

Filtration and cooling the filtrate at  $-30\text{ }^{\circ}\text{C}$  for 3 days yielded yellow crystals of the product (0.065 g, 75%): mp  $144\text{--}146\text{ }^{\circ}\text{C}$ ; mass spectrum ( $65\text{ }^{\circ}\text{C}$ ,  $16\text{ eV}$ )  $\text{M}^+$  (base peak),  $(\text{M} - \text{CO})^+$ ,  $(\text{M} - 2\text{CO})^+$ ,  $(\text{M} - \text{C}_7\text{H}_7)^+$ ,  $\text{C}_7\text{H}_7^+$ . Anal. Calcd for  $\text{C}_{19}\text{H}_{22}\text{O}_2\text{Os}$ : C, 48.29; H, 4.69. Found: C, 48.41; H, 4.81.

**Preparation of  $[(\eta\text{-C}_5\text{H}_5)\text{Os}(\text{CO})_2(\text{CH}_3\text{CN})]\text{BF}_4$  (12).** The hydride  $(\eta\text{-C}_5\text{H}_5)\text{Os}(\text{CO})_2\text{H}$  (0.058 g, 0.19 mmol) was dissolved in 20 mL of  $\text{CH}_3\text{CN}$ , and then  $\text{Ph}_3\text{CPF}_6$  (0.061 g, 0.16 mmol) was added. After the solution was stirred for 30 min, the solvent was evaporated and the residue recrystallized from acetone–ether, giving  $[(\eta\text{-C}_5\text{H}_5)\text{Os}(\text{CO})_2\text{CH}_3\text{CN}]\text{BF}_4$  as an off-white solid (0.065 g, 80%), dec pt  $125\text{--}126\text{ }^{\circ}\text{C}$ . Anal. Calcd for  $\text{C}_9\text{H}_8\text{BF}_4\text{NO}_2\text{Os}$ : C, 24.61; H, 1.84. Found: C, 24.71; H, 1.89.

**Preparation of  $[(\eta\text{-C}_5\text{Me}_5)\text{Os}(\text{CO})_2(\text{THF})]\text{PF}_6$  (13).** The hydride (4) (0.071 g, 0.19 mmol) dissolved in a mixture<sup>33</sup> of 15 mL of  $\text{CH}_2\text{Cl}_2$  and 0.20 mL of THF was treated with  $\text{Ph}_3\text{CPF}_6$  (0.074 g, 0.19 mmol), and the resulting solution was stirred for 30 min. The volume of the mixture was reduced to 2 mL by evaporation, and then 15 mL of  $\text{Et}_2\text{O}$  was slowly added. The resulting pale yellow precipitate was collected, washed with 10 mL of  $\text{Et}_2\text{O}$ , and dried under vacuum. Recrystallization from  $\text{CH}_2\text{Cl}_2\text{--Et}_2\text{O}$  gave  $[(\eta\text{-C}_5\text{Me}_5)\text{Os}(\text{CO})_2\text{THF}]\text{PF}_6$  as an off-white solid (0.070 g, 63%), dec pt  $101\text{--}103\text{ }^{\circ}\text{C}$ . Anal. Calcd for  $\text{C}_{16}\text{H}_{23}\text{F}_6\text{O}_3\text{OsP}$ : C, 32.11; H, 3.87. Found: C, 32.46; H, 3.65.

**Preparation of  $[(\eta\text{-C}_5\text{H}_5)\text{Os}(\text{CO})_3]\text{BF}_4$  (16).** Anomalies in the reactions of one commercial sample of  $\text{Ph}_3\text{CBF}_4$  were cleared up when it was shown by  $^1\text{H NMR}$  to contain 1 mol of  $\text{H}_2\text{O}$  (to the limits of accuracy of the integration). Only a trace of the expected  $\text{Ph}_3\text{COH}$  hydrolysis product was observed. A solution of  $(\eta\text{-C}_5\text{H}_5)\text{Os}(\text{CO})_2\text{H}$

(0.225 g, 0.72 mmol) in 25 mL of  $\text{CH}_2\text{Cl}_2$  was added over 45 min to a sample of  $\text{Ph}_3\text{CBF}_4\cdot\text{H}_2\text{O}$  (0.255 g, 0.73 mmol) in 5 mL of  $\text{CH}_2\text{Cl}_2$ . The resulting yellow solution on the basis of spectroscopic results (Table I and text) contained  $[(\eta\text{-C}_5\text{H}_5)\text{Os}(\text{CO})_2(\text{OH}_2)]\text{BF}_4$  (15), but attempted isolation led only to pale yellow oils or tars. The solution was placed in the 500-mL stainless steel autoclave, pressurized to 210 atm with CO, and heated at  $40\text{ }^{\circ}\text{C}$  for 20 h. After cooling and depressurization, the contents of the bomb were removed, evaporated to dryness, and washed with 50 mL of  $\text{Et}_2\text{O}$ . The solid was recrystallized from acetone– $\text{Et}_2\text{O}$  to afford  $[(\eta\text{-C}_5\text{H}_5)\text{Os}(\text{CO})_3]\text{BF}_4$  as colorless crystals (0.150 g, 60%), dec pt  $>315\text{ }^{\circ}\text{C}$ . Anal. Calcd for  $\text{C}_8\text{H}_5\text{BF}_4\text{O}_3\text{Os}$ : C, 22.55; H, 1.18. Found: C, 22.48; H, 1.29.

The aquo cation is a necessary intermediate in this synthesis. No 16 was formed when 3 was treated with water-free  $\text{Ph}_3\text{CPF}_6$  in the presence of CO at 1 atm. Furthermore, when a  $\text{CH}_2\text{Cl}_2$  solution of  $\text{Ph}_3\text{CPF}_6$  and 4 in equimolar properties was subjected to high-pressure CO, only a small amount of 17 was formed.

**Preparation of  $[(\eta\text{-C}_5\text{Me}_5)\text{Os}(\text{CO})_3]\text{BF}_4$  (17).** The preparation was similar to that for 16, except for the final recrystallization of the product, which was performed from a minimum volume of  $\text{CH}_2\text{Cl}_2$ : yield 90%, dec pt  $>310\text{ }^{\circ}\text{C}$ . Anal. Calcd for  $\text{C}_{13}\text{H}_{15}\text{BF}_4\text{O}_3\text{Os}$ : C, 31.46; H, 3.05. Found: C, 31.86; H, 3.04.

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**Registry No.** 1, 81554-88-3; 2, 81554-89-4; 3, 42442-16-0; 4, 81554-96-3; 5, 81571-96-2; 6, 81554-97-4; 7, 81554-98-5; 8, 81571-98-4; 9, 81555-00-2; 10, 81555-01-3; 11, 81555-02-4; 12, 81555-04-6; 13, 81554-80-5; 14, 81554-82-7; 15, 81554-84-9; 16, 81554-85-0; 17, 81554-87-2;  $(\text{CO})_4\text{OsBr}_2$ , 14878-21-8;  $\text{Os}_3(\text{CO})_{12}$ , 15696-40-9;  $(\text{C}_5\text{H}_6)_2$ , 21423-86-9.

(33) Pure THF was unsatisfactory as the solvent because of a reaction with  $\text{Ph}_3\text{CPF}_6$  that led to darkening. Use of a dilute  $\text{CH}_2\text{Cl}_2$  solution avoids this problem.

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## Reactivity of $\mu$ -Silanediyl Iron Carbonyl Complexes with Alkynes. Molecular Structure of $(\text{CO})_4\text{FeSiPh}_2\text{CET}=\text{CETSiPh}_2$ and of $(\text{CO})_3\text{FeCMe}=\text{CMeSiPh}_2\text{CMe}=\text{CMeFe}(\text{CO})_3$

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The diiron complex  $[\text{Fe}_2(\text{CO})_8(\text{SiPh}_2)_2]$  containing two bridging diphenylsilyl ligands has been prepared photochemically by reaction of iron pentacarbonyl and diphenylsilane. A related compound  $[\text{Fe}_2(\text{CO})_7(\text{SiMePh})_2]$  with one bridging carbonyl ligand has been obtained from methylphenylsilane.  $[\text{Fe}_2(\text{CO})_8(\text{SiPh}_2)_2]$  readily reacts with alkynes, yielding new mono- and diiron carbonyl complexes  $(\text{CO})_4\text{FeSiPh}_2\text{CR}=\text{CRSiPh}_2$  ( $\text{R} = \text{Ph}, \text{Et}, \text{Me}$ ) and  $(\text{CO})_3\text{FeCMe}=\text{CMeSiPh}_2\text{CMe}=\text{CMeFe}(\text{CO})_3$ . The crystal structures of two of these new compounds have been determined by X-ray diffraction studies. The complex  $(\text{CO})_4\text{FeSiPh}_2\text{CET}=\text{CETSiPh}_2$  crystallizes in the triclinic space group  $P\bar{1}$  with  $Z = 2$ . The unit cell parameters are  $a = 11.748$  (2) Å,  $b = 17.246$  (3) Å,  $c = 8.602$  (3) Å,  $\alpha = 86.70$  (2)°,  $\beta = 110.94$  (2)°,  $\gamma = 107.68$  (2)°,  $V = 1548$  Å<sup>3</sup>,  $d_{\text{calcd}} = 1.324$  g cm<sup>-3</sup>, and  $d_{\text{obsd}} = 1.32$  (1) g cm<sup>-3</sup>. The molecule has no rigorous element of symmetry. Some of the principal bond lengths are Fe–Si 2.405 (3) and 2.418 (2) Å and Fe–C average 1.782 Å; the angle Si–Fe–Si' is 81.92 (2)°. The compound  $(\text{CO})_3\text{FeCMe}=\text{CMeSiPh}_2\text{CMe}=\text{CMeFe}(\text{CO})_3$  crystallizes in the monoclinic system. The crystallographic parameters are as follows: space group  $P2_1/c$ ,  $a = 11.163$  (3) Å,  $b = 16.191$  (2) Å,  $c = 15.165$  (3) Å,  $\beta = 109.02$  (2)°,  $V = 2591$  Å<sup>3</sup>,  $Z = 4$ ,  $d_{\text{calcd}} = 1.461$  g cm<sup>-3</sup>,  $d_{\text{obsd}} = 1.45$  (1) g cm<sup>-3</sup>. The molecule has an approximate twofold axis. The important bond lengths are Fe–Fe' 2.517 (1) Å, Fe–C(CO) average 1.785 Å, Fe–C( $\sigma$  bonded) average 2.003 Å, and Fe–C( $\pi$  bonded) 2.093 (5)–2.191 (4) Å. The structures were solved by the heavy-atom method and refined by full-matrix least squares to  $R = 0.047$  and 0.038, respectively, for 1962 and 2105 independent observed data.

### Introduction

Our current interest in the use of organosilyl–transition metal complexes in organic synthesis<sup>1,2</sup> led us to investigate the reactivity of these complexes with organic molecules. The silicon–transition metal bond is usually very stable. It can be cleaved by nucleophiles or electrophiles.<sup>3</sup> Since we were

interested in more reactive silicon–metal bonds, we set out to prepare dinuclear complexes containing  $\mu\text{-SiR}_2$  ligands. Only a few complexes of this type have been reported, and little attention has been paid to their chemical reactivity.<sup>4,5</sup> We

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wish to report here the reaction of a  $\mu$ -silanediyl iron carbonyl complex with alkynes and the molecular structure of two of the reaction products.

### Experimental Section

All complexes were handled under air-free conditions with use of standard techniques.<sup>6</sup> Solvents were dried and deoxygenated thoroughly prior to use. Infrared spectra were recorded on a Perkin-Elmer 298 spectrophotometer in the form indicated. The <sup>1</sup>H NMR spectra were measured on a Varian EM 360, chemical shifts  $\delta$  are relative to Me<sub>4</sub>Si. The mass spectra were obtained on a JEOL JMS D100 apparatus. Elemental analyses were carried out by the Service Central de Microanalyse du CNRS. All photochemical reactions were performed at room temperature, with use of an immersed Hanovia 450-W high-pressure mercury lamp in a quartz reaction vessel.

**Synthesis of [Fe<sub>2</sub>(CO)<sub>8</sub>(SiPh<sub>2</sub>)<sub>2</sub>].** A solution containing Ph<sub>2</sub>SiH<sub>2</sub> (13.8 g, 75 mmol) and Fe(CO)<sub>5</sub> (14.7 g, 75 mmol) in 600 mL of dry degassed hexane was irradiated with an immersed 450 W high-pressure mercury lamp. Insoluble orange crystals appeared rapidly. After 20 h, the orange crystals were allowed to settle, and the solution was removed by filtration under nitrogen. The crystals were washed three times with 70 mL of dry degassed hexane and dried in vacuo. The yellow-orange crystalline [Fe<sub>2</sub>(CO)<sub>8</sub>(SiPh<sub>2</sub>)<sub>2</sub>] (14.2 g, 54%) was collected under nitrogen and stored in the cold; mp 151–154 °C. Anal. Calcd for C<sub>32</sub>H<sub>20</sub>O<sub>8</sub>Si<sub>2</sub>Fe<sub>2</sub>: C, 54.9; H, 2.9; Fe, 16.0. Found: C, 54.6; H, 3.1; Fe, 16.3. IR (Nujol):  $\nu$ (CO) 2040, 2005, 1940 cm<sup>-1</sup>. Mass spectrum: parent ion M<sup>+</sup> centered at  $m/e$  700 (very weak) followed by successive loss of eight carbonyl groups.

**Synthesis of [Fe<sub>2</sub>(CO)<sub>7</sub>(SiMePh)<sub>2</sub>].** As for the previous preparation, PhMeSiH<sub>2</sub> (10.0 g, 82 mmol) and Fe(CO)<sub>5</sub> (16.0 g 82 mmol) in 600 mL of hexane were exposed to UV light for 15 h. The yellow-orange crystals were washed with hexane, dried, and collected, yielding Fe<sub>2</sub>(CO)<sub>7</sub>(SiMePh)<sub>2</sub> (9.8 g, 22%), mp 198–200 °C. Anal. Calcd for C<sub>21</sub>H<sub>16</sub>O<sub>7</sub>Si<sub>2</sub>Fe<sub>2</sub>: C, 46.0; H, 2.9. Found: C, 45.8; H, 3.0. IR (Nujol):  $\nu$ (CO) 2040, 1995, 1950, 1820 cm<sup>-1</sup>. NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.5 (5, br m), 0.3 (2, br s). Mass spectrum: parent ion M<sup>+</sup> centered at  $m/e$  548 followed by successive loss of seven carbonyl groups.

**Reaction of [Fe<sub>2</sub>(CO)<sub>8</sub>(SiPh<sub>2</sub>)<sub>2</sub>] with Triphenylphosphine.** A solution of [Fe<sub>2</sub>(CO)<sub>8</sub>(SiPh<sub>2</sub>)<sub>2</sub>] (0.9 g, 1.3 mmol) and PPh<sub>3</sub> (0.68 g, 1.3 mmol) in 20 mL of dry degassed toluene was heated at 80 °C for 10 h, giving a bright red solution. The solvent was then removed in vacuo and the residue dissolved in 20 mL of dichloromethane. Then 40 mL of hexane was added and the mixture allowed to stand at -30 °C. The red crystals were washed with pentane and recrystallized from toluene, giving 0.95 g (62%) of [Fe<sub>2</sub>(CO)<sub>6</sub>(PPh<sub>3</sub>)<sub>2</sub>(SiPh<sub>2</sub>)<sub>2</sub>], mp 195 °C. Anal. Calcd for C<sub>66</sub>H<sub>50</sub>O<sub>6</sub>P<sub>2</sub>Si<sub>2</sub>Fe<sub>2</sub>: C, 67.8; H, 4.3. Found: C, 68.0; H, 4.6. IR (Nujol):  $\nu$ (CO) 1965, 1955, 1945, 1875 cm<sup>-1</sup>.

**Reaction of [Fe<sub>2</sub>(CO)<sub>8</sub>(SiPh<sub>2</sub>)<sub>2</sub>] with Diphenylacetylene.** A solution containing [Fe<sub>2</sub>(CO)<sub>8</sub>(SiPh<sub>2</sub>)<sub>2</sub>] (0.9 g, 1.3 mmol) and PhC≡CPh (0.23 g, 1.3 mmol) in 20 mL of toluene was refluxed for 1 h. The volume of the solvent was reduced to 5 mL and the solution allowed to stand at 0 °C. The brown crystals were recrystallized from toluene, giving (CO)<sub>4</sub>FeSiPh<sub>2</sub>CPh=CPhSiPh<sub>2</sub> (0.55 g, 60%) as off-white crystals, mp 219–220 °C. Anal. Calcd for C<sub>42</sub>H<sub>30</sub>O<sub>4</sub>Si<sub>2</sub>Fe: C, 71.0; H, 4.25. Found: C, 70.8; H, 3.9. IR (Nujol):  $\nu$ (CO) 2100, 2015, 1995 cm<sup>-1</sup>. NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.6 (4, m), 7.3 (6, m), 6.85 (5, br s). Mass spectrum: parent ion M<sup>+</sup> centered at  $m/e$  710 and successive loss of four carbonyl groups.

**Reaction of [Fe<sub>2</sub>(CO)<sub>8</sub>(SiPh<sub>2</sub>)<sub>2</sub>] with Hex-3-yne.** A solution containing [Fe<sub>2</sub>(CO)<sub>8</sub>(SiPh<sub>2</sub>)<sub>2</sub>] (0.41 g, 0.6 mmol) and an excess 0.5 mL of hex-3-yne in 20 mL of toluene was stirred at room temperature for 2 h and then heated at 60 °C for 30 min. The reaction mixture was pumped to dryness, and the residue was dissolved in 10 mL of toluene. The solution was passed through a short (5 cm) acid alumina column. Elution with toluene gave, after removal of the solvent, a red residue, which was dissolved in 10 mL of hexane. The solution was then allowed to stand at -30 °C. The pale yellow crystals obtained at this stage were recrystallized from hexane, giving (CO)<sub>4</sub>-FeSiPh<sub>2</sub>C≡C≡C≡SiPh<sub>2</sub> (0.24 g, 65%) as colorless crystals, mp 160 °C. Anal. Calcd for C<sub>34</sub>H<sub>30</sub>O<sub>4</sub>Si<sub>2</sub>Fe: C, 66.4; H, 4.9. Found: C,

66.1; H, 4.9. IR (Nujol):  $\nu$ (CO) 2100, 2010, 1990 cm<sup>-1</sup>. NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.85 (4, m), 7.2 (6, m), 2.6 (2.9,  $J$  = 7 Hz), 0.7 (3, t,  $J$  = 7 Hz). Mass spectrum: parent ion M<sup>+</sup> centered at  $m/e$  614 and successive loss of four carbonyl groups.

**Reaction of [Fe<sub>2</sub>(CO)<sub>8</sub>(SiPh<sub>2</sub>)<sub>2</sub>] with But-2-yne.** A solution containing [Fe<sub>2</sub>(CO)<sub>8</sub>(SiPh<sub>2</sub>)<sub>2</sub>] (1.4 g, 2 mmol) and an excess (1 mL) of but-2-yne in 30 mL of toluene was stirred at room temperature for 2 h and then heated up to 60 °C. The reaction mixture was pumped to dryness and the residue dissolved in hot hexane (50 mL). Subsequent concentration and cooling of the hexane solution afforded

colorless crystals of (CO)<sub>4</sub>FeSiPh<sub>2</sub>CMe=CMeSiPh<sub>2</sub> (0.35 g, 30%) and a red filtrate. The filtrate was chromatographed over acid alumina. Elution with a 1:9 CH<sub>2</sub>Cl<sub>2</sub>/hexane mixture allowed separation of a yellow and a red band. The first yellow solution gave, upon concentration, yellow crystals of the known [Fe<sub>2</sub>(CO)<sub>6</sub>(Me<sub>2</sub>C<sub>2</sub>)] complex.<sup>7</sup> The red solution deposited, after concentration and cooling, orange crystals of (CO)<sub>3</sub>FeCMe=CMeSiPh<sub>2</sub>CMe=CMeFe(CO)<sub>3</sub> (0.08 g, 11%), mp 156–158 °C.

(CO)<sub>4</sub>FeSiPh<sub>2</sub>CMe=CMeSiPh<sub>2</sub>: Anal. Calcd for C<sub>32</sub>H<sub>26</sub>O<sub>4</sub>Si<sub>2</sub>Fe: C, 65.5; H, 4.5. Found: C, 65.3; H, 4.4. IR (Nujol):  $\nu$ (CO) 2100, 2060, 2050, 1990 cm<sup>-1</sup>. NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.85 (4, m), 7.2 (6, m), 2.1 (3, s). Mass spectrum: parent ion M<sup>+</sup> centered at  $m/e$  586 and successive loss of four carbonyl groups.

(CO)<sub>3</sub>FeCMe=CMeSiPh<sub>2</sub>CMe=CMeFe(CO)<sub>3</sub>: Anal. Calcd for C<sub>26</sub>H<sub>22</sub>O<sub>6</sub>Si<sub>2</sub>Fe<sub>2</sub>: C, 54.7; H, 3.9; Fe, 19.6. Found: C, 55.3; H, 3.9; Fe, 19.9. IR (Nujol):  $\nu$ (CO) 2060, 2025, 1980 cm<sup>-1</sup>. NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.5 (2, m), 7.2 (3, m), 3.0 (3, s), 1.3 (3, s). Mass spectrum: parent ion M<sup>+</sup> centered at  $m/e$  570 and successive loss of six carbonyl groups and two iron atoms.

**Reactions of (CO)<sub>4</sub>FeSiPh<sub>2</sub>C≡C≡SiPh<sub>2</sub> With Triphenylphosphine.** A solution of the disilylated iron complex (0.6 g, 1 mmol) and triphenylphosphine (0.26 g, 1 mmol) in 70 mL of degassed hexane was exposed to UV light for 12 h. The solution was then concentrated, affording colorless microcrystalline (CO)<sub>3</sub>(Ph<sub>3</sub>P)FeSiPh<sub>2</sub>-C≡C≡C≡SiPh<sub>2</sub> (0.77 g, 91%), mp 202–204 °C. Anal. Calcd for C<sub>51</sub>H<sub>45</sub>O<sub>3</sub>PSi<sub>2</sub>Fe: C, 72.2; H, 5.3. Found: C, 72.6; H, 5.5. IR (Nujol):  $\nu$ (CO) 2020, 1960, 1945 cm<sup>-1</sup>. Mass spectrum: parent ion M<sup>+</sup> centered at  $m/e$  848.

**With Dimethylphenylphosphine.** The procedure was as above, using dimethylphenylphosphine. Colorless crystals of (CO)<sub>3</sub>(Me<sub>2</sub>PhP)-FeSiPh<sub>2</sub>C≡C≡C≡SiPh<sub>2</sub> (0.49 g, 68%) were obtained. Anal. Calcd for C<sub>41</sub>H<sub>41</sub>O<sub>3</sub>PSi<sub>2</sub>Fe: C, 67.9; H, 5.7. Found: C, 68.1; H, 5.9. IR (Nujol):  $\nu$ (CO) 2010, 1955, 1940 cm<sup>-1</sup>. Mass spectrum: parent ion M<sup>+</sup> centered at  $m/e$  724.

**Crystal Preparation.** Crystals of complex 5 were grown by careful evaporation of a degassed heptane solution by a slow stream of nitrogen at room temperature. Preliminary X-ray photography established a triclinic unit cell. A small block cut from a needle was sealed inside a Lindeman glass capillary with the [001] direction parallel to the  $\phi$  axis of the diffractometer.

Compound 7 is extremely soluble in usual solvents like pentane or carbon tetrachloride. In these solvents, very thin plates were obtained by either slow cooling or slow evaporation of concentrated solutions. Solubility is so high in benzene that only an oil could be recovered by the above techniques. However, a benzene solution of complex 7 slowly diluted with methanol by vapor diffusion produced a very large (0.6 × 4 × 4 mm) plate. Weissenberg photographs of a small block cleaved from this plate (mp 131–134 °C) showed a monoclinic system ( $a$  = 20.68 Å,  $b$  = 9.01 Å,  $c$  = 15.06 Å,  $\beta$  = 103°, space group  $P2_1/c$ ,  $V$  = 2734 Å<sup>3</sup>). Unfortunately the crystals stored in vacuo were efflorescent and gave an orange powder, which was identified as complex 7 by mass spectroscopy.

Good-quality crystals (mp 156–158 °C) were eventually grown by slow cooling of a boiling solution of the orange powder in 2-propanol. Weissenberg photography showed again the space group to be  $P2_1/c$ , but with a smaller unit cell ( $V$  = 2591 Å<sup>3</sup>). A unit cell with four molecules of the complex (C<sub>26</sub>H<sub>22</sub>Fe<sub>2</sub>O<sub>6</sub>Si, mol wt 570.2) gives a calculated density of 1.461 g cm<sup>-3</sup>. As measured by flotation in aqueous potassium iodide solution, the density of the crystals is 1.45

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**Table I.** Summary of Crystal Data, Intensity Collection, and Refinement

	$C_{34}H_{30}FeO_4Si_2$	$C_{26}H_{22}Fe_2O_6Si$
formula	$C_{34}H_{30}FeO_4Si_2$	$C_{26}H_{22}Fe_2O_6Si$
cryst system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
<i>a</i> , Å	11.748 (2)	11.163 (3)
<i>b</i> , Å	17.246 (3)	16.191 (2)
<i>c</i> , Å	8.602 (3)	15.165 (3)
$\alpha$ , deg	86.70 (2)	
$\beta$ , deg	110.94 (2)	109.02 (2)
$\gamma$ , deg	107.68 (2)	
vol, Å <sup>3</sup>	1548	2591
mol wt	614.6	570.2
<i>Z</i>	2	4
$d_{\text{calcd}}$ , g cm <sup>-3</sup>	1.324	1.461
$d_{\text{measd}}$ , g cm <sup>-3</sup>	1.32 (1)	1.45 (1)
cryst size, mm <sup>3</sup>	0.31 × 0.25 × 0.10	0.35 × 0.35 × 0.30
cryst color	colorless	orange
recrystn solvent	heptane	2-propanol
mp, °C	160	156–158
method of data collection	moving cryst, moving counter	moving cryst, moving counter
radiation (graphite monochromated)	Mo K $\alpha$	Mo K $\alpha$
$\mu$ , cm <sup>-1</sup>	5.96	11.95
2 $\theta$ limits, deg	6–40	4–44
no. of unique reflcns	2875	3312
no. of obsd reflcns	1962	2105
final no. of variables	379	316
$R_F$	0.047	0.038
$R_{wF}$	0.070	0.056
error of fit	2.18	1.12

$\pm 0.01$  g cm<sup>-3</sup>.<sup>8</sup> A cubic block of approximate edge 0.35 mm was mounted inside a capillary with the [100] direction parallel to the  $\phi$  axis of the goniometer.

**X-ray Data Collection.** Data were collected on a CAD-4 automated diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71069$  Å). For both compounds, lattice constants given in Table I came from a least-squares refinement of 25 reflections obtained at medium and high angles. The intensities of three standard reflections were monitored after intervals of 60 min. In either case, no significant change in their intensities occurred during data collection. The structure amplitudes were obtained after the usual Lorentz and polarization reduction. No absorption corrections were applied because of the relatively small values of  $\mu$ .

Of the 2875 unique reflections recorded with compounds **5**, 1962 were found to have  $\sigma(I)/I < 0.3$  and were employed in solving and refining the structure. A total of 3511 scans including 199 redundant data were measured with compound **7**. Equivalent reflections were averaged to give 2259 unique observed intensities [ $\sigma(I)/I < 0.4$ ].

**Structure Determination and Refinement.** The centric space group ( $P\bar{1}$ ) was initially chosen for the complex  $(CO)_4FeSiPh_2CEt=CEtSiPh_2$ , an assumption supported by the successful refinement of its structure. Iron and silicon atom positions were determined by Patterson methods. The remaining non-hydrogen atoms were located from three successive difference Fourier syntheses. The atomic scattering factors were taken from Doyle and Turner.<sup>9</sup> Two cycles of full-matrix anisotropic refinement of all non-hydrogen atoms converged to  $R = 0.058$ . At this point two disordered positions were introduced for the methyl group C(12). These were given occupancies of 0.65 and 0.35, later refined to 0.63 and 0.37, respectively. The final least-squares cycle gave  $R = 0.047$  and  $R_w = 0.070$  where  $R_w = (\sum w\Delta^2 / \sum wF_o^2)^{1/2}$ ; the weights were derived from the instrument instability constant and the counting statistics. The maximum  $\delta/\sigma$  for the last cycle was 0.04. The final values of the positional atomic parameters are listed in Table II. Lists of anisotropic thermal parameters (Table VIII) and observed and calculated structure factors (Table IX) are available as supplementary material.

The structure of the complex  $(CO)_3FeCMe=CMeSiPh_2-$

**Table II.** Fractional Atomic Coordinates  $\times 10^4$  for Compound **5**<sup>a</sup>

atom	x	y	z
Fe	1759.7 (9)	1516.8 (6)	2891.8 (12)
Si(1)	741.4 (16)	2444.0 (11)	3392.6 (23)
Si(2)	3640.2 (16)	2480.0 (11)	4811.4 (22)
C(1)	2015 (6)	2151 (4)	1299 (10)
O(1)	2180 (5)	2531 (4)	203 (7)
C(2)	1555 (6)	1071 (4)	4757 (10)
O(2)	1382 (5)	764 (3)	5892 (8)
C(3)	235 (8)	885 (5)	1539 (10)
O(3)	-743 (5)	474 (4)	669 (8)
C(4)	2779 (7)	969 (4)	2752 (9)
O(4)	3438 (5)	627 (3)	2608 (7)
C(9)	1965 (6)	3338 (4)	4757 (8)
C(10)	3215 (6)	3360 (4)	5356 (8)
C(11)	1511 (9)	3991 (6)	5252 (12)
C(12)	1586 (15) <sup>b</sup>	4704 (10)	4278 (20)
C(13)	4221 (9)	4103 (6)	6479 (13)
C(14)	5551 (9)	4145 (6)	7303 (13)
C(51)	-128 (6)	2886 (4)	1425 (8)
C(52)	-1474 (6)	2600 (4)	607 (9)
C(53)	-2081 (8)	2962 (5)	-817 (10)
C(54)	-1369 (9)	3613 (6)	-1466 (11)
C(55)	-5 (9)	3902 (5)	-662 (11)
C(56)	575 (7)	3538 (5)	770 (9)
C(61)	-402 (6)	1921 (4)	4480 (9)
C(62)	-1529 (7)	1292 (4)	3705 (9)
C(63)	-2368 (8)	912 (5)	4579 (12)
C(64)	-2008 (9)	1191 (6)	6248 (12)
C(65)	-861 (9)	1791 (5)	7058 (11)
C(66)	-73 (7)	2158 (5)	6153 (9)
C(71)	4275 (5)	1958 (4)	6770 (8)
C(72)	4122 (6)	2147 (4)	8228 (8)
C(73)	4557 (7)	1784 (5)	9717 (10)
C(74)	5147 (7)	1177 (5)	9756 (10)
C(75)	5275 (7)	953 (5)	8308 (11)
C(76)	4838 (6)	1341 (4)	6813 (9)
C(81)	4931 (6)	2911 (4)	3896 (8)
C(82)	4799 (7)	3533 (4)	2763 (9)
C(83)	5712 (8)	3871 (4)	2026 (10)
C(84)	6810 (8)	3607 (5)	2454 (11)
C(85)	6961 (7)	3011 (5)	3585 (11)
C(86)	6030 (7)	2662 (4)	4287 (9)

<sup>a</sup> Estimated standard deviations are in parentheses. <sup>b</sup> Only the atomic position having the occupancy of 0.63 was retained (see text).

$CMe=CMeFe(CO)_3$  was solved by the heavy-atom technique. The atomic positions of the Fe and Si atoms were isotropically refined with fixed thermal parameters. A subsequent difference Fourier map revealed all the oxygen and carbon atoms. Three cycles of full-matrix isotropic refinement gave a residual of  $R = 0.092$ . All the nonhydrogen atoms were then given anisotropic thermal parameters. The scale factor and the positional and thermal atomic parameters were refined by minimizing the function  $\sum w(|F_o| - |F_c|)^2$ , where  $w = [(0.5\sigma(F_o))^2 + (0.05|F_o|)^2]^{-1}$ . After two cycles of least-squares refinement, 154 weak reflections ( $|F_o| < 11.0$ ) were excluded, leaving 2105 data. A very strong reflection, (002), showing extinction effect was given zero weight in the three last cycles of the refinement. The residual  $R$  and  $R_w$  along with the error of fit appear in Table I. The ratios of parameter shifts to standard deviations in the last cycle were less than 0.1. The final atomic coordinates are listed in Table III. Anisotropic thermal parameters (Table X) and a list of observed and calculated structure factors (Table XI) are available as supplementary material.

## Results and Discussion

**Synthesis of  $\mu$ -Silanediyl Iron Carbonyl Complexes.** Hydrosilanes have been shown to react with iron pentacarbonyl to give oxidative addition products.<sup>10</sup> The reaction of dihydrosilanes thus could be a convenient source of iron carbonyl complexes containing bridging silyl ligands. We found that a hexane solution of diphenylsilane and iron pentacarbonyl,

(8) It is likely that the previous crystals, mp 131 °C, contained several benzene molecules per unit cell, but no evidence of this could be given since their density was not measured before decomposition.

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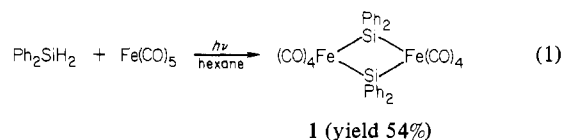
(10) Jetz, W.; Graham, W. A. G. *Inorg. Chem.* **1971**, *10*, 4.

**Table III.** Fractional Atomic Coordinates  $\times 10^4$  for Compound 7<sup>a</sup>

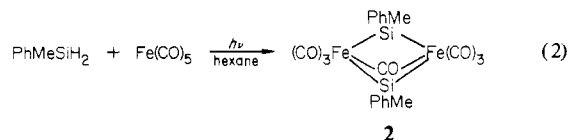
atom	x	y	z
Fe(1)	294.7 (6)	1849.8 (4)	2504.0 (5)
Fe(2)	278.6 (6)	305.6 (4)	2309.9 (4)
Si	3087 (1)	1056 (1)	3011 (1)
C(1)	1124 (5)	2651 (4)	3257 (4)
O(1)	1656 (4)	3169 (3)	3743 (3)
C(2)	-1183 (6)	1844 (4)	2716 (4)
O(2)	-2142 (5)	1862 (4)	2819 (4)
C(3)	-460 (5)	2478 (4)	1503 (4)
O(3)	-933 (4)	2890 (3)	874 (4)
C(4)	-456 (5)	-297 (3)	2983 (4)
O(4)	-961 (4)	-693 (3)	3384 (3)
C(5)	1059 (5)	-529 (3)	1958 (3)
O(5)	1560 (5)	-1060 (3)	1742 (3)
C(6)	-1219 (5)	286 (3)	1405 (3)
O(6)	-2169 (4)	256 (3)	855 (3)
C(7)	977 (4)	1024 (3)	3531 (3)
Me(7)	544 (6)	1008 (4)	4371 (4)
C(8)	1994 (5)	527 (3)	3500 (3)
Me(8)	2530 (6)	-186 (4)	4215 (4)
C(9)	894 (4)	1135 (3)	1577 (3)
Me(9)	374 (5)	1154 (4)	507 (3)
C(10)	1939 (4)	1624 (3)	2053 (3)
Me(10)	2423 (5)	2319 (4)	1574 (4)
C(11)	4237 (4)	1715 (3)	3920 (3)
C(12)	4114 (5)	1875 (4)	4776 (4)
C(13)	4982 (6)	2397 (5)	5423 (5)
C(14)	5981 (6)	2723 (5)	5209 (5)
C(15)	6136 (6)	2558 (5)	4366 (5)
C(16)	5270 (5)	2054 (4)	3711 (4)
C(21)	4076 (4)	373 (3)	2530 (4)
C(22)	3865 (5)	266 (4)	1583 (4)
C(23)	4649 (7)	-236 (5)	1277 (5)
C(24)	5641 (6)	-653 (5)	1908 (6)
C(25)	5864 (7)	-549 (5)	2846 (5)
C(26)	5089 (6)	-49 (4)	3143 (4)

<sup>a</sup> Estimated standard deviations are in parentheses.

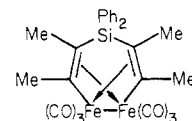
when exposed to UV light, deposited air-sensitive yellow-orange crystals of a  $\mu$ -diphenylsilanediyl iron carbonyl complex **1** (eq 1). The analytical data for compound **1** are consistent with



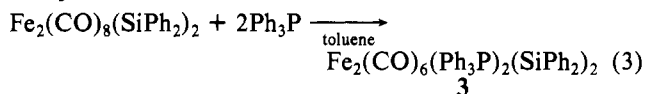
the stoichiometry  $[\text{Fe}_2(\text{CO})_8(\text{SiPh}_2)_2]$ . Its infrared spectrum did not show the presence of a bridging carbonyl ligand as in the case of  $[\text{Fe}_2(\text{CO})_7(\text{GePh}_2)_2]$ .<sup>11</sup> When heated, a solution of **1** in toluene showed the appearance of a bridging carbonyl ligand as monitored by infrared spectroscopy. However, no pure product could be isolated from this solution. The reaction of phenylmethylsilane led to highly air-sensitive yellow-orange crystals of complex **2** in 22% yield (eq 2). Compound **2** has



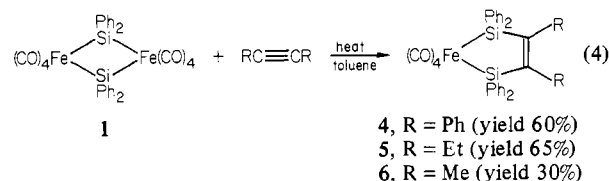
characteristics similar to those of the known  $\mu$ -dimethylsilanediyl complex  $[\text{Fe}_2(\text{CO})_7(\text{SiMe}_2)_2]$ .<sup>5</sup> The <sup>1</sup>H NMR spectrum of compound **2** exhibited a broad singlet for the methyl groups, and we were unable to show the presence of several isomers as demonstrated for  $[\text{Fe}_2(\text{CO})_7(\text{SnMePh})_2]$ .<sup>12</sup>

**Figure 1.** Representation of compound 7.

Complex **1** readily reacted with triphenylphosphine in toluene solution, leading to a bis(triphenylphosphine) complex, **3** (eq 3).



**Reactions of  $\mu$ -Diphenylsilanediyl Iron Carbonyl Complex 1 with Alkynes.** The reaction of disubstituted alkynes with **1** resulted in the formation of disilaferracyclopentenes **4–6** (eq 4). The disilylated iron carbonyl complexes **4–6** are isolated



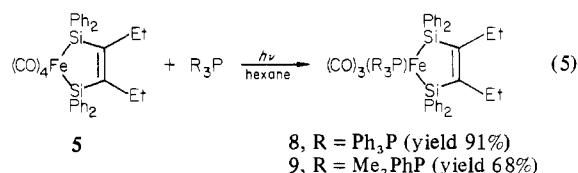
as air stable colorless crystals. The structure of compound **5** was established by X-ray diffraction study (vide infra).

These disilaferracyclopentenes arise probably from an insertion of an alkyne molecule in two iron-silicon bonds causing a cis-silylation of the acetylenic molecule. Analogous metallacycles have been obtained recently by insertion of a carbonylmetal unit into disilacyclobutene.<sup>13,14</sup> A related reaction yielding similar platinum complexes has been mentioned by Eaborn and his co-workers.<sup>15</sup> From reaction 4 the known acetylenic iron carbonyl complexes  $[\text{Fe}_2(\text{CO})_6(\text{R}_2\text{C}_2)_2]$  were also isolated.<sup>7</sup>

The reaction of complex **1** with but-2-yne also allowed recovery of an orange crystalline compound, **7**, which analyzed as  $[\text{Fe}_2(\text{CO})_6(\text{Me}_2\text{C}_2)_2(\text{SiPh}_2)_2]$ . The structure of **7** was determined by a single-crystal X-ray diffraction study (vide infra). As represented in Figure 1, compound **7** is a diferrasilacycloheptadiene in which each carbon-carbon double bond of the divinylsilane unit is coordinated to one iron atom.

The silicon-iron bonds in complex **1** are thus shown to be very reactive. Alkynes readily insert into these bonds, leading to iron complexes containing vinylsilyl ligands. Phenylacetylene ( $\text{PhC}\equiv\text{CH}$ ) also reacted with complex **1**, but only triphenylbenzene, arising from the trimerization of the starting alkyne, was isolated.

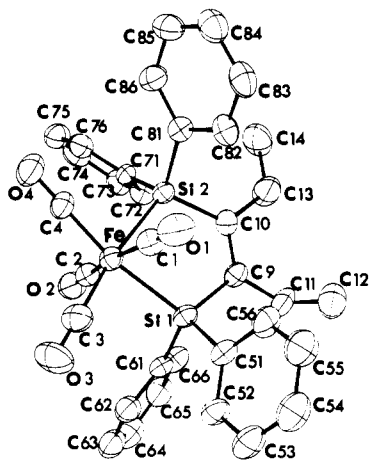
The disilylated iron complexes **4–6** are very stable. They do not exhibit thermal reactivity toward two-electron ligands. However, under photochemical conditions, substitution of one carbonyl group by a phosphine ligand can be achieved. Complex **5** was shown to react with triphenylphosphine and dimethylphenylphosphine, leading to phosphine complexes **8** and **9** in good yields (eq 5).



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(15) Eaborn, C.; Metham, T. N.; Pidcock, A. *J. Organomet. Chem.* **1977**, *131*, 1977.

(11) Elder, M. *Inorg. Chem.* **1969**, *8*, 2703.

(12) Marks, T. J.; Grynkeiwich, G. W. *J. Organomet. Chem.* **1975**, *91*, C9. Grynkeiwich, G. W.; Marks, T. J. *Inorg. Chem.* **1976**, *15*, 1307.



**Figure 2.** ORTEP diagram of  $(\text{CO})_4\text{FeSiPh}_2\text{CET}=\text{CETSiPh}_2$ , showing 40% probability ellipsoids.

**Table IV.** Bond Lengths (Å) and Selected Bond Angles (Deg) in the Ferradisilacyclopentene Moiety for Complex 5 (Esd's in Parentheses)

Fe-Si(1)	2.4049 (26)	Si(2)-C(10)	1.867 (8)
Fe-Si(2)	2.4176 (16)	Si(1)-C(51)	1.891 (7)
Fe-C(1)	1.757 (8)	Si(1)-C(61)	1.886 (8)
Fe-C(2)	1.801 (9)	Si(2)-C(71)	1.882 (7)
Fe-C(3)	1.794 (7)	Si(2)-C(81)	1.890 (8)
Fe-C(4)	1.774 (9)	C(9)-C(10)	1.360 (10)
C(1)-O(1)	1.157 (10)	C(9)-C(11)	1.521 (14)
C(2)-O(2)	1.136 (11)	C(11)-C(12)	1.446 (19)
C(3)-O(3)	1.155 (8)	C(10)-C(13)	1.542 (10)
C(4)-O(4)	1.147 (11)	C(13)-C(14)	1.447 (14)
Si(1)-C(9)	1.865 (6)		
Si(1)-Fe-Si(2)	81.95 (2)	Fe-Si(1)-C(9)	110.10 (26)
Si(1)-Fe-C(4)	169.3 (2)	Fe-Si(2)-C(10)	109.94 (19)
Si(2)-Fe-C(3)	171.6 (4)	Fe-Si(1)-C(51)	113.04 (28)
Si(1)-Fe-C(1)	85.6 (3)	Fe-Si(1)-C(61)	110.17 (25)
Si(2)-Fe-C(1)	87.2 (2)	Fe-Si(2)-C(71)	108.80 (17)
Si(1)-Fe-C(2)	84.2 (3)	Fe-Si(2)-C(81)	112.41 (20)
Si(2)-Fe-C(2)	84.3 (2)	C(51)-Si(1)-C(61)	109.8 (3)
C(3)-Fe-C(4)	100.9 (4)	C(71)-Si(2)-C(81)	109.9 (3)
C(1)-Fe-C(2)	167.5 (4)	Si(1)-C(9)-C(10)	119.2 (6)
Fe-C(1)-O(1)	176.1 (8)	Si(1)-C(9)-C(11)	118.3 (5)
Fe-C(2)-O(2)	177.1 (5)	C(10)-C(9)-C(11)	122.4 (6)
Fe-C(3)-O(3)	179.5 (9)	Si(2)-C(10)-C(9)	118.6 (4)
Fe-C(4)-O(4)	177.5 (7)	Si(2)-C(10)-C(13)	122.6 (6)
		C(9)-C(10)-C(13)	118.8 (8)

Moreover the silicon-iron bonds in complex **5** are very stable. No reaction of this compound with hex-3-yne, either thermally or photochemically, leading to the expected 1,4-disilahexadiene<sup>13</sup> was observed. However we recently showed that the disilyl ligand in complexes **4-6** could be photochemically transferred to nitriles, which in turn can be converted to disilylated aldehyde enamines.<sup>1,2</sup>

**Description of the Structure of Complex 5.** The labeling of the atoms is given in Figure 2. The molecular configuration is best seen in Figure 3. Bond lengths and bond angles are listed in Tables IV and V. The complex possess an imperfect mirror plane going through the iron atom and bisecting the C(9)-C(10) bond. This symmetry is in fact broken by the different conformations of the ethyl groups C(11)-C(12) and C(13)-C(14). The silicon atoms appear to have a normal tetrahedral geometry. Angles around C(9) and C(10) are very close to 120°, the expected value for  $\text{sp}^2$  carbons. The coordinations of the iron atom is octahedral with only mirror distortion, compared to that of complex  $\text{cis-Fe}(\text{CO})_4(\text{SiMe}_3)_2$ .<sup>16</sup> A very large Si-Fe-Si angle (111.8°) was found

**Table V.** Bond Lengths (Å) and Bond Angles (Deg) in the Phenyl Groups for Complex 5 (Esd's in Parentheses)

C(51)-C(52)	1.418 (9)	C(71)-C(72)	1.399 (11)
C(52)-C(53)	1.399 (11)	C(72)-C(73)	1.388 (10)
C(53)-C(54)	1.401 (13)	C(73)-C(74)	1.413 (14)
C(54)-C(55)	1.434 (13)	C(74)-C(75)	1.396 (14)
C(55)-C(56)	1.394 (12)	C(75)-C(76)	1.415 (11)
C(56)-C(51)	1.400 (10)	C(76)-C(71)	1.405 (11)
C(61)-C(62)	1.398 (8)	C(81)-C(82)	1.413 (10)
C(62)-C(63)	1.430 (14)	C(82)-C(83)	1.399 (13)
C(63)-C(64)	1.412 (15)	C(83)-C(84)	1.416 (14)
C(64)-C(65)	1.392 (11)	C(84)-C(85)	1.381 (12)
C(65)-C(66)	1.402 (14)	C(85)-C(86)	1.398 (12)
C(66)-C(61)	1.400 (11)	C(86)-C(81)	1.405 (11)
C(56)-C(51)-C(52)	118.3 (6)	C(76)-C(71)-C(72)	117.7 (6)
C(51)-C(52)-C(53)	120.7 (7)	C(71)-C(72)-C(73)	123.0 (8)
C(52)-C(53)-C(54)	120.6 (7)	C(72)-C(73)-C(74)	118.8 (8)
C(53)-C(54)-C(55)	119.3 (8)	C(73)-C(74)-C(75)	119.7 (8)
C(54)-C(55)-C(56)	119.0 (8)	C(74)-C(75)-C(76)	120.3 (8)
C(55)-C(56)-C(51)	122.1 (7)	C(75)-C(76)-C(71)	120.5 (8)
C(66)-C(61)-C(62)	119.2 (7)	C(86)-C(81)-C(82)	117.5 (7)
C(61)-C(62)-C(63)	120.9 (7)	C(81)-C(82)-C(83)	121.2 (8)
C(62)-C(63)-C(64)	117.5 (7)	C(82)-C(83)-C(84)	119.7 (7)
C(63)-C(64)-C(65)	122.2 (10)	C(83)-C(84)-C(85)	119.5 (9)
C(64)-C(65)-C(66)	118.6 (9)	C(84)-C(85)-C(86)	120.4 (8)
C(65)-C(66)-C(61)	121.6 (6)	C(85)-C(86)-C(81)	121.6 (7)

in this complex, due to repulsion between the trimethylsilyl groups. In complex **5**, the iron atom is part of a ferradisilacyclopentene ring and ring constraints close the Si(1)-Fe-Si(2) angle down to ca. 82°.

As is common in other carbonyl complexes,<sup>17-19</sup> the carbonyl ligands are displaced toward silicon (or germanium). Thus, the angle between the axial carbonyl carbons, C(1)-Fe-C(2), is 167.5 (4)°; the angles between the silicon atoms and the equatorial carbonyl carbons, Si(1)-Fe-C(4) and Si(2)-Fe-C(3), are 169.3 (4) and 171.6 (4)°, respectively. The ferradisilacyclopentene ring is not perfectly planar. Least-squares planes calculations show that the plane defined by iron and the two silicon atoms makes a dihedral angle of 3.1° with the Si(1)-C(9)-C(10)-Si(2) mean plane.

Some similar structural features have also been reported for the compound  $(\text{CO})_4\text{FeC}(\text{O})\text{CET}=\text{CETC}(\text{O})$ ,<sup>20</sup> where the ring is not perfectly planar and the C(O)-Fe-C(O) angle is as low as 81.1°.

The iron-silicon mean bond length, 2.411 (3) Å, is very close to the value observed in  $\text{cis-Fe}(\text{CO})_4(\text{SiMe}_3)_2$ <sup>16</sup> (2.456 (2) Å). The iron-silicon bond lengths observed in halogenosilyl-iron complexes ( $\eta^5\text{-C}_5\text{H}_5$ )Fe(CO)H(SiCl<sub>3</sub>)<sub>2</sub>,<sup>21</sup> 2.252 (3) Å, [Fe(CO)<sub>2</sub>SiCl<sub>3</sub>](NEt<sub>4</sub>),<sup>19</sup> 2.224 (9) Å, and ( $\eta^5\text{-C}_5\text{H}_5$ )Fe(CO)H(SiF<sub>2</sub>Me)<sub>2</sub>,<sup>22</sup> 2.249 (1) Å, are all shorter than the present iron-silicon distance. The mean Fe-C (1.78 (1) Å) and corresponding C-O (1.15 (1) Å) bond lengths for the carbonyl groups do not differ markedly from values obtained in other silyl-substituted iron carbonyls.<sup>16,19,22</sup> Unsatisfactory bond distances is the ethyl groups are probably due to the noninclusion of the hydrogen atoms in the refinement of the structure and to disorder observed for the methyl groups.

**Description of the Structure of Complex 7.** Figure 4 gives a perspective view of the molecule with the numbering of the atoms. Interatomic distances and main bond angles are listed in Tables VI and VII. Although not required by the crys-

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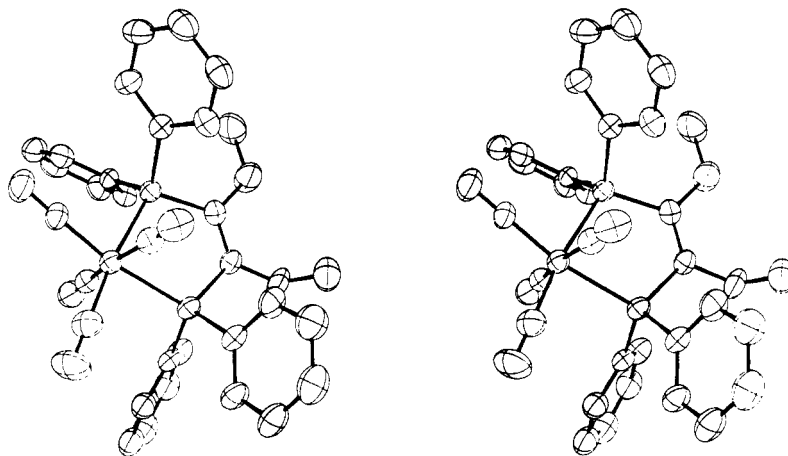


Figure 3. Stereoscopic view of complex 5.

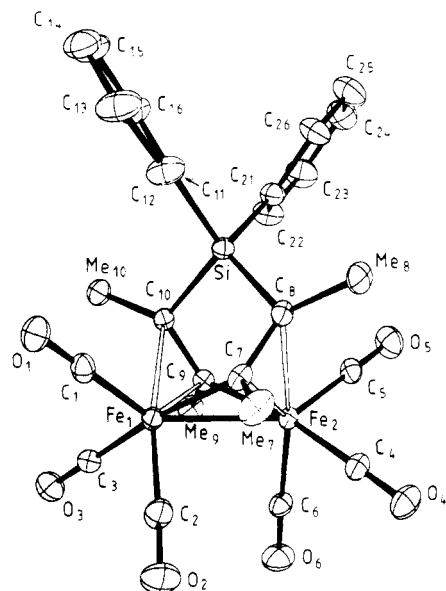


Figure 4. ORTEP representation of  $(\text{CO})_3\text{FeCMe}=\text{CMeSiPh}_2\text{-CMe}=\text{CMeFe}(\text{CO})_3$ . Ellipsoids are at the 20% probability level.

talline arrangement, the complex exhibits nearly exact  $C_2$  symmetry, as shown by Figure 5. The overall geometry is of the helix type with the side  $\text{Fe}(1)\text{-C}(7)\text{-C}(8)\text{-Si}$  equivalent to  $\text{Fe}(2)\text{-C}(9)\text{-C}(10)\text{-Si}$ . Since the binary axis goes through the silicon atom and the middle of the  $\text{Fe}(1)\text{-Fe}(2)$  bond, the

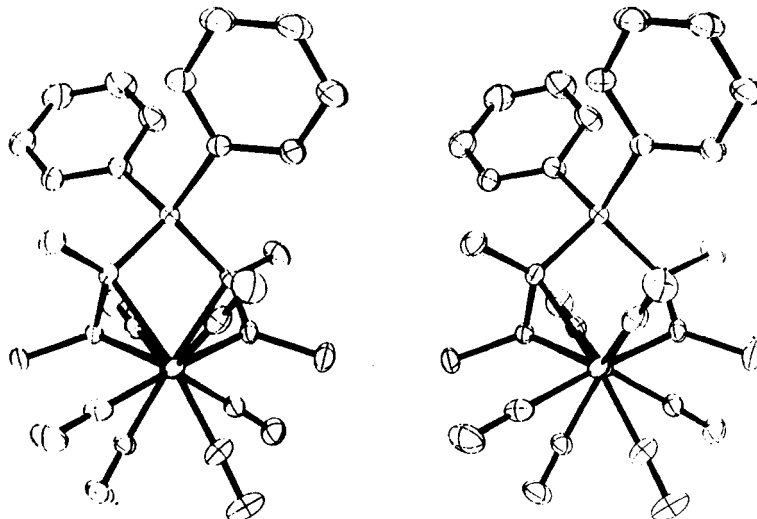


Figure 5. Stereoscopic view of complex 7 down the  $\text{Fe}(1)\text{-Fe}(2)$  axis.

Table VI. Bond Lengths (Å) for Complex 7 (Esd's in Parentheses)<sup>a</sup>

$\text{Fe}(1)\text{-Fe}(2)$	2.5170 (9)		
$\text{Fe}(1)\text{-C}(1)$	1.777 (6)	$\text{Fe}(2)\text{-C}(4)$	1.792 (6)
$\text{Fe}(1)\text{-C}(2)$	1.780 (6)	$\text{Fe}(2)\text{-C}(5)$	1.782 (6)
$\text{Fe}(1)\text{-C}(3)$	1.793 (6)	$\text{Fe}(2)\text{-C}(6)$	1.785 (5)
$\text{Fe}(1)\text{-C}(7)$	2.005 (5)	$\text{Fe}(2)\text{-C}(9)$	2.002 (5)
$\text{Fe}(1)\text{-C}(9)$	2.093 (5)	$\text{Fe}(2)\text{-C}(7)$	2.110 (4)
$\text{Fe}(1)\text{-C}(10)$	2.188 (4)	$\text{Fe}(2)\text{-C}(8)$	2.191 (4)
$\text{Fe}(1)\text{-M}(2)$	2.02	$\text{Fe}(2)\text{-M}(1)$	2.03
$\text{C}(1)\text{-O}(1)$	1.146 (7)	$\text{C}(4)\text{-O}(4)$	1.150 (7)
$\text{C}(2)\text{-O}(2)$	1.132 (7)	$\text{C}(5)\text{-O}(5)$	1.131 (6)
$\text{C}(3)\text{-O}(3)$	1.143 (7)	$\text{C}(6)\text{-O}(6)$	1.116 (6)
$\text{Si-C}(8)$	1.833 (5)	$\text{C}(11)\text{-C}(12)$	1.373 (8)
$\text{Si-C}(10)$	1.839 (5)	$\text{C}(12)\text{-C}(13)$	1.412 (8)
$\text{Si-C}(11)$	1.880 (5)	$\text{C}(13)\text{-C}(14)$	1.367 (10)
$\text{Si-C}(12)$	1.869 (5)	$\text{C}(14)\text{-C}(15)$	1.371 (10)
		$\text{C}(15)\text{-C}(16)$	1.400 (9)
$\text{C}(7)\text{-C}(8)$	1.406 (7)	$\text{C}(16)\text{-C}(11)$	1.403 (8)
$\text{C}(9)\text{-C}(10)$	1.400 (7)	$\text{C}(21)\text{-C}(22)$	1.389 (8)
		$\text{C}(22)\text{-C}(23)$	1.382 (9)
$\text{C}(7)\text{-Me}(7)$	1.502 (7)	$\text{C}(23)\text{-C}(24)$	1.381 (10)
$\text{C}(8)\text{-Me}(8)$	1.563 (7)	$\text{C}(24)\text{-C}(25)$	1.371 (11)
$\text{C}(9)\text{-Me}(9)$	1.535 (6)	$\text{C}(25)\text{-C}(26)$	1.365 (10)
$\text{C}(10)\text{-Me}(10)$	1.531 (7)	$\text{C}(26)\text{-C}(21)$	1.387 (8)

<sup>a</sup>  $\text{M}(1)$  = middle of  $\text{C}(7)\text{-C}(8)$ ;  $\text{M}(2)$  = middle of  $\text{C}(9)\text{-C}(10)$ .

carbonyl ligands and the methyl and phenyl carbon atoms are also related to each other in pairs.

Slight strain is evident in the organosilyl ligand, where the angle at Si is  $99.7^\circ$ , significantly less than the tetrahedral

**Table VII.** Important Bond Angles (Deg) for Complex 7 (Esd's in Parentheses)

C(3)-Fe(1)-C(7)	172.1 (2)	C(4)-Fe(2)-C(9)	170.0 (2)
C(2)-Fe(1)-C(10)	167.5 (2)	C(6)-Fe(2)-C(8)	170.0 (2)
C(2)-Fe(1)-Fe(2)	92.5 (2)	C(6)-Fe(2)-Fe(1)	94.4 (2)
C(1)-Fe(1)-C(7)	90.1 (2)	C(5)-Fe(2)-C(9)	93.0 (2)
C(1)-Fe(1)-C(2)	102.0 (3)	C(5)-Fe(2)-C(6)	100.6 (2)
C(1)-Fe(1)-C(3)	97.6 (3)	C(5)-Fe(2)-C(4)	96.7 (2)
C(1)-Fe(1)-C(10)	90.5 (2)	C(5)-Fe(2)-C(8)	89.4 (2)
C(2)-Fe(1)-C(3)	87.0 (3)	C(6)-Fe(2)-C(4)	86.6 (2)
C(2)-Fe(1)-C(7)	89.8 (3)	C(6)-Fe(2)-C(9)	89.4 (2)
C(7)-Fe(1)-C(9)	91.7 (2)	C(9)-Fe(2)-C(7)	91.3 (2)
C(7)-Fe(1)-C(10)	89.2 (2)	C(9)-Fe(2)-C(8)	89.0 (2)
C(3)-Fe(1)-C(10)	92.4 (2)	C(4)-Fe(2)-C(8)	93.4 (2)
Fe(1)-C(7)-C(8)	117.5 (3)	Fe(2)-C(9)-C(10)	118.1 (3)
Fe(1)-C(7)-Me(7)	121.7 (4)	Fe(2)-C(9)-Me(9)	121.4 (3)
C(8)-C(7)-Me(7)	120.4 (5)	C(10)-C(9)-Me(9)	119.9 (4)
C(7)-C(8)-Si	113.4 (3)	C(9)-C(10)-Si	112.0 (3)
C(7)-C(8)-Me(8)	122.0 (5)	C(9)-C(10)-Me(10)	122.3 (4)
Si-C(8)-Me(8)	118.1 (4)	Si-C(10)-Me(10)	118.6 (3)
C(8)-Si-C(10)	99.7 (2)	C(11)-Si-C(21)	105.8 (2)
C(8)-Si-C(11)	110.7 (2)	C(10)-Si-C(21)	109.6 (2)
C(8)-Si-C(21)	115.9 (2)	C(10)-Si-C(11)	115.4 (2)

angle. The torsion angles between the methyl groups Me(7)-Me(8) and Me(9)-Me(10) are 13.0 and 13.5°, respectively. Moreover, least-squares mean planes through Si, C(8), Me(8), C(7), and Si, C(10), Me(10), C(9) make dihedral angles of 28 and 29.5° with the mean planes C(8), C(7), Me(7), Fe(1) and C(10)-C(9)-Me(9)-Fe(2). Despite this strain, emphasis must be given on the high stability observed; the compound is perfectly air stable in the solid state, and the attempts to obtain crystals suitable for X-ray experiments were all conducted from the same amount of ca. 0.4 g of material. An attempt to grow crystals by sublimation (not described in the Experimental Section) showed a good thermal stability in vacuo up to 180 °C.

It is noteworthy that the Fe(1)-C(7) and Fe(2)-C(9) mean  $\sigma$ -bond length (2.003 Å) is nearly the same as the Fe(1)-M(2) and Fe(2)-M(1)  $\pi$ -coordination distances (2.02 and 2.03 Å).

Carbonyl groups cis or trans to the divinylsilyl ligand do not exhibit marked differences: iron-carbon and carbon-oxygen distances are randomly distributed around the average values 1.785 and 1.136 Å.

The best comparisons can be made with other diiron-hexacarbonyl complexes with analogous bridging ligands.<sup>23</sup> Structure determinations were achieved for two of them with :C=O<sup>24</sup> and :C=CH<sub>2</sub><sup>25</sup> replacing the :SiPh<sub>2</sub> moiety. The molecules of these red-orange complexes have also a non-crystallographic twofold axis. The average of the iron-iron interatomic distances, 2.507 (8) and 2.527 (6) Å, is just the same as the Fe-Fe bond length (2.517 (1) Å) determined in the present work. It is likely that the diphenylsilyl moiety, with an easier deformation of the C(8)-Si-C(10) angle compared with the values of 119 and 111° reported for the :C=O and :C=CH<sub>2</sub> bridged ligands,<sup>24,25</sup> could induce a better coordination geometry. This may account for the high stability of complex 7.

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**Supplementary Material Available:** Listings of anisotropic thermal parameters (Tables VIII and X) and structure factor amplitudes (Tables IX and XI) (28 pages). Ordering information is given on any current masthead page.

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