

Synthesis and Structure of η^4 -1-Functionally Substituted-2,3,4,5-Tetraphenyl-1-Silacyclopentadienyl Complexes of Irontricarbonyl. Crystal Structure of (η^4 -exo-Cyclopentadienyldicarbonyliron-endo-1-Methyl-2,3,4,5-Tetraphenyl-1-Silacyclopentadienyl)Tricarbonyliron

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New silicon-monosubstituted (η^4 -2,3,4,5-tetraphenyl-1-silacyclopentadiene)transition metal complexes are described. The new (silole-transition metal complex)Fe(CO)₃ was obtained from the reaction of silole-transition metal complex and Fe(CO)₃. We have determined the crystal structure of (η^4 -exo-cyclopentadienyldicarbonyliron-endo-1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)tricarbonyliron by using graphite-monochromated Mo-K α radiation. The compound was crystallized in the monoclinic space group *P2₁/c* with *a*=8.925(1), *b*=18.689(3), *c*=19.930(3) Å, and β =102.02(1)°. The iron moiety CpFe(CO)₂ on silicon is in an axial position. The (silole-transition metal complex) Fe(CO)₃ was also prepared through the reaction of (η^4 -1-chloro-2,3,4,5-tetraphenylsilacyclopentadiene)Fe(CO)₃ and metal complex nucleophile. The structure configuration was studied by conventional spectroscopy.

Introduction

Transition metal complexes of nonfunctional siloles have been documented¹, and the silole functions as an η^4 -ligand in all complexes reported thus far². Transition-metal complexes of siloles [Ph₄C₄Si(Cl)MLn] draw our attention because they are presumed to function as a silylene precursor or as precursors for the generation or detection of an (η^5 -silacyclopentadienyl)metal complexes containing transition metals. In the substitution reaction at coordinated siloles with use of active hydrogen, numerous studies have been carried out³. Nevertheless, little was known about the chemistry accompanying the reaction of transition-metal complexes of siloles with transition-metal nucleophiles. In such a reaction transition-metal nucleophiles bind to the silicon to give the silole-bridged heterobimetallic complexes. Because the product was presumed to be a good candidate for an (η^5 -silacyclopentadienyl) metal complex by removing Cl, we turned to the syntheses of transition-metal-substituted siloles. We also report the syntheses of (silole-transition metal complex) Fe(CO)₃ by two synthetic approaches: the substitution reaction of a coordinated (η^4 -silole) Fe(CO)₃ by metal nucleophiles or the reaction of metal carbonyl with silole containing transition metal complex.

Experimental Section

All manipulations of air-sensitive materials were carried out under an argon atmosphere with use of standard Schlenk or vacuum line technique or a Mebraun MB150 glovebox. ¹H-NMR spectra were recorded on a Bruker WM-250 spectrometer in CDCl₃. Chemical shifts were referenced relative to an internal standard Me₄Si. IR spectra were measured on a Perkin-Elmer 1310 spectrometer by a KBr method.

Mass spectra were measured on a high resolution VG 70-VSEG spectrometry. Elemental analyses were carried out at the Basic Science Research Center. Reagent grade tetrahydrofuran (THF) and toluene were distilled under argon from ketyl. The Ph₄C₄SiCl₄⁴, Ph₄C₄SiMeCp⁵, Ph₄C₄SiMeCpFe(CO)₂⁶ were prepared according to literature methods. The [CpFe(CO)₂]₂, Fe(CO)₅, CO₂(CO)₈, and [CpRu(CO)₂]₂ (Strem Chemicals) reagents were used without further purification.

(1-Chloro-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)-cyclopentadienyldicarbonyliron (I). A 0.25 g of [CpFe(CO)₂]₂ in 15 ml of THF was stirred with sodium amalgam prepared from 1 ml of Hg and 0.12 g of Na. After 2 hr, this solution was transferred to a stirred THF (10 ml) solution of 1,1-dichloro-2,3,4,5-tetraphenylsilacyclopentadiene (0.6 g, 1.32 mmol). The solution was stirred for 3 hr. The solution was filtered and evaporated to the dryness. The pale yellow powder was crystallized from a toluene and hexane (5 ml/25 ml) mixture. The yield was 37%. mp. 206°C. ¹H-NMR (CDCl₃) δ 7.4-6.6 (m, 20H), 4.65 (s, 5H); IR (on KBr pellet; cm⁻¹) ν (CO) 1998, 1956; mass spectrum, *m/e* (relative intensity) 597 (M⁺, 34), 541 (M⁺-2CO, 82), 420 (M⁺-FeCp(CO)₂, 26), 385 (M⁺-FeCp(CO)₂-Cl, 14). Anal. Calcd. for C₃₅ClFeH₂₅O₂F₂: C, 69.96; H, 4.16. Found: C, 70.62; H, 4.29.

(η^4 -exo-Cyclopentadienyldicarbonyliron-endo-1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)tricarbonyliron (IV). To a stirred toluene (30 ml) solution of (silole)methyl FeCp(CO)₂ (0.3 g, 0.52 mmol) was added Fe(CO)₅ (0.8 ml). The solution was refluxed for 48 hr and evaporated to dryness. The orangish-red solution was obtained by extraction of hexane (30 ml) and the volume was reduced to ca. 6 ml. The orange crystals were obtained by leaving the solution in a refrigerator at 0°C. the yield was 12%. mp. 176°C. ¹H-NMR (CDCl₃) δ 7.4-6.7 (m, 20H, aromatic), 4.52 (s, 5H, C₅H₅), 1.28 (s, 3H, CH₃); IR (on KBr pellet;

cm^{-1}) $\nu(\text{CO})$ 2040, 1995, 1980, 1945. $\nu(\text{C}=\text{C})$ 1594; mass spectrum, m/e (relative intensity) 716 (M^+ , 16), 632 ($M^+-3\text{CO}$, 62), 576 ($M^+-2\text{CO}$, 54). Anal. Calcd. for $\text{C}_{38}\text{H}_{28}\text{O}_5\text{Fe}_2\text{Si}$: C, 65.38; H, 3.91. Found: C, 65.86; H, 4.06.

(1-Methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)cyclopentadienyldicarbonylruthenium (II). The same procedure was taken as described in the preparation of I. The yield was 28%. mp. 208°C . $^1\text{H-NMR}$ (CDCl_3) δ 7.4-6.7 (m, 20H), 4.48 (s, 5H), 1.16 (s, 3H); IR (on KBr pellet; cm^{-1}) $\nu(\text{CO})$ 1992, 1943; mass spectrum, m/e (relative intensity) 621 (M^+ , 22), 565 ($M^+-2\text{CO}$, 64), 399 ($M^+-\text{RuCp}(\text{CO})_2$, 17). Anal. Calcd. for $\text{C}_{36}\text{H}_{28}\text{O}_5\text{SiRu}$: C, 69.53; H, 4.51. Found: C, 68.71; H, 4.29.

(1-Chloro-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)cyclopentadienyldicarbonylruthenium (III). The same procedure was taken as described in the preparation of I. The yield was 34%. mp. 212°C . $^1\text{H-NMR}$ (CDCl_3) δ 7.3-6.6 (m, 20H), 4.68 (s, 5H); IR (on KBr pellet; cm^{-1}) $\nu(\text{CO})$ 2004, 1954; mass spectrum, m/e (relative intensity) 641 (M^+ , 24), 585 ($M^+-2\text{CO}$, 72), 445 ($M^+-\text{RuCp}(\text{CO})_2$, 54). Anal. Calcd. for $\text{C}_{35}\text{H}_{25}\text{ClO}_5\text{SiRu}$: C, 65.44; H, 3.90. Found: C, 64.72; H, 3.62.

(η^4 -exo-Cyclopentadienyldicarbonylruthenium endo-1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)tricarbonyliron (VI). The same procedure was taken as described in the preparation of IV. The yield was 14%. mp. 180°C . $^1\text{H-NMR}$ (CDCl_3) δ 7.3-6.7 (m, 20H), 4.48 (s, 5H), 1.22 (s, 3H); IR (on KBr pellet; cm^{-1}) $\nu(\text{CO})$ 2037, 1990, 1982, 1940. Anal. Calcd. for $\text{C}_{38}\text{H}_{28}\text{O}_5\text{FeRuSi}$: C, 61.52; H, 3.68. Found: C, 60.49; H, 3.49.

(η^4 -exo-Cyclopentadienyldicarbonyliron-endo-1-chloro-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)tricarbonyliron (V). The same procedure was taken as described in the preparation of IV. The yield was 18%. mp. 180°C . $^1\text{H-NMR}$ (CDCl_3) δ 7.3-6.6 (m, 20H), 4.69 (s, 5H); IR (on KBr pellet; cm^{-1}) $\nu(\text{CO})$ 2035, 1998, 1978, 1951; mass spectrum, m/e (relative intensity) 736 (M^+ , 24), 652 ($M^+-3\text{CO}$, 72), 596 ($M^+-5\text{CO}$, 48); Anal. Calcd. for $\text{C}_{38}\text{ClFe}_2\text{H}_{28}\text{O}_5\text{Si}$: C, 61.93; H, 3.39. Found: C, 62.74; H, 3.49.

(η^4 -exo-Tetracarbonylcobalt-endo-1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)tricarbonyliron (VII). A 0.15 g (0.44 mmol) of $\text{Co}_2(\text{CO})_8$ in 20 ml of THF was stirred with sodium amalgam prepared from 1 ml of Hg and 0.1 g of Na. After 1 h, this solution was transferred to a stirred THF (15 ml) solution of IV (0.15 g, 0.88 mmol). The solution was stirred for 4 h and evaporated to dryness. The brownish residue was extracted with hexane (40 ml). The volume was reduced to ca. 30 ml. Brown crystals were obtained at 0°C overnight. The yield was 22%. mp. 148°C . $^1\text{H-NMR}$ (CDCl_3) δ 7.4-6.6 (m, 20H), 4.58 (s, 5H); IR (on KBr pellet; cm^{-1}) $\nu(\text{CO})$ 2045, 2005, 1990, 1951; mass spectrum, m/e (relative intensity) 710 (M^+ , 18), 628 ($M^+-3\text{CO}$, 72), 514 ($M^+-7\text{CO}$, 82); Anal. Calcd. for $\text{C}_{36}\text{FeH}_{23}\text{O}_5\text{CoFe}$: C, 60.83; H, 3.24. Found: C, 59.72; H, 3.04.

(η^4 -exo-Chloro-endo-1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)tricarbonyliron (VIII). To stirred toluene (30 ml) solution of η^4 -exo-methyl-endo-1-chloro-2,3,4,5-tetraphenyl-1-silacyclopentadienyl (0.5 g, 1.15 mmol) was added $\text{Fe}(\text{CO})_5$ (2 ml). The solution was refluxed for 72 h. The greenish yellow solution was evaporated to dryness. The residue was extracted by hexane (60 ml). The yield was 48%. mp. 162°C . $^1\text{H-NMR}$ (CDCl_3) δ 7.5-6.8 (m, 20H), 1.26

(s, 3H); IR (on KBr pellet; cm^{-1}) $\nu(\text{CO})$ 2038, 1982; mass spectrum, m/e (relative intensity) 575 (M^+ , 14), 491 ($M^+-3\text{CO}$, 72); Anal. Calcd. for $\text{C}_{32}\text{ClFeH}_{23}\text{O}_5\text{Si}$: C, 66.87; H, 4.00. Found: C, 65.91; H, 3.84.

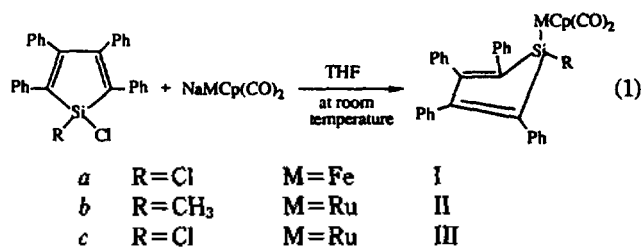
Crystal structure of II. The Crystal of II was grown from hexane at -20°C . The crystallized compound II possessed in the monoclinic space group $P2_1/c$ (systematic absences $0k0$: $k=\text{odd}$ and $h0l$: $l=\text{odd}$) with $a=8.925$ (1), $b=18.689$ (3), $c=19.930$ (3), \AA , $\beta=102.02$ (1°), $V=3251$ (1) \AA^3 , $Z=4$ and $d_{\text{calc}}=1.463$ g/cm^3 . The cell constants were determined from a least square fit of the setting angles for 25 accurately centered reflections. X-ray intensity data were collected on an Enraf-Nonius CAD4 diffractometer employing graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda=0.71073$ \AA) and using the ω - 2θ scan technique. A total of 8177 reflections were measured over the ranges: $4\leq 2\theta\leq 55^\circ$, $0\leq h\leq 11$, $-24\leq k\leq 0$, $-25\leq l\leq 25$. Three standard reflections measured every 3500 sec of X-ray exposure showed no intensity decay over the course of data collection.

The intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied. Of the reflections measured a total of 5267 unique reflection with $F^2 < 3\sigma(F^2)$ were used during subsequent structure refinement.

The structure was solved by standard heavy atom Patterson Techniques followed by weighted Fourier syntheses. Refinement was done by full-matrix least squares techniques based on F to minimize the quantity $\sum w(|F_o| - |F_c|)^2$ with $w=1/\sigma^2(F)$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included as constant contributions to the structure factors and were not refined. Refinement converged to $R_1=0.034$ and $R_2=0.045$.

Results and Discussion

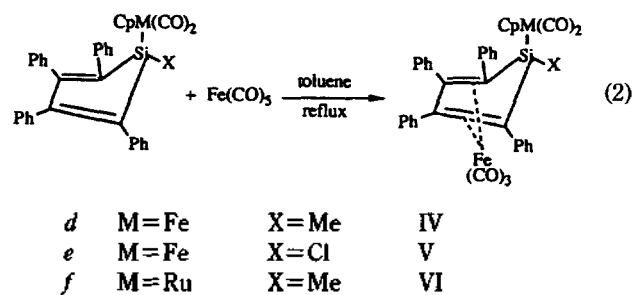
The silicon-monosubstituted (η^4 -2,3,4,5-tetraphenyl-1-silacyclopentadienyl)transition metal complexes have been prepared according to Eq. (1).



The reaction of silole with $\text{NaFeCp}(\text{CO})_2$ at room temperature gave a pale yellow solution. The iron-silole complex was isolated as air-stable pale yellow solid in 37% yield. The structure of compound I was deduced from its $^1\text{H-NMR}$, IR and mass spectra. The chloro adduct I had the similar spectral characteristics ($^1\text{H-NMR}$ and IR spectra) to the known methyl authentic material.⁶ The compound I was robust enough to give the expected molecular ion of m/e (597) in its electron impact (70 eV) mass spectrum. The spectral data of both the compounds II and III were quite similar to those of compound I.

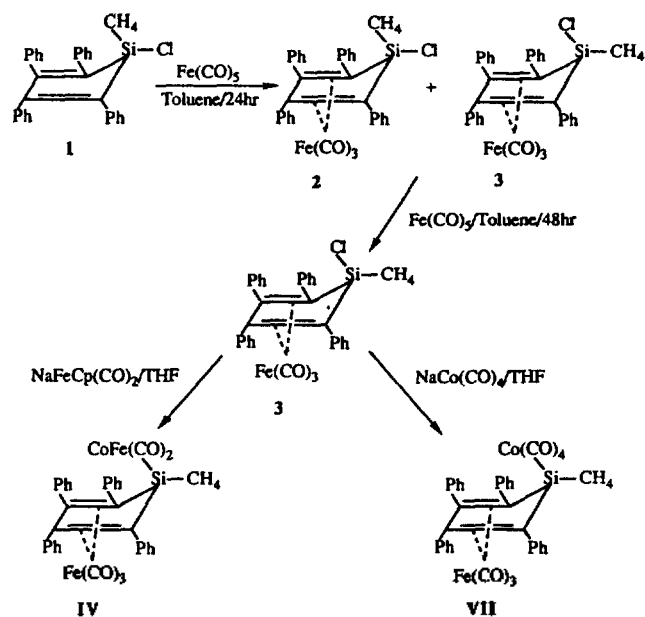
The (η^4 -exo-cyclopentadienyldicarbonyliron (or ruthenium)-endo-1-methyl(or chloro)-2,3,4,5-tetraphenylsilacyclopentadienyl)tricarbonyliron complexes have been prepared according

to Eq. (2).



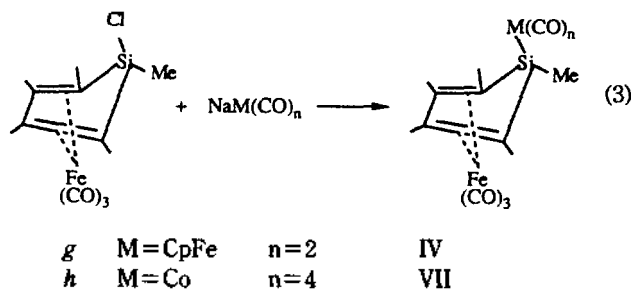
A toluene (30 ml) solution of $\text{Fe}(\text{CO})_5$ and compound *d* was refluxed under Ar for 48 h, and then dried. The dark powder was extracted with hexane (40 ml). The red solution was reduced to ca. 10 ml. Slow cooling of the solution gave red, air-stable crystal of IV, which was characterized by its $^1\text{H-NMR}$, IR, mass spectra, and elemental analysis. The $^1\text{H-NMR}$ spectrum of IV exhibits resonances of Cp at δ 4.52 and CH_3 at 1.28, which are shifted to downfield compared with those of (1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)cyclopentadienyldicarbonyliron. The infrared spectrum of IV clearly indicates the presence of two moieties of $\text{CpFe}(\text{CO})_2$ and $\text{Fe}(\text{CO})_3$. Two peaks at 1995 and 1945 cm^{-1} are CO stretching frequencies in $\text{CpFe}(\text{CO})_2$ moiety, as found in the complex $\text{CpFe}(\text{CO})_2\text{SiMe}_3$.⁷ Two peaks at 2040 and 1960 cm^{-1} are assigned to the CO stretching mode in $\text{Fe}(\text{CO})_3$ moiety, which are quite similar to those (2052 and 1965 cm^{-1}) of the diene complex $(\text{C}_4\text{Ph}_4\text{CO})\text{Fe}(\text{CO})_3$.⁸ The CO stretching frequencies of IV are compared to those of the thiophene-bridged $\text{Cp}^*(\text{CO})_2\text{Re}(\mu\text{-SC}_4\text{H}_4)\text{Fe}(\text{CO})_3$ and $[\eta^4\text{-exo-1-(dicarbonyl}(\eta^5\text{-cyclopentadienyl)ferrio]-endo-1-methyl-2,5-diphenylsilo}]$ tricarbonyliron¹⁰. The spectral patterns of compounds V and VI are quite similar to that of IV. Although these data support their formulation as complexes with the silole-bridged $\text{CpFe}(\text{CO})_2(\text{Ph}_4\text{C}_4\text{SiX})\text{Fe}(\text{CO})_3$, the iron moiety $\text{CpFe}(\text{CO})_2$ on silicon center is not certain as to whether it is located in an exo or endo-position. Thus, the crystal structure of IV was determined, and it was found that the bulky iron moiety was in an exo position as expected (see crystallographic work).

Another synthetic approach to the silole-bridged heterobimetallic complexes may be achieved by the substitution reaction of coordinated η^4 -silole by metal-complex nucleophiles. Indeed, the (η^4 -exo-metalcarbonyl-endo-chloro-2,3,4,5-tetraphenylsilacyclopentadienyl) tricarbonyliron complexes have been prepared according to Eq. (3). For this purpose, the reaction of silole $\text{Ph}_4\text{C}_4\text{Si}(\text{CH}_3)\text{Cl}$ with $\text{Fe}(\text{CO})_5$ was examined and the results are summarized in Scheme 1. The treatment of silole 1 (0.97 mmol) with 10 equiv. of $\text{Fe}(\text{CO})_5$ in toluene (30 ml) under refluxing condition gave a good yield (68%) of a 60 : 40 mixture of the exo-methyl complex 2 and exochlorine complex 3. In the purpose of raising the yield of the reaction between silole and metal-complex nucleophile, the compound 2 was completely converted to the complex 3, the mixture 2 and 3 was refluxed in toluene under prolonged reaction time (48 h), where interestingly, the compound 2 was completely converted to the compounds. The greenish yellow solution was evaporated to dryness and the residue was extracted in hexane. The geometrical isomer of the methyl group on silicon, *i.e.*, endo or exo with respect



Scheme 1.

to the $\text{Fe}(\text{CO})_3$ moiety was able to be unequivocally assigned by the $^1\text{H-NMR}$ spectroscopy.



The reaction of $\text{Fe}(\text{Ph}_4\text{C}_4\text{SiMeCl})(\text{CO})_3$ with $\text{NaCpFe}(\text{CO})_2$ in tetrahydrofuran at room temperature proceeds to give the complex IV. The product was purified by chromatography on silica gel. The $^1\text{H-NMR}$ and IR spectra were exactly identical to the complex IV obtained from the previous different synthetic method. Similarly, the reaction of compound 3 and $\text{NaCo}(\text{CO})_4$ in THF gave a brown solution. After the removal of solvent, the brownish residue was extracted with hexane. Brown crystals formed once the solution was cooled. The IR spectrum of compound VII was exactly identical to the authentic silole-cobalt complex prepared by the reaction of (η^4 -exo-1-hydro-endo-methyl-2,5-diphenylsilacyclopentadienyl)tricarbonyliron and $\text{Co}_2(\text{CO})_8$.³ In order to extend the syntheses of other transition metal complex-siloles, the reactions of compound 3 with transition metal complex-siloles such as $\text{NaRe}(\text{CO})_5$, $\text{NaCpMo}(\text{CO})_3$, and $\text{NaMn}(\text{CO})_5$ was examined. Unfortunately, dimer and several unidentified products which could not be separated by conventional method were obtained.

Crystallographic Work. To get a geometrical information of the complex IV in the solid state, X-ray diffraction work was carried out. The structure and atom labelling of the (η^4 -exo-cyclopentadienyldicarbonyliron-endo-1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadienyl)tricarbonyliron are shown in Figure 1. Selected interatomic distances and bond angles

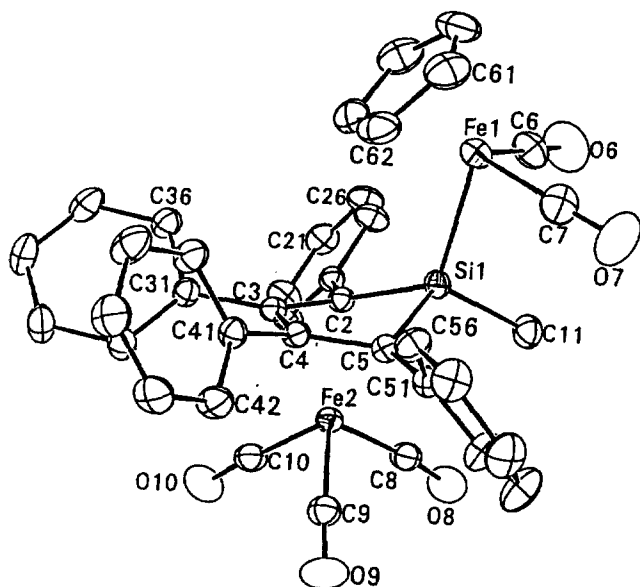


Figure 1. View of the structure of IV with the atomic numbering scheme.

are listed in Table 1 and 2, respectively. The four carbon atoms C2, C3, C4, and C5 constituting the diene portion of the five-membered ring containing the silicon atom are almost coplanar. The C4SiC25 butadiene dihedral angle has

Table 1. Bond Distances (Å)

Fe1-Si1	2.357 (1)	C3-C4	1.442 (3)	C34-C35	1.374 (4)
Fe1-C6	1.735 (3)	C3-C31	1.502 (3)	C35-C36	1.385 (4)
Fe1-C7	1.736 (3)	C4-C5	1.445 (3)	C41-C42	1.379 (3)
Fe1-C61	2.114 (4)	C4-C41	1.496 (3)	C41-C46	1.385 (4)
Fe1-C62	2.088 (3)	C5-C51	1.496 (3)	C42-C43	1.390 (4)
Fe1-C63	2.096 (3)	C6-O6	1.146 (4)	C43-C44	1.356 (5)
Fe1-C64	2.090 (3)	C7-O7	1.152 (4)	C44-C45	1.375 (4)
Fe1-C65	2.121 (4)	C8-O8	1.140 (4)	C45-C46	1.383 (4)
Fe2-C2	2.195 (2)	C9-O9	1.138 (3)	C51-C52	1.392 (3)
Fe2-C3	2.081 (2)	C10-O10	1.137 (3)	C51-C56	1.378 (4)
Fe2-C4	2.082 (2)	C21-C22	1.388 (4)	C52-C53	1.376 (4)
Fe2-C5	2.134 (2)	C21-C26	1.391 (4)	C53-C54	1.373 (5)
Fe2-C8	1.794 (3)	C22-C23	1.380 (4)	C54-C55	1.368 (4)
Fe2-C9	1.785 (2)	C23-C24	1.370 (4)	C55-C56	1.384 (4)
Fe2-C10	1.791 (3)	C24-C25	1.369 (4)	C61-C62	1.411 (5)
Si1-C2	1.902 (2)	C25-C26	1.387 (4)	C61-C65	1.387 (5)
Si1-C5	1.877 (2)	C31-C32	1.398 (3)	C62-C63	1.385 (4)
Si1-C11	1.880 (3)	C31-C36	1.386 (3)	C63-C64	1.388 (5)
C2-C3	1.441 (3)	C32-C33	1.379 (4)	C64-C65	1.405 (5)
C2-C21	1.492 (3)	C33-C34	1.372 (4)		

Table 2. Bond Angles (deg)

Si1-Fe1-C6	87.8 (1)	C5-Fe2-C9	92.7 (1)	C22-C23-C24	120.6 (3)
Si1-Fe1-C7	83.1 (1)	C5-Fe2-C10	157.5 (1)	C23-C24-C25	118.8 (3)
Si1-Fe1-C61	134.8 (1)	C8-Fe2-C9	94.5 (1)	C24-C25-C26	120.9 (3)
Si1-Fe1-C62	98.5 (1)	C8-Fe2-C10	93.5 (1)	C21-C26-C25	121.2 (2)
Si1-Fe1-C63	91.3 (1)	C9-Fe2-C10	90.1 (1)	C3-C31-C32	121.0 (2)
Si1-Fe1-C64	119.9 (1)	Fe1-Si1-C2	120.5 (1)	C3-C31-C36	120.6 (2)
Si1-Fe1-C65	156.4 (1)	Fe1-Si1-C5	114.5 (1)	C32-C31-C36	118.1 (2)
C6-Fe1-C7	91.6 (1)	Fe1-Si1-C11	107.9 (1)	C31-C32-C33	120.4 (2)
C6-Fe1-C61	137.3 (2)	C2-Si1-C5	85.1 (1)	C32-C33-C34	120.8 (3)
C6-Fe1-C62	158.8 (1)	C2-Si1-C11	113.7 (1)	C33-C34-C35	119.5 (3)
C6-Fe1-C63	121.5 (1)	C5-Si1-C11	114.0 (1)	C34-C35-C36	120.4 (2)
C6-Fe1-C64	94.6 (1)	Fe2-C2-Si1	89.6 (1)	C31-C36-C35	120.8 (2)
C6-Fe1-C65	102.3 (1)	Fe2-C2-C3	66.1 (1)	C4-C41-C42	124.2 (2)
C7-Fe1-C61	95.7 (1)	Fe2-C2-C21	125.3 (1)	C4-C41-C46	117.3 (2)
C7-Fe1-C62	109.2 (1)	Si1-C2-C3	108.6 (2)	C42-C41-C46	118.5 (2)
C7-Fe1-C63	146.2 (1)	Si1-C2-C21	125.2 (2)	C41-C42-C43	120.1 (2)
C7-Fe1-C64	156.3 (1)	C3-C2-C21	123.2 (2)	C42-C43-C44	120.7 (2)
C7-Fe1-C65	117.4 (1)	Fe2-C3-C2	74.6 (1)	C43-C44-C45	120.0 (3)
C61-Fe1-C62	39.2 (1)	Fe2-C3-C4	69.8 (1)	C44-C45-C46	119.6 (3)
C61-Fe1-C63	65.2 (1)	Fe2-C3-C31	125.9 (2)	C41-C46-C45	121.0 (2)
C61-Fe1-C64	64.7 (1)	C2-C3-C4	112.8 (2)	C5-C51-C52	120.9 (2)
C61-Fe1-C65	38.2 (1)	C2-C3-C31	125.8 (2)	C5-C51-C56	121.8 (2)
C62-Fe1-C63	38.7 (1)	C4-C3-C31	121.3 (2)	C52-C51-C56	117.2 (2)
C62-Fe1-C64	64.7 (1)	Fe2-C4-C3	69.7 (1)	C51-C52-C53	121.0 (3)
C62-Fe1-C65	65.0 (1)	Fe2-C4-C5	71.9 (1)	C52-C53-C54	120.6 (3)
C63-Fe1-C64	38.7 (1)	Fe2-C4-C41	133.9 (2)	C53-C54-C55	119.2 (3)
C63-Fe1-C65	65.2 (1)	C3-C4-C5	112.5 (2)	C54-C55-C56	120.1 (3)
C64-Fe1-C65	39.0 (1)	C3-C4-C41	121.2 (2)	C51-C56-C55	121.6 (2)

opened up to 46.8° , so that the silicon atom is out of the diene plane by 0.943 \AA . This value is relatively large compar-

C2-Fe2-C3	39.3 (1)	C5-C4-C41	125.6 (2)	Fe1-C61-C62	69.4 (2)
C2-Fe2-C4	68.2 (1)	Fe2-C5-Si1	92.2 (1)	Fe1-C61-C65	71.1 (2)
C2-Fe2-C5	72.3 (1)	Fe2-C5-C4	68.1 (1)	C62-C61-C65	107.8 (3)
C2-Fe2-C8	93.9 (1)	Fe2-C5-C51	125.4 (2)	Fe1-C62-C61	71.4 (2)
C2-Fe2-C9	164.5 (1)	Si1-C5-C4	108.5 (1)	Fe1-C62-C63	71.0 (2)
C2-Fe2-C10	102.3 (1)	Si1-C5-C51	125.4 (2)	C61-C62-C63	108.4 (3)
C3-Fe2-C4	40.5 (1)	C4-C5-C51	121.0 (2)	Fe1-C63-C62	70.4 (2)
C3-Fe2-C5	69.4 (1)	Fe1-C6-O6	178.3 (3)	Fe1-C63-C64	70.4 (2)
C3-Fe2-C8	132.8 (1)	Fe1-C7-O7	176.8 (3)	C62-C63-C64	107.5 (3)
C3-Fe2-C9	132.2 (1)	Fe2-C8-O8	172.5 (3)	Fe1-C64-C63	70.9 (2)
C3-Fe2-C10	92.4 (1)	Fe2-C9-O9	176.8 (2)	Fe1-C64-C65	71.7 (2)
C4-Fe2-C5	40.1 (1)	Fe2-C10-O10	178.1 (2)	C63-C64-C65	108.9 (3)
C4-Fe2-C8	146.5 (1)	C2-C21-C22	124.7 (2)	Fe1-C65-C61	70.6 (2)
C4-Fe2-C9	97.9 (1)	C2-C21-C26	118.7 (2)	Fe1-C65-C64	69.3 (2)
C4-Fe2-C10	117.4 (1)	C22-C21-C26	116.6 (2)	C61-C65-C64	107.3 (3)
C5-Fe2-C8	108.5 (1)	C21-C22-C23	121.9 (2)		

ed with those of the complexes $\text{Ru}(\text{C}_4\text{Ph}_2\text{H}_2\text{SiMe}_2)(\text{CO})_3^{11}$, $[\text{Co}(\text{C}_4\text{Me}_2\text{H}_2\text{SiMe}_2)(\text{PMe}_2)_3]^+^{12}$ and $(\eta^4\text{-exo-phenyl-endo-chloro-2,3,4,5-tetraphenyl-1-silacyclopentadienyl})\text{tricarbonyliron}^{13}$, where the dihedral angle is 32° , 41.3° , and 41.8° , respectively. The difference may be attributable to the steric bulkiness of the iron moiety.^{10,11} The iron moiety on silicon is in an axial position. The carbon-carbon distances in the five-membered ring on the silole show considerable conjugation, the formally single C-C bond (1.462 Å) being only slightly longer than common double carbon-carbon bond (1.440 Å). The Fe2-C2 and Fe2-C5 distances (2.195 and 2.134 Å, respectively) are longer than Fe2-C3 and Fe2-C4 distances (2.081 and 2.082 Å, respectively). This is consistent with a similar observation of Mills and Robinson¹⁴. The significant difference of Fe2-C2 and Fe2-C5 distances compared with the Fe2-C3 and Fe2-C4 distances may be attributable to the ineffective overlap of *p-d* orbitals due to the title of *p* orbital on C2 and C5. The coordination geometry around the iron atom seems to be in a distorted tetrahedron if the centroid of the four carbon diene moiety is taken as the fourth ligand site for the Fe atom, the other three sites being the carbons of the three carbonyls.

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