Synthesis and Properties of *s*-Alkyl-Substituted Silanediyl-Bridged and Silanetriyl-Bridged Diiron Complexes, $Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(X)CHR_2]$ and $Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(DMAP)CHR_2]^+I^-$ (X = H, I; R = Et, Ph; DMAP = 4-(Dimethylamino)pyridine)

Lung-Shiang Luh, Yuh-Sheng Wen,† Hiromi Tobita,* and Hiroshi Ogino*

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-77

†Institute of Chemistry, Academia Sinica, Taipei, 11529, Taiwan, ROC

(Received May 12, 1997)

Photolysis of 2 molar amounts of $CpFe(CO)_2SiMe_3$ (= $FpSiMe_3$, **1**) with *s*-alkylsilanes R_2CHSiH_3 (**2a**: R = Et; **2b**: R = Ph) produces the silylene (or silanediyl)-bridged diiron complexes $Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(H)CHR_2]$ (**3a**: R = Et; **3b**: R = Ph) which exist mainly in *cis*-form. The treatment of *cis*-**3** with an excess amount of CH_2I_2 stereoselectively affords the iodosilylene-bridged diiron complexes $Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(I)CHR_2]$ (**4a**: R = Et; **4b**: R = Ph) in *cis*-form. The reaction of complexes **4** with 4-(dimethylamino)pyridine (= DMAP) gives the base-stabilized silylyne (or silanetriyl)-bridged diiron complexes $Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(DMAP)CHR_2]^+I^-$ (**5a**: R = Et; **5b**: R = Ph) in 35 and 43% yields, respectively. The *cis–trans* isomerization of complexes **3** was studied under thermal and photochemical reaction conditions. The molar ratios of the *cis* and *trans* isomers of complexes **3** in the thermal equilibrium at 50 °C were 95 : 5 (**3a**) and 78 : 22 (**3b**), respectively, and in the photostationary state at 10 °C were 80 : 20 and 30 : 70, respectively. The structures of complexes **3b** and **4b** have been characterized by X-ray diffraction.

Compounds with transition metal-silicon bonds have attracted a considerable number of researchers continuously 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. These complexes represent very rich chemistry and have important applications in a number of catalytic processes.[2]

The oxidative addition of Si–H bonds of mono-, di-, or tri-substituted silanes 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] It is now clear that coordination compounds of subvalent silicon ligands play a key role in many reactions and have important applications in industrial processes.[5] Bimetallic complexes with silylene (or silanediyl) as bridging ligand have been known for some time;[6] however, the investigations of silylyne (or silanetriyl)-bridged one have been few. We have previously reported the preparation of the silylene-bridged diiron complexes $Cp'_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}SiHR)$ (Cp′ = C_5H_5, R = *t*-Bu, $(CMe_2)_2H$; Cp′ = C_5Me_5, R = *p*-Tol) via the photolytic reaction of $Cp'Fe(CO)_2SiMe_3$ and $RSiH_3$.[7] Furthermore, we have succeeded in the synthesis of the first base-stabilized silylyne-bridged diiron complexes $Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(Base)t\text{-}Bu]^+I^-$ by the reaction of $Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(I)t\text{-}Bu]$ with Lewis bases, such as DMAP and *N*-methylimidazole (= NMI).[8] Herein, we would like to report some results of the photolysis of $FpSiMe_3$ in the presence of the secondary alkylsilanes R_2CHSiH_3 to give silylene-bridged diiron complexes $Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(X)CHR_2]$ (X = H, I; R = Et, Ph). The syntheses of silylyne-bridged diiron complexes $Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(DMAP)CHR_2]^+I^-$ (R = Et, Ph) from the corresponding iodo-substituted silylene-bridged diiron complexes are also reported.

Experimental

All manipulations were performed under an atmosphere of prepurified nitrogen with standard Schlenk techniques, and all solvents were distilled from an appropriate drying agent.[9] 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) or CD_3CN (1.95 ppm). The ^{29}Si NMR spectra were obtained on the Bruker ARX 300 spectrometer by using a DEPT pulse sequence. Mass spectra were recorded on a JEOL JMS HX-110 spectrometer. $FpSiMe_3$ (**1**)[1] and 1-ethylpropyl chloride[10] were prepared according to the literature procedures. Other reagents were obtained from commercial sources and used without further purification.

Preparation of Silanes R_2CHSiH_3 (2a: R = Et; 2b: R = Ph). (a) 1-Ethylpropylsilane, Et_2CHSiH_3 (2a): A 250 cm^3 flask was equipped with a condenser and a dropping funnel. 1-Ethylpropyl

chloride (10 g, 94 mmol) in 10 cm^3 of pentane placed in the funnel was added dropwise to the suspension of Li powder (2.5 g, 0.36 mmol) with 5% Na dispersion in 100 cm^3 of pentane at 36 °C over 1 h; then the solution was refluxed for an additional 2 h. After the solution was cooled to room temperature, it was filtered under nitrogen. The resultant orange filtrate (1-ethylpropyllithium), whose concentration was determined by the titration with 1.0 M *s*-BuOH to be 0.71 M (1 M = 1 mol dm^{-3}), was transferred to another dropping funnel via a cannula and added dropwise to the stirred solution of $SiCl_4$ (24 g, 0.14 mmol) in 100 cm^3 of THF placed in a 500 cm^3 flask over 2 h. After the addition was completed, the solution was refluxed for 2 h and then cooled to room temperature. Most of the solvent was distilled under atmospheric pressure and the yellowish residue was distilled under reduced pressure to afford trichloro(1-ethylpropyl)silane (7.2 g, 35 mmol, 37%) as a colorless liquid, bp 101—104 °C/85 mmHg (1 mmHg = 133.322 Pa).

To the suspension of $LiAlH_4$ (3.23 g, 85 mmol) in 150 cm^3 of THF, a solution of trichloro(1-ethylpropyl)silane (7.0 g, 34 mmol) in 20 cm^3 of THF was added dropwise through a dropping funnel over 30 min. After the addition was completed, the solution was heated to 80 °C for 2 h and then cooled by an ice-bath. Then, 4 cm^3 of water, 4 cm^3 of 15% aqueous NaOH, and 13 cm^3 of water were added successively while stirring vigorously. The white precipitate was then filtered by frit and washed with THF (20 $cm^3 \times 3$). The filtrate and washings were combined, placed in a separatory funnel, and washed with a dilute NaCl solution and then with water to wash off THF until the volume of the organic layer did not change (12 times). The organic layer was then washed with a saturated NaCl solution and dried over $MgSO_4$. The resulting crude product was distilled to give 1-ethylpropylsilane (**2a**) (1.68 g, 16.5 mmol, 49%) as a colorless liquid, bp 46—48 °C. IR (hexane, cm^{-1}) 2150 (ν_{Si-H}); ^{1}H NMR (C_6D_6) δ = 0.67 (m, 1H, –C*H*), 0.86 (t, 6H, –CH_3), 1.35 (m, 4H, –CH_2), 3.62 (d, J_{HH} = 3.2 Hz, 3H, –Si–*H*); ^{29}Si NMR (C_6D_6) δ = −55.1 (s). Found: C, 58.21; H, 13.6%. Calcd for $C_5H_{14}Si$: C, 58.73; H, 13.8%.

(b) (Diphenylmethyl)silane, Ph_2CHSiH_3 (2b): Ph_2CH_2 (8.4 cm^3, 50 mmol) was dissolved in 100 cm^3 of THF and the solution was maintained at −78 °C. *n*-BuLi (1.6 M in hexane, 35 cm^3, 55 mmol) in 50 cm^3 of hexane was added dropwise to the solution. After the addition was completed, the orange solution was stirred for 2 h at 0 °C before being warmed up to room temperature. The resultant orange solution (Ph_2CHLi) was transferred to another dropping funnel via a cannula and then added dropwise to the solution of $SiCl_4$ (25.5 g, 0.15 mol) in 100 cm^3 of THF over 3 h. After the addition was completed, the solution was refluxed for 2 h. The solution was distilled under reduced pressure after being cooled to room temperature to give $Ph_2CHSiCl_3$ (3.02 g, 10 mmol, 20%) as a colorless liquid, bp 89–90 °C/0.15 mmHg (1 mmHg = 133.322 Pa), and 8.5 g of $(Ph_2CH)_2SiCl_2$ as a white solid.

To the suspension of $LiAlH_4$ (0.95 g, 25 mmol) in 100 cm^3 of Et_2O, $Ph_2CHSiCl_3$ (3.0 g, 10 mmol) in 20 cm^3 of Et_2O was added dropwise over 30 min. After the addition was completed, the solution was refluxed for 2 h and then cooled in an ice-bath. 6.5 cm^3 of water was added dropwise carefully while stirring vigorously to quench any excess of $LiAlH_4$ and then the solution was filtered by frit and washed with Et_2O (10 $cm^3 \times 3$). The filtrate and washings were combined, dried over $MgSO_4$, and distilled under reduced pressure to give Ph_2CHSiH_3 (**2b**) (1.68 g, 8.5 mmol, 85%) as a colorless liquid, bp 65—68 °C/0.15 mmHg. IR (hexane, cm^{-1}) 2164 (ν_{Si-H}); ^{1}H NMR (C_6D_6) δ = 3.61 (q, J_{HH} = 1.7 Hz, 1H, –C*H*), 3.91 (d, J_{HH} = 1.7 Hz, 3H, –Si–*H*), 7.01–7.46 (m, 20H, Ph); ^{29}Si NMR (C_6D_6) δ = −51.0 (s). Found: C, 79.31; H, 7.26%. Calcd for $C_{13}H_{14}Si$: C, 78.73; H, 7.11%.

Preparation of $Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(H)CHEt_2]$ (3a). The mixture of Et_2CHSiH_3 (**2a**) (0.23 g, 2.20 mmol) and $FpSiMe_3$ (1.00 g, 4.00 mmol) was dissolved in 100 cm^3 of pentane and the solution was irradiated with a 450 W medium-pressure Hg lamp at 10 °C. The yellow solution changed to red with liberation of CO and red crystals precipitated during irradiation. After the solution had been irradiated for 5 h, two-thirds of the solvent was removed under vacuum, and then cooled to −46 °C. After 2 h, the mother liquor was transferred via a cannula and the precipitate was washed with pentane (5 $cm^3 \times 2$) and then dried under vacuum to give 600 mg (1.41 mmol) of red *cis*-$Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(H)CHEt_2]$ (**3a**) as the exclusive product in 70% yield. IR (toluene, cm^{-1}) 1996 (w, ν_{Si-H}), 1969 (vs, ν_{CO_t}), 1932 (m, ν_{CO_t}), 1776 (s, ν_{CO_b}); ^{1}H NMR (C_6D_6) δ = 1.24 (t, 6H, –CH_3), 1.69 (m, 1H, –C*H*), 1.97 (m, 4H, –CH_2), 4.11 (s, 10H, –C_5H_5), 7.18 (d, J_{HH} = 6.6 Hz, 1H, –Si–*H*); ^{13}C NMR (C_6D_6) δ = 14.1 (s, –CH_3), 26.6 (s, –CH_2), 39.4 (s, –CH), 84.0 (s, –C_5H_5), 212.8 (s, CO_t), 275,4 (s, CO_b); ^{29}Si NMR (C_6D_6) δ = 237.2 (s). Mass (FAB, Xe, *m*-nitrobenzyl alcohol matrix) 426 (M^+; 55), 398 (M^+−CO; 44), 370 (M^+−2CO; 71), 342 (M^+−3CO; 6). Found: C, 50.80; H, 5.27%. Calcd for $C_{18}H_{22}Fe_2O_3Si$: C, 50.73; H, 5.20%.

Preparation of $Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(I)CHEt_2]$ (4a). Complex **3a** (0.250 g, 0.587 mmol) was dissolved in 2 cm^3 of CH_2Cl_2 and then 1 cm^3 of CH_2I_2 was added via a syringe. The flask was wrapped in aluminum foil to prevent the decomposition of the desired product to $CpFe(CO)_2I$ by light. The solution was stirred at room temperature and the reaction was monitored by silica gel TLC (toluene/hexane = 2 : 1 as eluent). After 60 h, the crude product was purified by silica gel flash chromatography with toluene/hexane = 2 : 1 as eluent to give 187 mg (0.34 mmol) of red *cis*-$Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(I)CHEt_2]$ (**4a**) in 58% yield and FpI in trace amount. IR (toluene, cm^{-1}) 1983 (vs, ν_{CO_t}), 1950 (m, μ_{CO_t}), 1794 (s, ν_{CO_b}); ^{1}H NMR (C_6D_6) δ = 1.21 (t, 6H, –CH_3), 1.32 (tt, 1H, –C*H*), 1.92, 2.13 (qdd, 2H×2, –C*HH*), 4.19 (s, 10H, –C_5H_5); ^{13}C NMR (C_6D_6) δ = 14.0 (s, –CH_3), 27.8 (s, –CH_2), 48.2 (s, –CH), 87.8 (s, –C_5H_5), 212.1 (s, CO_t), 271.1 (s, CO_b); ^{29}Si NMR (C_6D_6) δ = 266.1 (s). Mass (FAB, Xe, *m*-nitrobenzyl alcohol matrix) 552 (M^+; 54), 524 (M^+−CO; 100), 496 (M^+−2CO; 21), 468 (M^+−3CO; 38), 425 (M^+−I; 10), 398 (M^+−I−CO; 13), 369 (M^+−I−2CO; 5). Found: C, 39.07; H, 3.86%. Calcd for $C_{18}H_{21}Fe_2IO_3Si$: C, 39.16; H, 3.83%.

Preparation of $Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(DMAP)CHEt_2]^+\text{-}I^-$ (5a). In an NMR tube, 1 cm^3 of CD_3CN was transferred to the mixture of complex **4a** (26 mg, 47.1 μmol) and DMAP (6.0 mg, 50 μmol) under vacuum and then sealed by flame. The reaction was monitored by ^{1}H NMR spectroscopy. After the solution was heated at 40 °C for 8 h, the starting material was consumed completely. It was then cooled to −50 °C for 3 d to crystallize the product. After opening the sealed tube in the glove box, the supernatant fluid was removed by a syringe and the red crystals were washed with Et_2O (1 $cm^3 \times 2$) and dried under vacuum to give 11.2 mg (16.5 μmol) of red $Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(DMAP)CHEt_2]^+I^-$ (**5a**) in 35% yield. IR (KBr, cm^{-1}) 1967 (s, ν_{CO_t}), 1934 (m, ν_{CO_t}), 1759 (s, ν_{CO_b}); ^{1}H NMR (CD_3CN) δ = 1.14 (m, 1H, –C*H*), 1.19 (t, 6H, –CHHCH_3), 1.47, 2.35 (m, 2H×2, –C*HH*CH_3), 3.15 (s, 6H, –N(CH_3)), 5.04 (s, 10H, –C_5H_5), 6.79, 8.42 (d, 2H×2, pyridine ring); ^{13}C NMR (CD_3CN) δ = 15.2 (s, –CH_2CH_3), 26.4 (s, –CH_2CH_3), 39.4 (s, –N(CH_3)), 47.5 (s, –CH), 86.4 (s, –C_5H_5), 106.7, 146.1, 156.5 (pyridine ring), 212.9 (s, CO_t), 269.6 (s, CO_b); ^{29}Si NMR (CD_3CN) δ = 264.0 (s). Found: C, 44.54; H, 4.63; N, 4.15%. Calcd for $C_{25}H_{31}Fe_2IN_2O_3Si$: C, 44.68; H, 4.60; N, 4.32%.

Preparation of $Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(H)CHPh_2]$ (3b). The procedures are similar to those of the preparation of **3a**. Ph_2CHSiH_3 (**2b**) (0.79 g, 4.00 mmol) and $FpSiMe_3$ (2.00 g, 8.00 mmol) were dissolved in 270 cm^3 of pentane. A red precipitate formed and stuck to the inner wall of the immersion well during irradiation. After the solution had been irradiated for 6 h, the mother liquor was transferred via a cannula and the precipitate was washed with pentane (5 $cm^3 \times 2$) and then dried under vacuum to give 1.30 g (2.5 mmol) of red *cis*-$Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(H)CHPh_2]$ (*cis*-**3b**) as the exclusive product in 41% yield. The mother liquor was dried under vacuum to afford the oily residue, which was purified by silica gel flash chromatography with toluene/hexane = 2 : 1 as eluent to give, according to the order of appearance, three products: 2 mg (3.83 μmol) of purple *trans*-**3b** in 0.96% yield, trace amount of Fp_2, and 439 mg (0.84 mmol) of *cis*-**3b** in 21% yield.

Spectroscopic data for *cis*-**3b**: IR (toluene, cm^{-1}) 1996 (w, ν_{Si-H}), 1969 (vs, ν_{CO_t}), 1932 (m, ν_{CO_t}), 1780 (s, ν_{CO_b}); ^{1}H NMR (C_6D_6) δ = 3.98 (s, 10H, $-C_5H_5$), 4.58 (d, J_{HH} = 6.7 Hz, 1H, $-CH$), 7.10 (t, 2H, H_{para}), 7.25 (t, 4H, H_{meta}), 7.49 (d, J_{HH} = 6.7 Hz, 1H, Si–*H*), 7.72 (d, 4H, H_{ortho}); ^{13}C NMR (C_6D_6) δ = 51.3 (s, –CH), 84.0 (s, $-C_5H_5$), 125.8, 128.7, 129.3, 144.4 (phenyl region), 212.6 (s, CO_t), 272.7 (s, CO_b); ^{29}Si NMR (C_6D_6) δ = 227.4 (s). Mass (FAB, Xe, *m*-nitrobenzyl alcohol matrix) 522 (M^+; 9), 466 (M^+-2CO; 14), 438 (M^+-3CO; 3). Found: C, 60.00; H, 4.53%. Calcd for $C_{26}H_{22}Fe_2O_3Si$: C, 59.80; H, 4.25%.

trans-**3b**: IR (toluene, cm^{-1}) 2004 (w, ν_{Si-H}), 1971 (m, ν_{CO_t}), 1930 (vs, ν_{CO_t}), 1778 (s, ν_{CO_b}); ^{1}H NMR (C_6D_6) δ = 4.08, 4.23 (s, 5H×2, $-C_5H_5$), 4.45 (d, J_{HH} = 6.7 Hz, 1H, $-CH$), 7.02—7.25 (m, 2H×2, H_{para} and H_{meta}), 7.36 (d, J_{HH} = 6.7 Hz, 1H, –Si–*H*), 7.62—7.68 (d, 4H×2, H_{ortho}); ^{13}C NMR (C_6D_6) δ = 54.2 (s, –CH), 85.2, 85.3 (s, $-C_5H_5$), 125.8, 126.4, 128.8, 129.3, 129.3 130.2, 144.2, 145.6 (phenyl region), 212.7, 213.1 (s, CO_t), 271.6 (s, CO_b); ^{29}Si NMR (C_6D_6) δ = 226.1 (s).

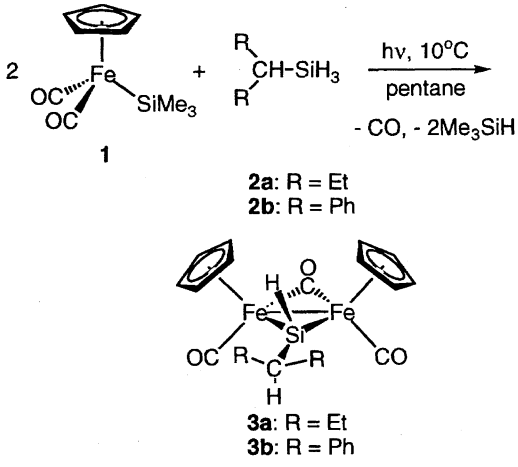
Preparation of $Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(I)CHPh_2]$ (4b). The procedures are similar to those of the preparation of **4a**. The *cis*-**3b** (0.29 g, 0.56 mmol) was used. After stirring at room temperature for 48 h, the red crude product was purified by silica gel flash chromatography with toluene/hexane = 3 : 1 as eluent to give 35 mg (0.115 mmol, 20%) of black FpI and 65 mg (0.10 mmol, 18%) of red *cis*-$Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(I)CHPh_2]$ (**4b**). IR (toluene, cm^{-1}) 1979 (vs, ν_{CO_t}), 1942 (m, ν_{CO_t}), 1786 (s, ν_{CO_b}); ^{1}H NMR (C_6D_6) δ = 4.15 (s, 10H, $-C_5H_5$), 4.93 (s, 1H, $-CH$), 7.14 (t, 2H, H_{para}), 7.24 (t, 4H, H_{meta}), 7.79 (d, 4H, H_{ortho}); ^{13}C NMR (C_6D_6) δ = 57.5 (s, –CH), 87.9 (s, $-C_5H_5$), 126.3, 128.5, 129.8, 143.5 (phenyl region), 212.0 (s, CO_t), 270.5 (s, CO_b); ^{29}Si NMR (C_6D_6) δ = 246.1 (s). Mass (FAB, Xe, *m*-nitrobenzyl alcohol matrix) 648 (M^+; 20), 620 (M^+-CO; 13), 592 (M^+-2CO; 100), 564 (M^+-3CO; 8), 521 (M^+-I, 3). Found: C, 48.15; H, 3.45%. Calcd for $C_{26}H_{21}Fe_2IO_3Si$: C, 48.18; H, 3.27%.

Preparation of $Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(DMAP)CHPh_2]^+I^-$ (5b). In an NMR tube, 1 cm^3 of CD_3CN was transferred to the mixture of complex **4b** (20.3 mg, 31.4 μmol) and DMAP (4.0 mg, 33 μmol) under vacuum and then sealed by flame. The reaction was monitored by ^{1}H NMR. The starting material dissolved gradually and was consumed completely after the solution was heated at 40 °C for 80 h, then it was cooled to −60 °C for 2 d. After opening the sealed tube in the glove box, the supernatant fluid was removed by a syringe and the red precipitate was washed with Et_2O (1 $cm^3 \times 2$) and dried under vacuum to give 10.3 mg (13.5 μmol) of $Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(DMAP)CHPh_2]^+I^-$ (**5b**) in 43 % yield. IR (KBr, cm^{-1}) 1969 (s, ν_{CO_t}), 1933 (m, ν_{CO_t}), 1760 (s, ν_{CO_b}); ^{1}H NMR (CD_3CN) δ = 3.17 (s, 6H, $-N(CH_3)$), 4.94 (s, 10H, $-C_5H_5$), 5.12 (s, 1H, –CH), 6.65 8.16 (d, 2H×2, pyridine ring), 7.29 (t, 2H, H_{para}), 7.38 (t, 4H, H_{meta}), 7.52 (d, 4H, H_{ortho}); ^{13}C NMR (CD_3CN) δ = 40.2 (s, $-N(CH_3)$), 61.4 (s, –CH), 86.8 (s, $-C_5H_5$), 106.6, 146.9, 156,7 (pyridine ring), 127.2, 129.8, 129.9, 143.8 (phenyl ring), 212.7 (s, CO_t), 269.9 (s, CO_b); ^{29}Si NMR (CD_3CN) δ = 245.3 (s). Found: C, 51.57; H, 4.38; N, 3.80%. Calcd for $C_{33}H_{31}Fe_2IN_2O_3Si$: C, 51.46; H, 4.06; N, 3.64%.

X-Ray Structure Analysis. The single crystals of complexes **3b** and **4b** were grown by a slow evaporation method in a mixture of benzene and hexane. The single-crystal X-ray diffraction measurements were performed on a Nonius CAD-4 automated diffractometer using graphite-monochromated Mo $K\alpha$ 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 $I_0 > 2.0\sigma(I_0)$ 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 Ψ 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 hydrogen atoms were placed isotropically at their calculated positions (C–H = 1.00 Å) and fixed in the calculations. Atomic scattering factor curves f_0, $\Delta f'$, and $\Delta f''$ of Fe, Si, O, and C and f_0 of H were taken from International Tables.[13] Crystal data and structure refinement details are summarized in Table 2. Selected bond lengths and angles for **3b** and **4b** are given in Tables 3 and 4, respectively. The tables of the bond distances and angles, the anisotropic temperature factors for non-hydrogen atoms, the atomic coordinates and the structural factors are deposited as Document No. 70033 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Preparation of Silylene-Bridged Diiron Complexes and Their Properties. Photolysis of 2 molar amounts of $FpSiMe_3$ with R_2CHSiH_3 produces the silylene-bridged diiron complexes $Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(H)CHR_2]$ (**3a**: R=Et; **3b**: R=Ph) in 70 and 62% yields, respectively (Eq. 1).



(1)

These complexes have been characterized by spectroscopic methods and mainly exist in *cis*-form because only

Table 1. Activation Parameters for *cis*⇌*trans* Isomerization of Complexes **3**[a] in C_6D_6

	3a		**3b**	
	cis → *trans*	*trans* → *cis*	*cis* → *trans*	*trans* → *cis*
$\Delta H^{\ddagger}$/kJ mol^{-1}	80.2±4.8	82.7±2.0	58.1±4.6	63.5±5.1
$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	−74.6±15.5	−42.4±16.4	−140.5±14.8	−115.1±16.5
$\Delta G^{\ddagger}_{298}$/kJ mol^{-1}	102.4±9.4	95.3±3.9	99.9±9.0	97.8±10.0
E_a/kJ mol^{-1}	82.8±4.8	85.3±2.0	60.7±4.5	66.0±5.1

a) The average molar ratio of the *cis* and *trans* isomers in the thermal equilibrium is 95 : 5 for **3a** and 75 : 25 for **3b**.

Table 2. Crystal Data and Refinement Details for Complexes $Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(H)CHPh_2]$ (**3b**) and $Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(I)CHPh_2]$ (**4b**)

Complex	**3b**	**4b**
Formula	$C_{26}H_{22}Fe_2O_3Si$	$C_{26}H_{21}Fe_2IO_3Si$
FW	522.24	648.13
Diffratometer used	Nonius	Nonius
Space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$
a/Å	6.689(3)	7.933(2)
b/Å	9.206(2)	15.968(2)
c/Å	19.743(5)	19.842(3)
α/deg	97.38(2)	
β/deg	96.25(3)	96.17(2)
γ/deg	106.10(2)	
V/Å^3	1145.0(6)	2498.8(9)
Z	2	4
D(calcd)/g cm^{-3}	1.515	1.732
λ/Å	0.7093	0.7093
F(000)	536	1280
2θ range/deg	15.54 — 21.60	15.32 — 34.43
Scan type	$\theta/2\theta$	$\theta/2\theta$
Scan width/deg	2(0.55+0.51tan θ)	2(0.70+0.35tan θ)
Scan speed/deg min^{-1}	1.65 — 16.48	1.48 — 8.42
2θ(max)	50.0	50.0
hkl ranges	$-7<h<7$	$-9<h<9$
	$0<k<10$	$0<k<18$
	$-23<l<23$	$0<l<23$
μ/cm^{-1}	13.43	24.56
Crystal size/mm	0.66×0.09×0.31	0.25×0.31×0.47
Transmission	0.969 — 1.000	0.831 — 1.000
Temperature/K	298	298
No. of measured reflections	4284	4719
No. of observed reflections ($I>2.0\sigma(I)$)	2880	3518
No. of unique reflections	4010	4380
R_f; R_w	0.034; 0.036	0.027; 0.035
GOF	1.37	1.72
Refinement program	NRCVAX	NRCVAX
No. of atoms	54	54
No. of refined parameters	290	298
The weight modifier K in KF_o^2	0.0001	0.0001
$(\delta/\sigma)_{max}$	0.002	0.001
(D-map) max; min/ e Å^{-3}	−0.24; 0.42	−0.72; 0.64

one Cp resonance was observed in the ^{1}H and ^{13}C NMR spectra, respectively, and the terminal CO stretching bands of the IR spectrum assigned to the symmetric vibration is stronger than the antisymmetric one.[14] However, monitoring the photolytic reaction in C_6D_6 by ^{1}H NMR spectra also revealed the formation of the *trans*-**3**, which exhibited two resonances of the Cp rings. Both of the *trans*-**3** are very soluble in nonpolar solvents, such as pentane and hexane, and easily isomerize to *cis*-form thermally. In the case of *trans*-**3a**, it is too sensitive to be isolated. As for *trans*-**3b**, it is less air sensitive than *trans*-**3a** and can be isolated by flash chromatography from the mother liquor but decomposes gradually into an unidentified yellow complex, even when it is kept under nitrogen at low temperature. The ^{1}H and ^{13}C NMR spectra show that

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(H)CHPh_2]$ (**3b**)

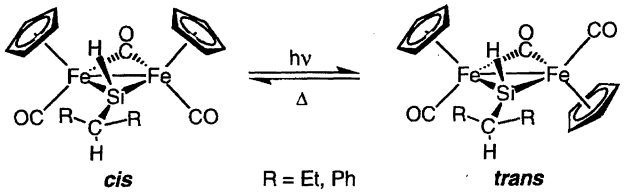
Bond lengths			
Fe(1)–Fe(2)	2.621(1)	Fe(1)–Si	2.257(1)
Fe(2)–Si	2.267(1)	Fe(1)–C(11)	1.918(4)
Fe(2)–C(11)	1.912(4)	Fe(1)–C(12)	1.739(4)
Fe(2)–C(13)	1.737(4)	Si–C(14)	1.910(4)
C(11)–O(11)	1.186(4)	C(12)–O(12)	1.149(5)
C(13)–O(13)	1.152(5)		
Bond angles			
Fe(1)–Fe(2)–Si	54.42(3)	Fe(2)–Fe(1)–Si	54.78(3)
Fe(1)–Si–Fe(2)	70.80(4)	Fe(1)–Fe(2)–C(11)	46.9(1)
Fe(2)–Fe(1)–C(11)	46.7(1)	Fe(1)–C(11)–Fe(2)	86.4(2)
Fe(1)–Si–C(14)	124.3(1)	Fe(2)–Si–C(14)	122.0(1)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(I)SHPh_2]$ (**4b**)

Bond lengths			
Si–I	2.526(1)	Fe(1)–Fe(2)	2.629(1)
Fe(1)–Si	2.262(1)	Fe(2)–Si	2.263(1)
Fe(1)–C(1)	1.754(4)	Fe(2)–C(2)	1.734(4)
Fe(1)–C(3)	1.925(4)	Fe(2)–C(3)	1.926(4)
Si–C(4)	1.926(3)	C(1)–O(1)	1.145(5)
C(2)–O(2)	1.148(4)	C(3)–O(3)	1.181(5)
Bond angles			
Fe(1)–Fe(2)–Si	54.47(3)	Fe(2)–Fe(1)–Si	54.49(3)
Fe(1)–Si–Fe(2)	71.04(3)	Fe(1)–Fe(2)–C(3)	46.9(1)
Fe(2)–Fe(1)–C(3)	47.0(1)	Fe(1)–C(3)–Fe(2)	86.1(2)
Fe(1)–Si–C(4)	121.1(1)	Fe(2)–Si–C(4)	124.1(1)
Fe(1)–Si–I	119.62(4)	Fe(2)–Si–I	116.39(4)
I–Si–C(4)	103.4(1)		

two Cp rings and two phenyl groups are nonequivalent, as it was expected. The trace amount of Fp_2 was also isolated in both cases. The formation of **3** from the photolysis of $FpSiMe_3$ with R_2CHSiH_3 would be explained by the mechanism proposed previously.[7] The photolysis of FpMe instead of $FpSiMe_3$ with R_2CHSiH_3 formed Fp_2 in a large amount and the reaction was not straightforward.

The *cis* and *trans* isomers of complexes **3a** and **3b** were found to undergo interconversion both thermally and photochemically (Eq. 2).



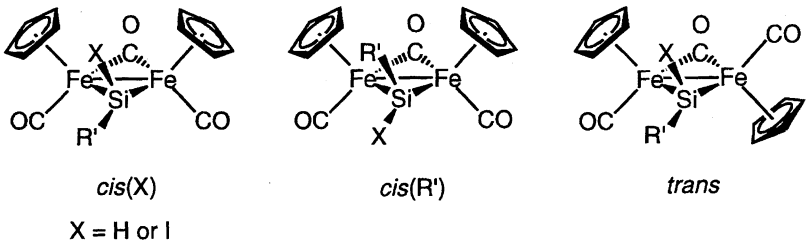
(2)

Starting from the pure *cis*-**3**, the ratios of the *cis* and *trans* isomers changed with time during irradiation, and the final *cis* : *trans* ratio in the photostationary state was 80 : 20 for **3a** and 30 : 70 for **3b**. Table 1 shows the activation parameters of thermal *cis*→*trans* and *trans*→*cis* isomerization of complexes **3**, which were obtained from the measurement of ^1H NMR spectral change of the resonances of Cp rings and methine proton in C_6D_6 at 50, 45, 40, 35, 30, and 25 °C.

These results indicate that the *cis* isomers are thermodynamically more stable than the *trans* isomers because of the smaller steric repulsion between two Cp rings and the R_2CH group on the silicon atom. On the other hand, the large negative activation entropies imply that the isomerization proceeds via cleavage of Fe–(μ-CO) and Fe–Fe bonds, followed by coordination of solvent to the coordinatively unsaturated Fe center, as was proposed for the isomerization mechanism of $Cp^*_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(H)p\text{-}Tol]$ (**6**)[7c] and $Cp_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}CH_2)$.[15] The behavior of **3a** is different from that of **3b**, in which the *cis* isomer is always dominating thermally and photochemically and the absolute values of negative activation entropies are smaller, apparently due to the larger steric repulsion between 3-pentyl group and Cp rings.

The signal of ^{29}Si NMR of *cis*-**3** appears at remarkably low fields, δ=237.2 for **3a** and 226.1 for **3b**. This behavior is similar to those of reported silylene-bridged diiron complexes with Fe–Fe bond, such as $Cp_2(CO)_2Fe_2(\mu\text{-}SiMe_2)_2$,[16] δ=229.5 (*trans* isomer), 243.8 (*cis* isomer); three isomers of $Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}SiMe(SiMe_3)]$ (**7**),[16] δ=232.1, 242.7, 245.5; **6**, δ=235.5 (*trans* isomer), 250.4 (*cis* isomer);[7c] $Cp_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}SiHR)$ R=*t*-Bu (**8a**), δ=254.4; R=$(CMe_2)_2$H (**8b**), δ=255.1; $Cp_2(CO)_2Fe_2(\mu\text{-}CO)$-[$\mu$-Si(X)*t*-Bu], X=Cl (**9a**), δ=276.3; X=Br (**9b**), δ=284.8; X=I (**9c**), δ=289.1; X=Me, δ=267.4.[7a]

Three possible geometrical isomers of silyene-bridged diiron complexes are shown in the Scheme 1.[17] Complexes **3a** and **3b** adopted the least sterically hindered *cis*(X)-geometry; the structure of **3b** has been determined by X-ray diffraction. A molecular plot of complex **3b** with atomic numbering sequence is shown in Fig. 1. This complex contains two bridges, one CO and one silylene ligand, and a direct Fe–Fe bond. The two Cp rings are mutually *cis* with the dihedral



Scheme 1. Three possible geometrical isomers of silylene-bridged diiron complexes.

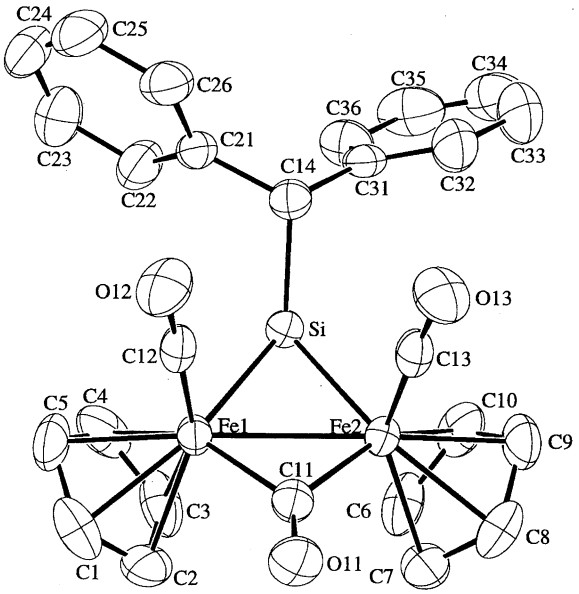
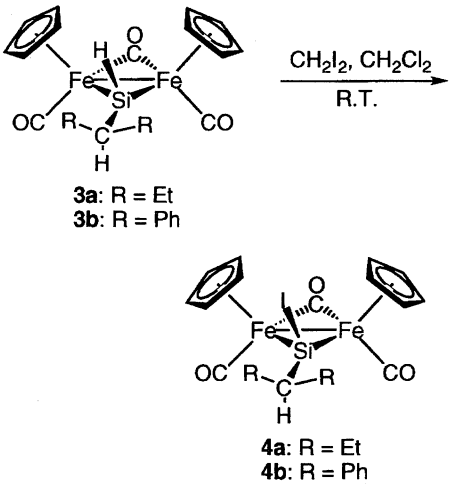


Fig. 1. Molecular plot of $Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(H)\text{-}CHPh_2]$ (**3b**) with the atomic numbering sequence. The thermal ellipsoids are drawn at the 50% level. The H atoms are omitted for clarity.

angle of 92.4° and the bond of C(14)–Si points away from the Cp rings to the opposite side of the plane of Fe(1), Si, and Fe(2). The angle between the C(14)–Si bond and the plane of Fe(1), Si, and Fe(2) is 132.2°. The distortion from ideal tetrahedron (125.3°) is apparently due to the steric repulsion between the Ph_2CH group and CO ligands. The angle of Fe(1)–Si–Fe(2) is 70.80(4)° and the dihedral angle between the Fe_2Si plane and the $Fe_2C(11)$ plane is 18.6(2)°. The Fe–Si bonds [2.257(1) and 2.267(1) Å] are shorter than those of closely related complexes, such as 2.270(1) and 2.272(1) Å in **8a** and 2.294(1) and 2.301(1) Å in **7**. The distance of Fe–Fe is 2.621(1) Å, which is similar to 2.622(1) Å in **7** and slightly longer than 2.614(1) Å n **8a** but significantly longer than those in carbon-bridged analogues 2.531(1) Å in $Cp_2(CO)_2Fe_2(\mu\text{-}CO)_2$[18] and 2.520(2) Å in $Cp_2(CO)_2Fe_2(\mu\text{-}CO)(\mu\text{-}CHMe)$.[19]

Preparation of Iodosilylene-Bridged Diiron Complexes. At room temperature, the iodination reaction of complexes **3** with an excess amount of CH_2I_2 in CH_2Cl_2 produces iodosilylene-bridged diiron complexes $Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(I)CHPh_2]$ (**4a**: R=Et; **4b**: R=Ph) in 58 and 18% yields, respectively (Eq. 3). These complexes are obviously more stable than the corresponding precursor *cis*-**3**, and can be isolated by flash chromatography. The complexes **4** exist exclusively in *cis*-form because only one Cp resonance was observed in the ^1H and ^{13}C NMR spectra, respectively. The assignment is also supported by the pattern of CO stretching bands in IR spectra which is similar to those of the corresponding *cis*-**3**. The chemical shift of ^{29}Si NMR of complexes **4a** and **4b** appears at lower field than that of *cis*-**3**, at δ=266.1 and 246.1, respectively. It is attributable to the decrease of the electron density at Si atom by displacement of hydrogen with iodine. This deshielding effect was also observed in the halogenation of **8a** to **9**.[8b]



(3)

The structure of complex **4b** has been determined by X-ray diffraction, which revealed that **4b** adopts *cis*(X)-geometry. A molecular plot of complex **4b** with an atomic numbering sequence is shown in Fig. 2. To our best knowledge, it is the first example of iodosilylene-bridged diiron complex characterized by X-ray diffraction. This complex has the same core structure as **3b**; one bridging CO, one bridging silylene ligand and a direct Fe–Fe bond. The diheral angle of two Cp rings is 84.33° and the angle between the C(4)–Si bond and the plane of Fe(1), Si, and Fe(2) is 131.5°. The angle of Fe(1)–Si–Fe(2) is 71.04(3)° and the dihedral angle between the Fe_2Si plane and the $Fe_2C(3)$ plane is 16.0°. The steric repulsion between two Cp rings and the substituents on the silylene ligand in **4b** is apparently larger than that in **3b**, but the Fe–Si bonds, the Fe–Fe bond, and the Fe–(μ-CO) bonds in **4b** are very close to those in **3b**. The most significant

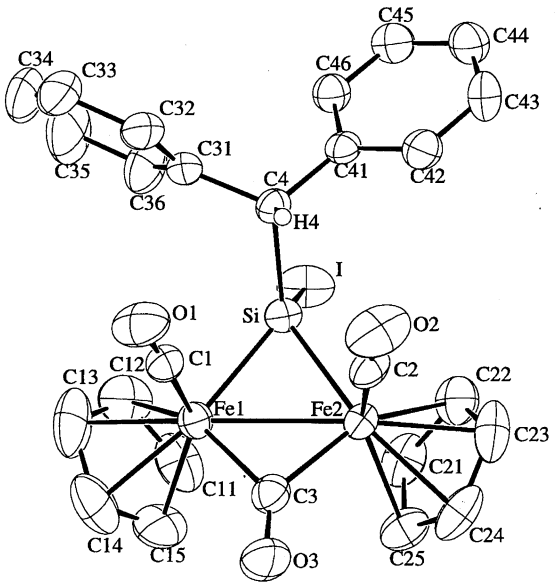
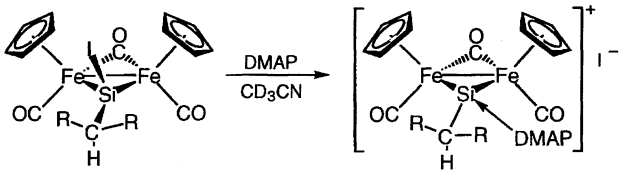


Fig. 2. Molecular plot of $Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(I)\text{-}CHPh_2]$ (**4b**) with the atomic numbering sequence. The thermal ellipsoids are drawn at the 50% level. The H atoms are omitted for clarity.

influence of this repulsion appears in the elongation of the Si–C bond from 1.910(4) Å in **3b** to 1.926(4) Å in **4b** along with the elongation of the Si–I bond [2.526(1) Å], which is substantially longer than averaged bond length 2.46 Å in R_3SiI.[20]

Preparation of Silylyne-Bridged Diiron Complexes. We recently have succeeded in the synthesis of the first base-stabilized silylyne and germylyne (or germanetriyl)-bridged diiron complexes $Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}E(Base)t\text{-}Bu]^+X^-$ (E=Si, Base=NMI and DMAP, X=I; E=Ge, Base=DMAP, X=OTf).[8,21] The structures of these complexes have been determined unequivocally by X-ray diffraction. As for the base-stabilized silylyne complexes with a terminal ≡SiR unit,[22] $[Cp^*(Me_3P)_2RuSi(N\sim N)(S\text{-}p\text{-}Tol)](OTf)_2$ (N∼N=bipyridine and phenanthroline; OTf=CF_3OSO_2) have been synthesized by displacement of two triflate ions with bidentate amines and the base-free silylyne and germylyne-bridged dinuclear complexes, $(OC)_4OsSi(S\text{-}p\text{-}Tol)[RuCp^*(PMe_3)_2]$[23] and $[CpWH(\mu\text{-}GeMe)(\mu\text{-}\eta^5,\eta^1\text{-}C_5H_4GeMe_2)WCp_2]^+OTf^-$[24] along with a base-free molybdenum–germylyne complex, $Cp(CO)_2Mo(GeC_6H_3\text{-}2,6\text{-}Mes_2)$[25] have also been reported.

In a sealed tube, the treatment of complexes **4** with DMAP at 40 °C gave the base-stabilized silylyne-bridged diiron complexes $Cp_2(CO)_2Fe_2(\mu\text{-}CO)[\mu\text{-}Si(DMAP)CHR_2]^+I^-$ (**5a**: R=Et; **5b**: R=Ph) in 35 and 43% yields, respectively (Eq. 4).



4a: R = Et
4b: R = Ph

5a: R = Et
5b: R = Ph

(4)

These complexes have been characterized by spectroscopic methods. The chemical shifts of ^1H NMR of the rings and coordinated DMAP were observed at lower field than those in the corresponding complexes **4** and free DMAP; such results indicate that the positive charge is delocalized over the $SiFe_2C$ four-membered ring and the coordinated DMAP. Since the electron-donating tendency of substitutents at silicon atom decreases in the order: $t\text{-}Bu > Et_2CH > Ph_2CH$, the replacement of neighboring iodine in **9c**, **4a**, and **4b** by a base to form the corresponding base-stabilized silylyne diiron complexes should reveal such an electronic influence. Parallel to the electron-donating tendency, the reaction time is in the following order: **4b**(80h)>**4a**(8h)>**9c**(0.5h).

This work was supported by the Kurata Research Grant from the Kurata Foundation and a Grant-in-Aid for Scientific Research No. 09440245 from the Ministry of Education, Science, Sports and Culture. We are grateful to Shin-Etsu Chemical Co., Ltd., for a gift of silicon compounds.

References

1) T. S. Piper, D. Lemal, and G. Wilkinson, *Naturwissenschaften*, **43**, 129 (1956).

2) a) T. D. Tilley, in "The Silicon-Heteroatom Bond," ed by S. Patai and Z. Rappoport, Willey, New York (1991), Chaps. 9 and 10, p. 245, 309; b) C. Zybill, H. Handwerck, and H. Friedrich, *Adv. Organomet. Chem.*, **36**, 229 (1994); c) H. K. Sharma and K. H. Pannell, *Chem. Rev.*, **95**, 1351 (1995); d) M. D. Curtis and P. S. Epstein, *Adv. Organomet. Chem.*, **19**, 213 (1981); e) J. L. Speier, *Adv. Organomet. Chem.*, **17**, 407 (1977); f) C. S. Cundy, B. M. Kingston, and M. F. Lappert, *Adv. Organomet. Chem.*, **11**, 253 (1973); g) B. J. Aylett, *Adv. Inorg. Chem. Radiochem.*, **25**, 1 (1982); h) U. Schubert, *Transition Met. Chem.*, **16**, 136 (1991).

3) H. Ogino and H. Tobita, *Adv. Organomet. Chem.*, in press and references therein.

4) a) W. A. G. Graham, *J. Organomet. Chem.*, **300**, 81 (1986); b) U. Schubert, *Adv. Organomet. Chem.*, **30**, 151 (1990); c) J. K. Hoyano, M. Elder, and W. A. G. Graham, *J. Am. Chem. Soc.*, **91**, 4568 (1969); d) M. Auburn, M. Ciriano, J. A. K. Howard, M. Murray, N. J. Pugh, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, **1980**, 659; e) C. J. Aitken, J. F. Harrod, and E. Samuel, *J. Am. Chem. Soc.*, **108**, 4059 (1986); f) R. Carreño, V. Riera, M. A. Ruiz, Y. Jeannin, and M. Philoche-Levisalles, *J. Chem. Soc., Chem. Commun.*, **1990**, 15; g) M. D. Fryzuk, L. Rosenberg, and S. J. Rettig, *Organometallics*, **10**, 2537 (1991); i) M. D. Fryzuk, L. Rosenberg, and S. J. Rettig, *Organometallics*, **15**, 2871 (1996); j) M. D. Fryzuk, L. Rosenberg, and S. J. Rettig, *Inorg. Chim. Acta*, **222**, 345 (1994); k) H. Suzuki, T. Takao, M. Tanaka, and Y. Moro-oka, *J. Chem. Soc., Chem. Commun.*, **1992**, 476; l) B. K. Campion, R. H. Heyn, and T. D. Tilley, *Organometallics*, **11**, 3918 (1992); m) R. Simons and C. A. Tessier, *Organometallics*, **15**, 2604 (1996).

5) a) K. A. Brown-Wensley, *Organometallics*, **6**, 1590 (1987); b) W. Büchner, *J. Organomet. Chem. Lib.*, **9**, 409 (1980); c) K. Yamamoto, H. Okinoshima, and J. Kumada, *J. Organomet. Chem.*, **27**, C31 (1971); d) I. Ojima, S. I. Inaba, T. Kogure, and Y. Nagai, *J. Organomet. Chem.*, **55**, C7 (1973); e) M. Kumada, *J. Organomet. Chem.*, **100**, 127 (1975); f) D. Seyferth, M. L. Shannon, S. C. Vick, and T. F. Lim, *Organometallics*, **4**, 57 (1985); g) H. Okinoshima, K. Yamamoto, and M. Kumada, *J. Am. Chem. Soc.*, **94**, 9263 (1972); h) H. Sakurai, Y. Kamiyama, and Y. Nakadaira, *J. Am. Chem. Soc.*, **99**, 3879 (1977); i) E. Hengge and M. Weinberger, *J. Organomet. Chem.*, **443**, 167 (1993).

6) a) C. Zybill, *Top. Curr. Chem.*, **160**, 1 (1991); b) D. D. Lickiss, *Chem. Soc. Rev.*, **1992**, 271.

7) a) Y. Kawano, H. Tobita, and H. Ogino, *J. Organomet. Chem.*, **428**, 125 (1992); b) H. Tobita, Y. Kawano, and H. Ogino, *Chem. Lett.*, **1989**, 2155; c) Y. Kawano, H. Tobita, and H. Ogino, *Organometallics*, **11**, 499 (1992); d) H. Tobita, H. Izumi, S. Ohnuki, M. C. Ellergy, M. Kikuchi, S. Inomata, and H. Ogino, *J. A. Chem. Soc.*, **117**, 7013 (1995).

8) a) Y. Kawano, H. Tobita, and H. Ogino, *Angew. Chem., Int. Ed. Engl.*, **11**, 843 (1991); b) Y. Kawano, H. Tobita, M. Shimoi, and H. Ogino, *J. Am. Chem. Soc.*, **116**, 8575 (1994).

9) D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals," Pergamon Press, Oxford (1981).

10) I. A. Rivero, R. Somanathan, and L. H. Hellberg, *Synth. Commun.*, **23**, 711 (1993).

11) P. Main, in "Crystallographic Computing 3: Data Collection, Structure Determination, Proteins and Databases," ed by G. M.

Sheldrick, C. Krueger, and R. Goddard, Charendon Press, Oxford (1985), pp. 206—215.

12) a) E. J. Gabe, Y. Le Page, P. S. White, and F. L. Lee, *Acta Crystallogr., Sect. A*, **A43**, S294 (1987); b) E. J. Gabe, Y. Le Page, and F. L. Lee, in "Crystallographic Computing 3: Data Collection, Structure Determination, Proteins and Databases," ed by G. M. Sheldrick, C. Krueger, and R. Goddard, Charendon Press, Oxford (1985), pp. 167—174.

13) J. A. Ibers and W. C. Hamilton, "International Tables for X-Ray Crystallography," Vol. 4, Kynoch, Birmingham (1974), Tables 2.2A, 2.3.1D.

14) a) M. D. Curtis and R. C. Job, *J. Am. Chem. Soc.*, **94**, 2153 (1972); b) R. D. Adams, M. D. Brice, and F. A. Cotton, *Inorg. Chem.*, **13**, 1080 (1974).

15) a) R. Korswagen, R. Alt, D. Speth, and M. L. Ziegler, *Angew. Chem., Int. Ed. Engl.*, **20**, 1049 (1981); b) M. I. Altbach, C. A. Muedas, R. P. Korswagen, and M. L. Ziegler, *J. Organomet. Chem.*, **306**, 375 (1986).

16) K. Ueno, N. Hamashima, M. Shimoi, and H. Ogino, *Organometallics*, **10**, 959 (1991).

17) W. Malisch and W. Ries, *Angew. Chem., Int. Ed. Engl.*, **17**, 120 (1978).

18) R. F. Bryan, D. T. Greene, M. J. Newlands, and D. S. Field, *J. Chem. Soc. A*, **1970**, 3068.

19) a) B. B. Meyer, P. E. Riley, and R. E. Davis, *Inorg. Chem.*, **20**, 3024 (1981); b) A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, **1983**, 1427.

20) A. J. Gordon and R. A. Ford, "The Chemist's Companion," John Wiley&Sons, New York (1972), p. 107.

21) J. Fujita, Y. Kawano, H. Tobita, and H. Ogino, *Chem. Lett.*, **1994**, 1353.

22) S. D. Grumbine, R. K. Chadha, and T. D. Tilley, *J. Am. Chem. Soc.*, **114**, 1518 (1992).

23) S. D. Grumbine, T. D. Tilley, and A. L. Rheingold, *J. Am. Chem. Soc.*, **115**, 358 (1993).

24) L. K. Figge, P. J. Carroll, and D. H. Berry, *Angew. Chem., Int. Ed. Engl.*, **35**, 435 (1996).

25) R. S. Simons and P. P. Power, *J. Am. Chem. Soc.*, **118**, 11966 (1996).