Preparation of Silanediyl-Bridged Fe–Fe and Fe–W Dinuclear Complexes.
X-Ray Structures of [$Cp^*Fe(CO)(\mu\text{-}CO)\{\mu\text{-}Si(H)CHPh_2\}(CO)_nMCp$] ($Cp^* = C_5Me_5$, $Cp = C_5H_5$, $M = Fe, n = 1; M = W, n = 2$)

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Photolysis of a 2 : 1 mixture of [$Cp^*Fe(CO)_2Me$] and Ph_2CHSiH_3 produces mainly the mononuclear silyl complex [$Cp^*Fe(CO)_2\{Si(H)_2CHPh_2\}$] (**1**) together with two silanediyl-bridged diiron complexes: *cis*- and *trans*-[$Cp^*{}_2(CO)_2Fe_2(\mu\text{-}CO)\{\mu\text{-}Si(H)CHPh_2\}$] (**2**), and [$\{Cp^*Fe(CO)_2\}_2$]. The *trans*-**2** complex isomerizes to *cis*-**2** photochemically, but no *cis–trans* isomerization occurs thermally below 100 °C. Photolysis of [$CpFe(CO)_2SiMe_3$] or [$CpW(CO)_3Me$] in the presence of **1** produces novel silanediyl-bridged complexes [$Cp^*Fe(CO)(\mu\text{-}CO)\{\mu\text{-}Si(H)CHPh_2\}(CO)_nMCp$] (**3**: M = Fe, *n* = 1; **4**: M = W, *n* = 2) in moderate yields. Complexes **3** and **4** have been characterized by X-ray diffraction analysis. To the best of our knowledge, complex **4** is the first example of a silanediyl-bridged Fe–W complex. The Cp and Cp* rings are mutually *cis* with the dihedral angle of 78.7(2)° in complex **3**, but they are *trans* with the dihedral angle of 13.1(6)° in complex **4**.

Compounds with transition metal–silicon bonds have attracted many researchers since the first example, [$CpFe(CO)_2SiMe_3$] (= $FpSiMe_3$), was reported in 1956.1) There has been remarkable progress over the last few years in the preparation of transition metal complexes containing unsaturated silicon ligands.2) The oxidative addition of Si–H bonds of polyhydrosilane to low-valent metal centers is one of the most important reactions in the formation of transition metal–silicon bonds.3) Many silyl(transition metal) complexes and several complexes with M···H···Si 3-center 2-electron bonds have been prepared.4) Due to the synthetic methods, silanediyl-bridged complexes are homometallic and symmetric in most cases.3,5) Much less effort has been made toward the synthesis and reactivity of heterometallic ones.6) Of these complexes, examples which have been characterized by X-ray diffraction analysis are very rare. We previously have reported the preparation of silanediyl-bridged diiron complexes [$CP_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}SiHR)$] (CP = Cp, R = *t*-Bu, $(CMe_2)_2H$, $CHPh_2$, $CHEt_2$; CP = Cp*, R = *p*-Tol) via the photolytic reaction of [$CPFe(CO)_2SiMe_3$] with $RSiH_3$.7) Herein we would like to report the preparation of a mononuclear silyl complex [$Cp^*Fe(CO)_2\{Si(H)_2CHPh_2\}$] by the photolysis of [$Cp^*Fe(CO)_2Me$] with Ph_2CHSiH_3, application of this complex toward the synthesis of asymmetric silanediyl-bridged Fe–Fe and Fe–W complexes, and the X-ray structural studies on these dinuclear complexes.

Experimental

All manipulations were performed under an atmosphere of prepurified nitrogen with standard Schlenk techniques, and all solvents were distilled from appropriate drying agents.8) Infrared spectra were recorded on a Horiba FT-200 spectrometer. The ^1H NMR spectra were obtained on a Bruker ARX 300 spectrometer, in which chemical shifts were reported in δ values relative to the residual solvent resonance of C_6D_6 (7.15 ppm). The ^{29}Si NMR spectra were obtained on a Bruker ARX 300 spectrometer by using a DEPT pulse sequence. Mass spectra were recorded on a JEOL JMS HX-110 spectrometer. [$Cp^*Fe(CO)_2Me$] (= [Fp^*Me]),9) [$FpSiMe_3$],1) [$CpW(CO)_3Me$],10) and $R_2CHSiH_3$7f) were prepared according to the literature procedures. Other reagents were obtained from commercial sources and used without further purification.

Photolysis of [$Cp^*Fe(CO)_2Me$] with Ph_2CHSiH_3. The mixture of [$Cp^*Fe(CO)_2Me$] (1.84 g, 7.0 mmol) and Ph_2CHSiH_3 (0.772 g, 3.5 mmol) was dissolved in 120 cm^3 of pentane and the solution was irradiated with a 450 W medium-pressure Hg lamp at 10 °C. The pale yellow solution changed to red with liberation of CO and red crystals precipitated during irradiation. After the solution had been irradiated for 30 min, it was filtered by frit and the precipitate was washed with pentane (10 $cm^3 \times 2$) to give 250 mg of red $Fp^*{}_2$ in 18.4% yield. The filtrate and washings were combined and dried under vacuum to afford a red oily residue, which was purified by silica gel flash chromatography with toluene/hexane = 1 : 1 eluent to give, according to the order of appearance, five products: 393 mg of unreacted yellow [Fp^*Me], trace amount of purple *trans*-[$Cp^*{}_2(CO)_2Fe_2(\mu\text{-}CO)\{\mu\text{-}Si(H)CHPh_2\}$] (*trans*-**2**), 1.08 g of yellow [$Cp^*Fe(CO)_2SiH_2CHPh_2$] (**1**) in 41% yield, 36 mg of red [$Fp^*{}_2$] in 2.6% yield, and 143 mg of orange-red *cis*-

[$Cp^*{}_2(CO)_2Fe_2(\mu$-CO)$\{\mu$-Si(H)$CHPh_2\}$] (*cis*-**2**) in 8.0% yield.

Spectroscopic data for **1**: IR (toluene) 2069 (w, ν_{Si-H}), 1986 (vs, ν_{COt}), 1932 cm^{-1} (vs, ν_{COt}); ^{1}H NMR δ = 1.35 (s, 15H, C_5Me_5), 4.14 (t, 1H, J_{HH} = 3.9 Hz, 1H, C*H*), 4.65 (d, J_{HH} = 3.9 Hz, 2H, Si–*H*), 7.05 (t, 2H, *H*para), 7.22 (t, 4H, *H*meta), 7.63 (d, 4H, *H*ortho); ^{13}C NMR δ = 8.9 (C_5Me_5), 45.6 (*C*H), 94.4 (C_5Me$_5$), 125.5, 128.7, 129.2, 145.6 (phenyl region), 216.2 (*C*O); ^{29}Si NMR δ = 27.4. Anal. Calcd for $C_{25}H_{28}FeO_2Si$: C, 67.56; H, 6.35%. Found: C, 67.28; H, 6.51%.

cis-**2**: IR (toluene) 2019 (w, ν_{Si-H}), 1950 (vs, ν_{COt}), 1909 (m, ν_{COt}), 1745 cm^{-1} (s, ν_{COb}); ^{1}H NMR δ = 1.41 (s, 30H, C_5Me_5), 4.67 (d, J_{HH} = 6.5 Hz, 1H, C*H*), 7.07 (t, 2H, *H*para), 7.24 (t, 4H, *H*meta), 7.48 (d, J_{HH} = 6.5 Hz, 1H, Si–*H*), 7.91 (d, 4H, *H*ortho); ^{13}C NMR δ = 10.0 (C_5Me_5), 53.9 (*C*H), 95.4 (C_5Me$_5$), 125.4, 128.7, 129.7, 145.9 (phenyl region), 215.0 (CO_t), 280.6 (CO_b); ^{29}Si NMR δ = 251.6. Mass (FAB, Xe, *m*-nitrobenzyl alcohol matrix) 662 (M$^+$; 25), 634 (M$^+$ − CO; 6), 606 (M$^+$ − 2CO; 24), 495 (M$^+$ − $CHPh_2$; 37), 167 ($CHPh_2$; 100). Anal. Calcd for $C_{36}H_{42}Fe_2O_3Si$: C, 65.27; H, 6.39%. Found: C, 64.84; H, 6.35%.

It was not possible to get pure *trans*-**2** owing to the contamination of **1**, but photolysis of the crude *trans*-**2** in C_6D_6 gave *cis*-**2** cleanly, as was observed by the ^{1}H NMR spectrum.

Photolysis of [$CpFe(CO)_2SiMe_3$] with [$Cp^*Fe(CO)_2SiH_2CHPh_2$]. In an NMR tube, the mixture of [$CpFe(CO)_2SiMe_3$] (50 mg, 0.20 mmol) and **1** (96 mg, 0.20 mmol) was dissolved in 1 cm^3 of degassed C_6D_6 and the solution was irradiated with a 450 W medium-pressure Hg lamp at 10 °C. The reaction was monitored by ^{1}H NMR spectra. After the solution had been irradiated for 20 h, it was purified by silica gel flash chromatography with toluene/hexane = 2 : 1 as eluent to give, according to the order of appearance, three products: 15 mg of unreacted **1**, 13 mg of red $Fp^*{}_2$, and 56.1 mg of red [Cp^*(CO)Fe(μ-CO)$\{\mu$-Si(H)$CHPh_2\}$Fe(CO)Cp] (**3**) in 57% yield.

Spectroscopic data for **3**: IR (toluene) 2038 (w, ν_{Si-H}), 1959 (vs, ν_{COt}), 1921 (m, ν_{COt}), 1763 cm^{-1} (s, ν_{COb}); ^{1}H NMR δ = 1.33 (s, 15H, C_5Me_5), 4.13 (s, 5H, C_5H_5), 4.61 (d, J_{HH} = 6.6 Hz, 1H, C*H*), 7.09 (t, 1H, *H*para), 7.10 (t, 1H, *H*para), 7.24 (t, 2H, *H*meta), 7.25 (t, 2H, *H*meta), 7.38 (d, J_{HH} = 6.6 Hz, 1H, Si–*H*), 7.80 (d, 4H, *H*ortho); ^{13}C NMR δ = 9.5 (C_5Me_5), 52.1 (*C*H), 82.8 (C_5H_5), 95.5 (C_5Me$_5$), 125.3, 125.8, 128.4, 128.6, 128.7, 130.3, 145.0, 145.0 (phenyl region), 212.4, 214.9 (CO_t), 277.6 (CO_b); ^{29}Si NMR δ = 239.8. Mass (FAB, Xe, *m*-nitrobenzyl alcohol matrix) 592 (M$^+$; 22), 564 (M$^+$ − CO; 11), 536 (M$^+$ − 2CO; 48), 508 (M$^+$ − 3CO; 11), 425 (M$^+$ − $CHPh_2$; 24). Anal. Calcd for $C_{31}H_{32}Fe_2O_3Si$: C, 62.86; H, 5.44%. Found: C, 63.15; H, 5.59%.

Photolysis of [$CpW(CO)_3Me$] with [$Cp^*Fe(CO)_2SiH_2CHPh_2$]. The procedures are similar to those of the preparation of [Cp^*(CO)Fe(μ-CO)$\{\mu$-Si(H)$CHPh_2\}$Fe(CO)Cp] (**3**). The mixture of $CpW(CO)_3Me$ (35 mg, 0.10 mmol) and **1** (48 mg, 0.10 mmol) was used. After the solution had been irradiated for 3.5 h, it was purified by silica gel flash chromatography with toluene/hexane = 1 : 1 as eluent to give, according to the order of appearance, three products: 6 mg of unreacted **1**, 6 mg of red $Fp^*{}_2$, and 28.3 mg of red [Cp^*(CO)Fe(μ-CO)$\{\mu$-Si(H)$CHPh_2\}$W(CO)$_2$Cp] (**4**) in 44.2% yield.

Spectroscopic data for **4**: IR (toluene) 2085 (w, ν_{Si-H}), 1940 (m, ν_{COt}), 1921 (vs, ν_{COt}), 1863 (vs, ν_{COt}), 1763 cm^{-1} (s, ν_{COb}); ^{1}H NMR δ = 1.44 (s, 15H, C_5Me_5), 4.07 (d, J_{HH} = 6.8 Hz, 1H, C*H*), 4.45 (s, 5H, C_5H_5), 7.00—7.06 (m, 2H, *H*para), 7.10—7.23 (m, 4H, *H*meta), 7.61 (d, 2H, *H*ortho), 7.66 (d, 2H, *H*ortho), 8.08 (d, J_{HH} = 6.8 Hz, 1H, Si–*H*); ^{13}C NMR δ = 9.3 (C_5Me_5), 54.7 (*C*H), 90.0 (C_5H_5), 97.0 (C_5Me$_5$), 125.5, 126.1, 128.4, 128.8, 129.0, 130.8, 145.0, 145.9 (phenyl region), 215.7 (Fe–CO_t), 222.8, 233.1 (J_{WC} = 150 Hz, W–CO_t), 274.0 (CO_b); ^{29}Si NMR δ = 228.1. Mass (FAB, Xe, *m*-nitrobenzyl alcohol matrix) 748 (M$^+$; 13), 720 (M$^+$ − CO; 6), 692 (M$^+$ − 2CO; 4), 664 (M$^+$ − 3CO; 9), 636 (M$^+$ − 4CO; 5), 581 (M$^+$ − $CHPh_2$; 100). Anal. Calcd for $C_{32}H_{32}FeO_4SiW$: C, 51.36; H, 4.31%. Found: C, 51.09; H, 4.21%.

X-Ray Structure Analysis. The single crystals of **3** and **4** were grown by slow evaporation from benzene/hexane. The single-crystal X-ray diffraction measurements were performed on a Nonius CAD-4 automated diffractometer using graphite-monochromated Mo $K\alpha$ (λ = 0.71069 Å) radiation; 25 high-angle reflections were used in a least-squares fit to obtain accurate cell constants. Diffraction intensities were collected up to $2\theta < 50°$ using the $\theta/2\theta$ scan technique, with background counts made for half the total scan time on each side of the peak. Three standard reflections measured every hour showed no significant decrease in intensity during data collection. The reflections with $I_o > 2.0\sigma(I_o)$ were judged as observations and were used for solution and structure refinement. Data were corrected for Lorentz-polarization factors. An empirical absorption correction based on a series of Y scans was applied to the data. The structure was solved by direct methods[11)] and refined by a full-matrix least-squares routine[12)] with anisotropic thermal parameters for all non-hydrogen atoms (weight = $1/[\sigma(F_o)^2+0.0001(F_o)^2]$, $\sigma(F_o)$ from counting statistics). All of the hydrogen atoms were placed isotropically at their calculated positions (C–H = 1.00 Å) and fixed in the calculation. Atomic scattering factor curves f_o, $\Delta f'$, and $\Delta f''$ of W, Fe, P, Si, O, C, and f_o of H were taken from International Tables.[13)] Crystal data and refinement details are summarized in Table 1. Selected bond lengths and angles for **3** and **4** are given in Tables 2 and 3, respectively. The tables of the final atomic coordinates, mean square displacement tensors, bond distances and angles, the least-squares planes, dihedral angles, and the structural factors are deposited as Document No. 71067 at the Office of the Editor of Bull. Chem. Soc. Jpn.

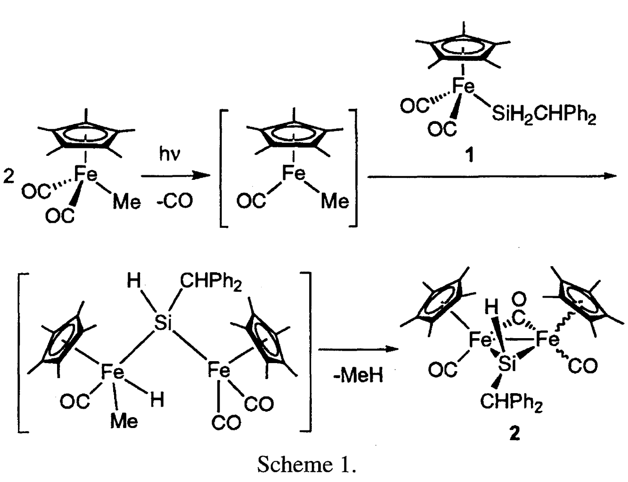
Results and Discussion

Synthesis and Characterization. Photolysis of two molar equivalents of [Fp^*Me] in the presence of Ph_2CHSiH_3 at 10 °C afforded [$Fp^*SiH_2CHPh_2$] (**1**) in 41% yield, *cis*-[$Cp^*{}_2(CO)_2Fe_2(\mu$-CO)$\{\mu$-Si(H)$CHPh_2\}$] (*cis*-**2**) in 8% yield together with a trace amount of the *trans* isomer, and [$Fp^*{}_2$] in 21% yield (Eq. 1). Mononuclear silyl complex **1** was a major product, while silanediyl-bridged dinuclear complexes **2** were obtained as minor products. This result is in contrast with the previously reported photolysis of $FpSiMe_3$ in the presence of Ph_2CHSiH_3 where dinuclear complex *cis*-[$Cp_2(CO)_2Fe_2(\mu$-CO)$\{\mu$-Si(H)$CHPh_2\}$] (*cis*-**5a**) was obtained as a major product in 62% yield.[7f)] A steric effect is thought to be responsible for this difference: A plausible mechanism for the formation of **2** involves the oxidative addition of **1** at the Si–H bond to a 16e intermediate [Cp^*Fe(CO)-Me] generated by photolysis of [Fp^*Me] (Scheme 1).[7)] Steric repulsion between bulky Cp^* ligands and a SiH_2CHPh_2 group strongly retards this reaction, while the corresponding reaction between complexes with Cp ligands instead of Cp^* may occur more smoothly. A similar steric effect has been also observed in the following reactions: Photolysis of [Fp^*SiMe_3] in the presence of *t*-$BuSiH_3$ afforded mononuclear [Fp^*SiH_2*t*-Bu] as a sole product,[7b)] whereas photol-

Table 1. Crystal Data and Refinement Details of Complexes [Cp*Fe(CO)(μ-CO){μ-Si(H)-CHPh$_2$}(CO)FeCp] (**3**) and [Cp*Fe(CO)(μ-CO){μ-Si(H)CHR$_2$}(CO)$_2$WCp]·1/2C$_6$D$_6$ (**4**·1/2C$_6$D$_6$)

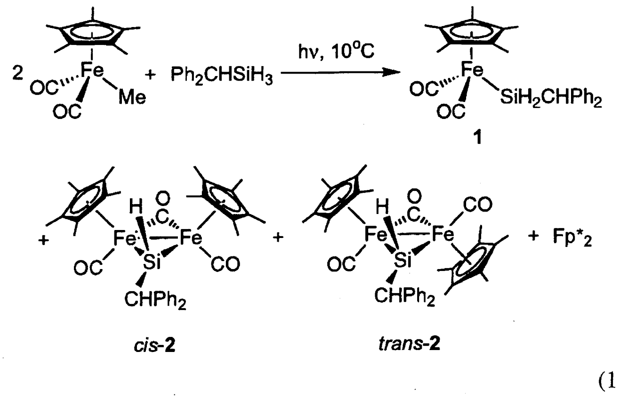
	3	**4**
Formula	$C_{31}H_{32}Fe_2O_3Si$	$C_{38}H_{38}FeO_4SiW$
F_W	592.37	826.50
Space group	Monoclinic $P2_1/n$	Triclinic $P\bar{1}$
a/Å	15.026(2)	8.906(4)
b/Å	10.096(1)	10.088(2)
c/Å	18.282(2)	19.946(4)
α/deg	90	79.80(2)
β/deg	98.04(1)	83.45(3)
γ/deg	90	62.86(3)
V/Å^3	2745.9(5)	1568.3(9)
Z	4	2
F(000)	1232	824
D_{calc}/g cm^{-3}	1.43	1.75
μ/mm^{-1}	1.13	4.28
λ/Å	0.71069	0.71069
Crystal size/mm	$0.31 \times 0.31 \times 0.38$	$0.19 \times 0.25 \times 0.34$
Scan type	θ–2θ	θ–2θ
2θ(max)	50.0	50.0
hkl ranges	$-17 < h < 17$	$-9 < h < 10$
	$0 < k < 11$	$0 < k < 11$
	$0 < l < 21$	$-22 < l < 23$
Diffractometer	Nonius	Nonius
No. of measured reflections	5006	5893
No. of unique reflections	4811	5504
No. of observed reflections ($I > 2.0\ \sigma(I)$)	3347	4426
Transmission factors	0.942—1.000	0.817—1.000
Temperature/K	298	298
No. of atoms	69	77
No. of params	338	383
Weights	Counting-statistic	Counting-statistic
Weight modifier	0.0001	0.0001
$R^{a)}$; $R_w^{b)}$	0.033; 0.037	0.031; 0.034
GOF $^{c)}$	1.63	1.49
$(\delta/\sigma)_{max}$	0.0003	0.0007
(D-map)$_{max}$; min/e Å^{-3}	−0.25; 0.31	−0.98; 1.21

a) $R = \sum(F_o - F_c)/\sum(F_o)$. b) $R_w = [\sum(w(F_o - F_c)^2)/\sum(wF_o)]^{1/2}$.
c) GOF $= [\sum(w(F_o - F_c)^2)/((\text{no. of reflns}) - (\text{no. of params}))]^{1/2}$.



Scheme 1.

yses using less bulky complex [FpSiMe$_3$][7a,7b] or silane p-TolSiH$_3$[7e] provided silanediyl-bridged dinuclear complexes [Cp$_2$(CO)$_2$Fe$_2$(μ-CO)(μ-SiHt-Bu)] and [Cp*$_2$(CO)$_2$Fe$_2$(μ-CO)(μ-SiHp-Tol)], respectively.



(1)

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [Cp*Fe(CO)(μ-CO){μ-Si(H)CHPh$_2$}(CO)FeCp] (**3**)

	Bond lengths		
Fe1–Fe2	2.647(1)	Fe1–Si	2.253(1)
Fe2–Si	2.266(1)	Fe1–C1	2.092(3)
Fe1–C2	2.098(3)	Fe1–C3	2.144(3)
Fe1–C4	2.157(3)	Fe1–C5	2.142(3)
Fe1–C16	1.732(4)	Fe1–C18	1.926(4)
Fe2–C11	2.082(4)	Fe2–C12	2.112(4)
Fe2–C13	2.113(4)	Fe2–C14	2.102(4)
Fe2–C15	2.077(4)	Fe2–C17	1.730(4)
Fe2–C18	1.925(4)	Si–C19	1.927(3)
	Bond angles		
Fe1–Fe2–Si	53.91(3)	Fe2–Fe1–Si	54.36(3)
Fe1–Si–Fe2	71.73(3)	Fe1–Fe2–C18	46.6(1)
Fe2–Fe1–C18	46.6(1)	Fe1–C18–Fe2	86.9(2)
Si–Fe1–C18	100.1(1)	Si–Fe2–C18	99.7(1)
Fe1–Si–C19	128.5(1)	Fe2–Si–C19	118.6(1)
Fe1–C18–O18	137.1(3)	Fe2–C18–O18	136.1(3)
Fe1–Fe2–C17	94.4(1)	Fe2–Fe1–C16	97.3(1)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [Cp*Fe(CO)(μ- CO){μ- Si(H)CHR$_2$}(CO)$_2$WCp]·1/2C$_6$D$_6$ (**4**·1/2C$_6$D$_6$)

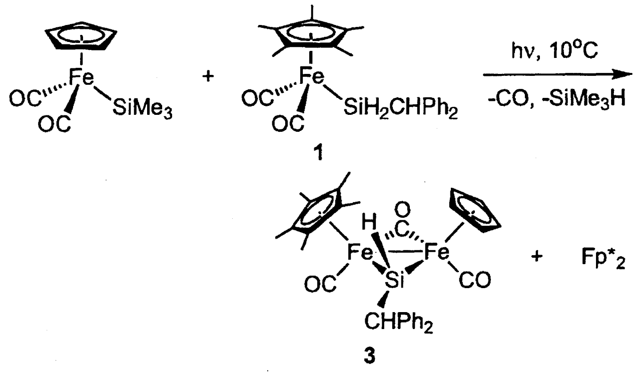
	Bond lengths		
W–Fe	2.935(1)	W–Si	2.519(2)
Fe–Si	2.259(2)	W–C11	2.350(8)
W–C12	2.309(8)	W–C13	2.284(8)
W–C14	2.297(8)	W–C15	2.341(8)
W–C17	1.965(7)	W–C18	1.959(7)
W–C19	2.275(6)	Fe–C1	2.089(5)
Fe–C2	2.101(5)	Fe–C3	2.145(5)
Fe–C4	2.138(5)	Fe–C5	2.140(5)
Fe–C16	1.733(6)	Fe–C19	1.866(6)
Si–C20	1.928(5)		
	Bond angles		
W–Fe–Si	56.23(4)	Fe–W–Si	48.21(4)
W–Si–Fe	75.6(1)	W–Fe–C19	50.8(2)
Fe–W–C19	39.5(1)	W–C19–Fe	89.7(2)
Si–Fe–C19	106.3(2)	Si–W–C19	87.2(2)
W–Si–S20	120.5(2)	Fe–Si–C20	123.6(2)
W–C19–O19	129.1(4)	Fe–C19–O19	141.2(5)
W–Fe–C16	97.5(2)	Fe–W–C17	99.4(2)
Fe–W–C18	93.0(2)	C17–W–C18	77.0(3)

Complexes **1** and *cis*-**2** have been characterized by spectroscopic methods. The IR spectrum of **1** exhibits two CO bands of nearly equal intensity, which is typical of [Fp*R], at 1986 and 1932 cm^{-1}, together with a weak $\nu_{\text{Si–H}}$ absorption at 2069 cm^{-1}. The ^{1}H NMR spectrum shows, in addition to the signals in the phenyl region, two mutually coupled signals with the intensity ratio of 1 : 2, a triplet at $\delta = 4.14$ and a doublet at $\delta = 4.65$, for the CH and SiH hydrogen atoms, respectively. The ^{29}Si NMR signal appears at $\delta = 27.4$. These are consistent with a mononuclear silyliron dicarbonyl structure of **1**. Photolysis of **1** in an NMR tube monitored by ^{1}H NMR did not show any significant change after 4 h. Obviously, the steric bulkiness hindered the further formation of silanediyl-bridged diiron complexes.

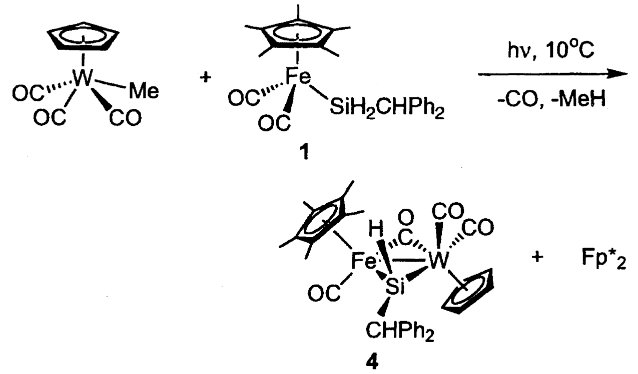
The IR spectrum of *cis*-**2** exhibits one weak $\nu_{\text{Si–H}}$ band at 2019 cm^{-1}, two terminal CO bands at 1950 (s, symmetric vibration) and 1909 (m, antisymmetric vibration) cm^{-1}, and one bridging CO band at 1745 cm^{-1}. The ^{1}H NMR spectrum of *cis*-**2** shows a Cp* resonance at $\delta = 1.41$ and two mutually coupled doublets in equal intensity at $\delta = 4.67$ and 7.48 for the CH and SiH hydrogen atoms, respectively. The ^{13}C NMR shows only one methyl resonance of Cp* at $\delta = 10.0$. The ^{29}Si NMR appears at relatively low field, $\delta = 251.6$. The ^{29}Si chemical shifts of reported silanediyl-bridged diiron complexes with an Fe–Fe bond are: [Cp$_2$(CO)$_2$Fe$_2$(μ-SiMe$_2$)$_2$] (**6**) (at $\delta = 243.8$ and 229.5 for *cis* and *trans* isomers, respectively),[14] three isomers of [Cp$_2$(CO)$_2$Fe$_2$(μ-CO){μ-SiMe(SiMe$_3$)}] (**7**) (at δ = 232.1, 242.7, and 245.5),[14] [Cp$^*_2$(CO)$_2$Fe$_2$(μ-CO){μ-Si(H)*p*-Tol)}] (**8**) (at $\delta = 250.4$ and 235.5 for *cis* and *trans* isomers, respectively),[7e] [Cp$_2$(CO)$_2$Fe$_2$(μ-CO)(μSiHR)] (**5**) (**a**: R = CHPh$_2$, 226.1; **b**: R = CHEt$_2$, 237.2; **c**: R = *t*-Bu, 254.4; R = (CMe$_2$)$_2$H, 255.1)[7a,7b,7e] and [Cp$_2$(CO)$_2$Fe$_2$(μ-CO)(μ-SiIR)] (**9**) (**a**: R = CHPh$_2$, 246.1; **b**: R = CHEt$_2$, 266.1; **c**: R = *t*-Bu, 289.1).[7c,7d,7f]

Thermal and photochemical interconversion between geometrical isomers of [CP$_2$(CO)$_2$Fe$_2$(μ-CO)(μ-ER$_2$)] (CP = Cp, Cp*; E = Si, Ge; R$_2$ = H, alkyl, halide etc.) have been reported.[7,15] Complex **2** is quite robust, however; no thermal *cis*–*trans* isomerization could be recorded below 100 °C, presumably attributed to the steric hindrance among the two Cp* ligands and the substituent group at the Si atom. In contrast, *trans*-**2** converted to *cis*-**2** on photolysis. Although obtained only in trace amount and contaminated with **1**, *trans*-**2** was unambiguously characterized based on this isomerization reaction as well as the spectroscopic data: The IR spectrum exhibits two terminal CO and one bridging CO bands at 1942, 1907, and 1753 cm^{-1}. As for two terminal CO bands, the one at 1907 cm^{-1} assigned to the antisymmetric vibration is stronger in intensity than the other at 1942 cm^{-1} assigned to the symmetric one. This spectroscopic pattern is typically observed in the *trans* isomer of this type of complexes.[7] In the ^{1}H NMR spectrum, two Cp* methyl chemical shifts are observed at $\delta = 1.38$ and 1.41, in equal intensity. The ^{13}C NMR spectrum shows two Cp* methyl resonances at $\delta = 9.8$ and 10.2.

The mechanism of forming silanediyl-bridged diiron complexes by photolysis of [FpSiMe$_3$] with RSiH$_3$ has been proposed previously.[7] Photochemical CO dissociation and oxidative addition of hydrosilane are the key steps. If **1** is an intermediate in this reaction as mentioned above, isolated **1** could then become a precursor for the synthesis of other silanediyl-bridged complexes. Thus, the photolysis of [CpFe(CO)$_2$SiMe$_3$] and [CpW(CO)$_3$Me] in the presence of **1** was investigated. These reactions afforded novel silanediyl-bridged asymmetric dinuclear complexes [Cp*Fe(CO)(μ-CO){μ-Si(H)CHR$_2$}(CO)$_n$MCp] (**3**: M = Fe, $n = 1$; **4**: M = W, $n = 2$) in 57 and 44% yields together with [Fp$^*_2$] (Eqs. 2 and 3).



(2)



(3)

Complexes **3** and **4** have been characterized by spectroscopic methods. The ν_{CO} stretching bands of **3** in the IR spectrum (1959, 1921, 1763 cm^{-1}) displays a pattern similar to those of *cis*-**2**, indicative of the formation of *cis* isomer, although slightly blue-shifted. Such a shift is attributable to the replacement of one of Cp* ligands in *cis*-**2** by a less electron-donating Cp ligand in **3** which weakens the back donation from the $\mathrm{Fe_2}$ unit to CO ligands. The ^{1}H NMR spectrum shows the Cp and Cp* resonances at $\delta = 4.13$ and 1.33. Two doublets of mutually coupled methine and Si–H protons appear at $\delta = 4.61$ and 7.38, respectively. The ^{13}C NMR spectrum shows two distinct terminal CO resonances at $\delta = 212.4$ and 214.9 due to asymmetric environment of two iron centers. On comparison to the corresponding terminal CO resonances of *cis*-**5a** with Cp ligands (at $\delta = 212.5$) and *cis*-**2** with Cp* ligands (at $\delta = 215.0$), the former signal of **3** is assigned to CpFe–CO, while the latter one is assigned to Cp*Fe–CO. The bridging CO resonance is observed at very low field ($\delta = 277.6$). The ^{29}Si NMR signal appears at $\delta = 239.8$, indicative of the existence of a bridging silanediyl ligand. It is interesting to discover that the IR ν_{CO} stretching bands and the ^{29}Si NMR chemical shift of **3** appear at the average of those of *cis*-**2** ($\delta = 251.6$) and *cis*-**5a** ($\delta = 226.1$). It seems that a linear relationship exists between the spectroscopic data and electronic characters.

The IR spectrum of **4** exhibits three terminal CO bands at 1940, 1921, and 1863 cm^{-1} and one bridging CO band at 1763 cm^{-1}. In the ^{1}H NMR spectrum, the peaks of Cp and Cp* are observed at $\delta = 4.45$ and 1.44. The mutually coupled methine proton and Si–*H* appear at $\delta = 4.07$ and 8.08 as two doublets. The ^{13}C NMR shows three terminal CO resonances at $\delta = 215.7$, 222.8, and 233.1. The first signal belongs to Fe–CO, in agreement with those of corresponding terminal CO's in *cis*-**2** and **3**. The remaining two signals are assigned to W–CO's on the basis of tungsten satellites ($J_{\mathrm{WC}} = 150$ Hz). The bridging CO shows the resonance at a typical low field region ($\delta = 274.0$). The ^{29}Si NMR signal appears at $\delta = 228.1$, inidcating the existence of a bridging silanediyl ligand. To our knowledge, this is the first synthesis of Fe–W complex with silanediyl and CO bridges. To clarify the geometry of **4**, the X-ray diffraction analysis has been undertaken and will be discussed later.

In contrast to $[\mathrm{Cp_2(CO)_2Fe_2}(\mu\text{-CO})(\mu\text{-SiHR})]$,[7c,7d] treatment of complexes **3** and **4** with $\mathrm{CH_2I_2}$ at room temperature for more than 80 h didn't afford the corresponding iodosilanediyl-bridged complexes but decomposition occurred, probably because the Si atoms are sterically blocked by the Cp* ligand and the substituent at the Si atom.

X-Ray Structures. A molecular plot of complex **3** with atomic numbering sequence is shown in Fig. 1. Four possible geometrical isomers of silanediyl-bridged asymmetric diiron complexes are shown in Scheme 2. Complex **3** adopts the least sterically hindered *cis*(H)-geometry. The butterfly-like core structure contains an Fe–Fe bond and two bridging ligands, namely one CO and one silanediyl. The substituent $\mathrm{Ph_2CH}$ at Si atom is directed away from the Cp* ligand with a torsion angle Cp*(centroid)–Fe–Si–C19 of 118.3(1)°. The Cp and Cp* rings adopt mutually *cis* configuration, probably to minimize the steric repulsion between these ligands and the bulky $\mathrm{Ph_2CH}$ group. The dihedral angle of two cyclopentadienyl rings (78.7(2)°) is smaller than those in $[\mathrm{Cp_2(CO)_2Fe_2}(\mu\text{-CO})(\mu\text{-SiXR})]$ (X = H, R = $\mathrm{CHPh_2}$ (**5a**) 92.4°,[7f] $\mathrm{CHEt_2}$ (**5b**) 91.45°;[16] *t*-Bu (**5c**) 91.3°,[7a,7b] X = I, R = $\mathrm{CHPh_2}$ (**9a**) 84.33°[7f]) but is larger than that in *cis*-

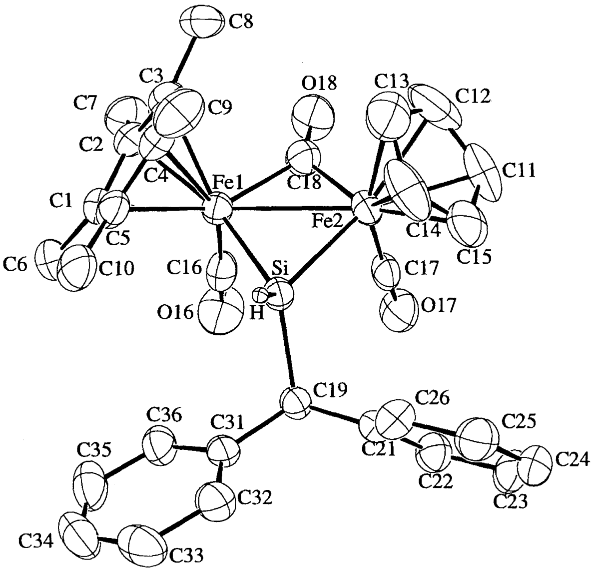
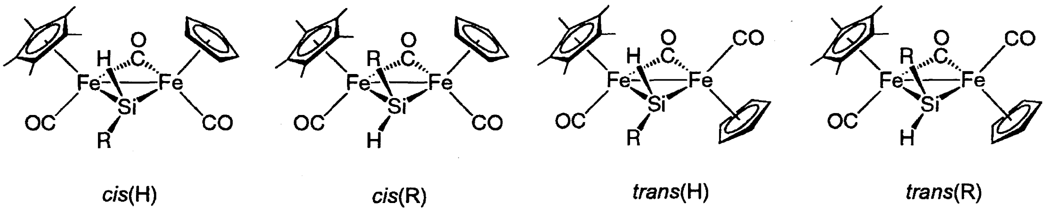


Fig. 1. Molecular plot of $[\mathrm{Cp^*Fe(CO)}(\mu\text{-CO})\{\mu\text{-Si(H)-CHPh_2}\}\mathrm{(CO)FeCp}]$ (**3**) with atomic sequence. The thermal ellipsoids are shown at the 50% probability level. The H atoms are omitted for clarity.



Scheme 2. Four possible geometrical isomers of silanediyl-bridged asymmetric diiron complexes.

[$Cp^*_2(CO)_2Fe_2(\mu$-$CO)(\mu$-SiH*p*-Tol)] (*cis*-**8**, 65.3°).[17] The interplanar angle between the Fe_2Si plane and the Fe_2C 18 plane is 167.3(2)°, which is larger than the reported values for [$Cp_2(CO)_2Fe_2(\mu$-$CO)(\mu$-SiXR)] (161.3°—164.0°),[7] but is smaller than that in *cis*-**8** (176.4°).[17] The distance of Fe1–Fe2 is 2.647(1) Å, which is significantly longer than 2.614(1) Å in **5c**,[7a,b] 2.621(1) Å in **5a**,[7f] 2.622(1) Å in **7**,[14] and 2.629(1) Å in **9a**,[7f] but is distinctly shorter than that of the bis-Cp* complex *cis*-**8** (2.693(1) Å).[17] All these structural differences can be explained by considering the steric repulsion between two cyclopentadienyl ligands, which increases in the following order: Cp–Cp < Cp–Cp* < Cp*–Cp*. The Fe1–Si–Fe2 angle (71.73(3)°) is in the normal range of silanediyl-bridged complexes with a metal-metal bond.[3] The distances of Fe1 to Cp* (centroid) and Fe2 to Cp (centroid) are 1.748(2) and 1.735(3) Å, respectively, which reflect the steric hindrance of the ligands. Since Fe1 is more electron-rich than Fe2 due to a stronger donating tendency of Cp*, Fe1 exhibits a greater π-back bonding to the bridging Si atom than Fe2. Hence, the bond length of Fe1–Si [2.253(1) Å] is shorter than that of Fe2–Si [2.266(1) Å].

A molecular plot of complex **4** with atomic numbering sequence is shown in Fig. 2. The crystal of **4** contains benzene as solvent of crystallization in the molar ratio of **4**: benzene = 2 : 1. The core structure resembles that of **3**, with bridging silanediyl and carbonyl ligands and a direct Fe–W bond. The substituent Ph_2CH at Si atom is directed away from the Cp* ligand with a torsion angle of Cp*(centroid)–Fe–Si–C20 of 113.5(2)°. The Cp and Cp* adopt *trans*(H) geometry, analogous to that shown in Scheme 2, with a dihedral angle of 13.1(6)°. This geometry is in sharp contrast with the *cis* geometry of diiron complex **3** and is apparently due to the existence of two carbonyl ligands on the tungsten atom: A cyclopentadienyl ligand is less sterically demanding than the two carbonyl ligands and is, therefore, located in the position *cis* to the bulky Ph_2CH group. The bridging carbonyl ligand C19–O19 bends away from the Fe atom (Fe–C19–O19 141.2(5)°, W–C19–O19 129.1(4)°) apparently due to the steric repulsion of Cp*. This geometry and/or the unsymmetrical distribution of electron density on the W–Fe bond may cause the unusually short bond length of Fe–C19 [1.866(6) Å] in comparison with the bond length of bridging Fe–CO [1.91—1.95 Å] in the derivatives of [$CP_2(CO)_2Fe_2(\mu$-CO)(μ-SiXR)] (CP = Cp*, Cp).[7,17] The interplanar angle of the Fe–W–Si plane and the Fe–W–C19 plane is 168.9(3)°, which is larger than the corresponding angle of **3**. The W–Si–Fe angle [75.6(1)°] is similar to the M–Si–M angles in silanediyl-bridged dinuclear complexes with a metal–metal bond.[3] The W–Fe bond length [2.935(1) Å] is longer than the reported 2.880 and 2.884 Å for two independent molecules in [CpFe(CO)(μ-η^2,η^2-$CH_2{=}C{=}CH_2$)$(CO)_2$WCp],[18] 2.831(2) Å in [$Fe(CO)_3(\mu$-$CO)(\mu$-$PPh_2)(CO)_2$WCp],[19] and 2.851(3) Å in [CpFe(CO)(μ-PPh_2)(μ-CO)W$(CO)_4$].[20] It is among the longest of W–Fe bond lengths from 19 structures, 64 fragments, containing a fragment of CpW$(CO)_2$Fe retrieved from the Cambridge Structural Database: The direct W–Fe distances are between 2.605 and 2.856 Å.[21] The bond length of Fe–Si [2.259(2) Å] is in the normal range,[7] while the W–Si bond length [2.519(2) Å] is shorter than 2.586 Å in [{$(CO)_4W(\mu$-$SiHEt_2)$}$_2$][22] and 2.533—2.633 Å in [Cp*W$(CO)_2$(silyl)(L)] and [$Cp_2W(SiMe_3)$(L)].[23]

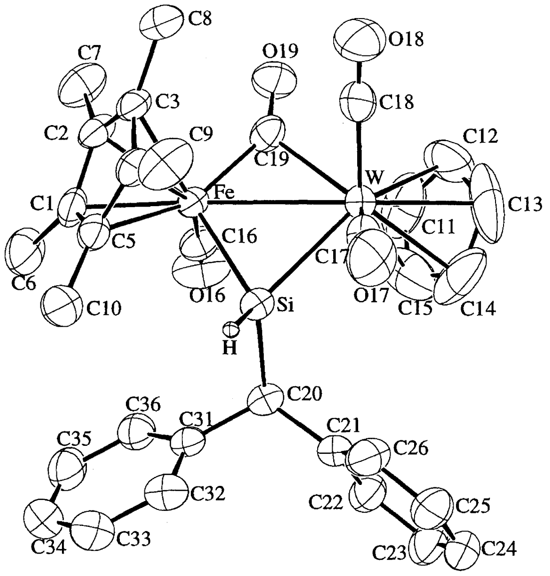


Fig. 2. Molecular plot of [Cp*Fe(CO)(μ-CO){μ-Si(H)-$CHPh_2$}$(CO)_2$WCp] (**4**) with atomic sequence. The thermal ellipsoids are shown at the 50% probability level. The H atoms and the atoms of the solvent molecules are omitted for clarity.

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