings, =C(*t*-Bu)SiF$_2$), 95.23 (d, d, d, =CHSiF, $^{4}J_{F,F}$ = 2.7 Hz, 1.2 Hz, $^{3}J_{F,P}$ = 2.7 Hz). ^{13}C NMR of **7b**: δ 30.62 (s(q), C(*C*H$_3$)$_3$), 36.28 (d(d,q), N(*C*H$_3$)$_2$, $^{2}J_{C,P}$ = 5 Hz), 38.10 (s(s), *C*(CH$_3$)$_3$), 77.49 (s(d), C$_5$H$_5$), 150.5 (d,(d,d), =CHSiF), 192.0 (m(m), =C(*t*-Bu)SiF$_2$), 215.78 (s(s), CO). $^{29}Si\{^{1}H\}$ NMR of **7a/7b**: δ 116.32 (d, SiF, $J_{Si,F}$ = 428.8 Hz), 68.96 (t, SiF$_2$, $J_{Si,F}$ = 358.7 Hz).

Preparation of (η^5-C_5H_5)(CO)(H)FeSiF$_2$C(*t*-Bu)=CHSiF$_2$ (8). Ten milliliters of 10% HMPT/benzene solution containing approximately 0.1 mmol of **7a/7b** was added with 0.1 mmol of dry HF in a quartz tube. After the tube was shaken for 30 min, the reaction mixture was subjected to concentration and distillation under vacuum; about 0.054 mmol of compound **8** was obtained with a yield of 54%. MS of **8**: 364 (M^+, $C_{12}H_{16}OSi_2F_4Fe^+$), 336 ($C_{11}H_{16}Si_2F_4Fe^+$), 280 ($C_{11}H_{16}Si_2F_4^+$), 270 ($C_6H_{10}Si_2F_4Fe^+$), 215 ($C_6H_{11}Si_2F_4^+$), 150 ($C_6H_6OFe^+$), 122 ($C_5H_6Fe^+$), 66 ($C_5H_6^+$), 57 ($C_4H_9^+$). ^{1}H NMR of **8**: δ −12.0 (m, 1 H, FeH), 1.33 (s, 9 H, *t*-Bu), 4.30 (s, 5 H, C_5H_5), 7.18 (m, 1 H, =CHSiF$_2$). $^{19}F\{^{1}H\}$ NMR of **8**: 84.81 (AB, =CHSiF$_2$), 93.40 (AX, =C(*t*-Bu)SiF$_2$). ^{13}C NMR of **8**: δ 30.23 (s(q), C(*C*H$_3$)$_3$), 38.17 (s(s), *C*(CH$_3$)$_3$), 83.23 (s(d), C$_5$H$_5$), 150.40 (t(d,t), =*C*HSiF$_2$), 189.43 (m(m), =C(*t*-Bu)SiF$_2$), 210.52 (s(s), CO). ^{29}Si NMR of **8**: δ 54.85 (t, J_{SiF} = 329.9 Hz), 57.50 (t, $J_{Si,F}$ = 359.8 Hz), two SiF$_2$ groups of **8**.

X-ray Structure Analysis. Single crystals of compound **6** were selected under dry argon atmosphere and sealed into Lindemann glass capillaries. A yellow crystal of approximate dimensions 0.50 × 0.50 × 0.46 mm was mounted on a Nicolet R3m/V diffractometer equipped with a graphite monochromator (Mo Kα radiation). Unit cell constants were determined from a least-squares fit to the automatically centered settings for 19 reflections with $14.2 \le 2\theta \le 26.4°$. Details of crystal data and intensity collection are listed in Table II.

The space group *Pbcn* was determined from the systematic absences: $0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; and $0kl$, $k + 1 = 2n + 1$. $\theta/2\theta$ scan data were collected at room temperature (24 °C). The data were corrected for a decay of 6% intensity (during 56 h of data collection time) and Lorentz and polarization effects.

The structure was solved by a direct method using SHELXTL PLUS.[19] Full-matrix least-squares refinement based on F with anomalous–dispersion corrections for atoms with atomic numbers greater than 16 was used. Neutral-atom-scattering form factors were taken from *International Tables for X-ray Crystallography*.[20] The weight had the form $w = [\sigma^2(F) + gF^2]^{-1}$ with g = 0.0002. All of the non-hydrogen atoms were obtained from E maps and refined anisotropically. All of the hydrogen atoms except one could be located on a E map, and their positional parameters were refined with a fixed U of 0.08 A^2. Final agreement factors are R = 0.0385, R_w = 0.0340, and GOF = 1.21. The final difference map was featureless with ρ_{max} = 0.36 e Å^{-3}. All calculations were performed on a MicroVAX II based Nicolet SHELXTL PLUS system.

Acknowledgment. The financial support of this work by the National Science Council is gratefully acknowledged. K.M.H. Thanks China Petroleum Co. for a postgraduate followship.

Supplementary Material Available: Tables of anisotropic thermal parameters and hydrogen coordinates (2 pages); tables of calculated and observed structure factors (16 pages). Ordering information is given on any current masthead page.

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