Reactions of 1,1-dichloro-, 1-chloro-1-phenyl- and 1-chloro-1-methylsilacyclopent-3-ene with Na[Cp(CO)₂Fe]. X-ray diffraction study of the 1-(dicarbonylcyclopentadienyl-ferrio)-1-[4-(dicarbonylcyclopentadienylferrio)but-1-oxy]sila-cyclopent-3-ene resulting from insertion of an opened THF molecule into a Si–Fe bond

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Abstract

The reaction of 1,1-dichlorosilacyclopent-3-ene (**1**), 1-chloro-1-phenylsilacyclopent-3-ene (**2**) and 1-chloro-1-methylsilacy-clopent-3-ene (**3**) with Na[Cp(CO)₂Fe] in a 1/1 ratio yielded yellow crystalline powders of the Cp(CO)₂Fe(ClSiC₄H₆) (**5**), Cp(CO)₂Fe(PhSiC₄H₆) (**6**) and Cp(CO)₂Fe(MeSiC₄H₆) (**7**) complexes, respectively. ¹H-NMR spectra indicated that the silacy-clopent-3-ene ring in all complexes is puckered in solution. When 1,1-dichlosilacyclopent-3-ene was reacted with two equivalents of Na[Cp(CO)₂Fe] in THF, a different complex **8** was produced, resulting from the insertion of an opened THF molecule into a Si–Fe bond. Its crystal structure was determined by single-crystal X-ray diffraction: triclinic, space group $P\bar{1}$, $a = 7.9334(12)$, $b = 11.596(2)$, $c = 12.939(3)$ Å, $\alpha = 75.73(2)$, $\beta = 75.38(2)$, $\gamma = 80.05(1)°$, $Z = 2$, $R = 0.040$, $Rw = 0.045$. Complex **8** contains two Cp(CO)₂Fe fragments, one of which is directly bonded to the Si atom of a silacyclopent-3-ene unit, whereas the other is at the carbon end of an opened THF molecule whose oxygen atom is bonded to same Si atom. Both iron(II) centres possess a pseudo-octahedral coordination created by one Cp ring, two *cis* CO ligands and, in one case, a Si atom and, in the other, the terminal CH₂ group of the opened THF molecule thus acting as a bridging unit between Si and a Cp(CO)₂Fe group. Under similar conditions, the above ligands failed to react with Na[Co(CO)₄], but the related Co(CO)₄(1,3-Me₂SiC₄H₅) molecule was synthesized from 1,3-dimethylsilacyclopent-3-ene via a hydrosilylation reaction. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Iron; Cobalt; Silacyclopentene; Opened THF; X-ray diffraction

1. Introduction

Alkyl- or aryl-substituted silacyclopent-3-enes have attracted a great deal of attention as monomeric precursors leading to inorganic polymers via ring opening processes (ROAP) (Scheme 1) [1].

Although these planar molecules present two potential metal coordination sites, namely the C=C bond and the Si atom, their ability to bind metal centers and their coordination chemistry are still poorly developed. In contrast, metal-coordinated alkyl and aryl silanes are

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numerous and compounds have been described in which nearly all transition metals form stable σ metal–silicon bonds. They were synthesized mainly via nucleophilic substitution of a silicon-bonded halogen atom by a metallate anion [2], a method that can be easily applied to silacyclopent-3-ene.

We report here the synthesis of the first compounds containing a silacyclopentene unit σ bonded to the 17-electron metallic fragment $Cp(CO)_2Fe$, which were isolated by reacting 1,1-dichlorosilacyclopent-3-ene (1), 1-chloro-1-phenylsilacyclopent-3-ene (2) and 1-chloro-1-methylsilacyclopent-3-ene (3) with $Na[Cp(CO)_2Fe]$ in 1/1 and 1/2 ratios. As expected, the reactions are highly sensitive to temperature, concentrations and the other experimental conditions. When 1,1-dichlorosilacyclopent-3-ene was reacted with two equivalents of the metal salt in THF, a different type of complex was precipitated, which is a scarce example of insertion of a THF molecule-after ring opening-into a Si–Fe bond. The X-ray structure of this complex is reported. Attemps were made to synthesize the related $Co(CO)_4$ complexes without success. Interestingly, the only compound of this type was obtained with 1,3-dimethylsilacyclopent-3-ene (4) via an hydrosilylation reaction.
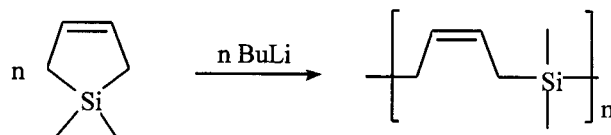
2. Experimental section

2.1. Reactants and methods

Solvent distillation and all other manipulations were performed in dry N_2 atmosphere using standard Schlenk techniques. Tetrahydrofuran, toluene and ether were stirred with sodium wire and distilled over Na/benzophenone prior to use. Pentane and hexane were distilled from Na just before use. Dichloromethane was dried over P_2O_5. All solvents were degassed by three freeze-thaw cycles.

1,1-Dichlorosilacyclopent-3-ene (1), 1-chloro-1-phenylsilacyclopent-3-ene (2) and 1-chloro-1-methylsilacyclopent-3-ene (3) were prepared by literature methods [3]. $[CpFe(CO)_2]_2$ and $Co_2(CO)_8$ (Strem) were used without purification. $Na[CpFe(CO)_2]$ and $Na[Co(CO)_4]$ were synthesized from the corresponding dimer by reduction with Na/Hg [4] or by reaction with $K[BH(sec-Bu)_3]$ [5].

The ^1H- and $^{13}C\{^1H\}$-NMR spectra were recorded on Bruker WM-200 or WH-80 spectrometers using $CDCl_3$ or C_6D_6 as solvent. The chemical shifts were referenced to the residual solvent signals: $CDCl_3$, $\delta(^1H) = 7.27$ ppm and $\delta(^{13}C) = 77.0$ ppm; C_6D_6, $\delta(^1H) = 7.25$ ppm and $\delta(^{13}C) = 128.0$ ppm.

Microanalyses were performed by the Service Cen-

tral de Microanalyses du CNRS, Lyon, and by the Service de Microanalyses du LCC, Toulouse.

2.2. Preparative work

2.2.1. 1-(Dicarbonylcyclopentadienylferrio)-1-chlorosilacyclopent-3-ene (5)

$[CpFe(CO)_2]_2$ (0.62 g, 1.75 mmol) in 40 mL of THF was stirred for 2 h with sodium amalgam (4 mL Hg/ 0.5 g Na). After filtration, the solution was cooled to $-40°C$ and added dropwise to a solution of 0.54 g (3.5 mmol) of 1 in 30 mL of THF. The mixture was stirred for 45 min, then warmed up slowly to r.t. and stirred again for 24 h. After removal of THF in vacuo, the solid was extracted with pentane. Cooling the solution to $-20°C$ gave 0.72 g of a yellow crystalline powder (yield: 70%). Anal: Calcd (Found) for $C_{11}H_{11}ClFeO_2Si$: C, 44.85 (44.95); H, 3.76 (3.77). IR (pentane): $v(CO)$, 2005 (vs), 1960 (vs) cm^{-1}. ^1H- and $^{13}C\{^1H\}$-NMR: see Table 3.

Table 1
Crystal data for compound 8

Formula	$C_{22}H_{24}Fe_2O_5Si$
Formula weight	508.21
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	7.9334(12)
b (Å)	11.596(2)
c (Å)	12.939(3)
α (°)	75.73(2)
β (°)	75.38(2)
γ (°)	80.05(1)
V (Å^3)	1108.4(4)
Z	2
D_{calc} (g cm^{-3})	1.523
Radiation (λ, Å)	1.54056
μ (mm^{-1})	11.34
Temperature (K)	295
No. measured reflections	8274
No. independent reflections	4205
No. reflections with $I > 3\sigma(I)$	3348
R[a]	0.040
Rw[a]	0.045

Table 2
Atomic coordinates and equivalent isotropic temperature factors
($\mathrm{\mathring{A}} \times 10^2$) for the non-hydrogen atoms of compound **8**

Atom	x	y	z	B_{iso}^a
Fe(1)	0.21874(7)	0.23017(5)	1.01816(5)	2.05(2)
Fe(2)	−0.29803(8)	0.79069(5)	0.54762(5)	2.51(2)
Si	0.39946(12)	0.28594(9)	0.8502 2(8)	2.03(4)
O(1)	0.2966(3)	0.3643(2)	0.7540(2)	2.5(1)
C(2)	0.1808(5)	0.4715(3)	0.7610(3)	2.7(2)
C(3)	0.1336(5)	0.5262(3)	0.6521(3)	2.5(2)
C(4)	−0.0207(5)	0.6257(4)	0.658 8(3)	2.9(2)
C(5)	−0.0594(5)	0.6834(4)	0.5469(3)	2.9(2)
C(6)	0.5901(5)	0.3654(4)	0.8434(3)	3.1(2)
C(7)	0.7328(5)	0.3105(4)	0.7623(4)	3.9(2)
C(8)	0.7075(6)	0.2150(4)	0.7354(4)	3.7(2)
C(9)	0.5385(5)	0.1633(3)	0.7848(3)	2.8(2)
O(10)	0.5339(4)	0.1546(3)	1.1026(3)	4.0(2)
C(10)	0.4087(5)	0.1854(3)	1.0682(3)	2.7(2)
O(20)	0.2080(4)	0.4768(3)	1.0313(3)	4.2(2)
C(20)	0.2094(5)	0.3779(4)	1.0265(3)	2.8(2)
O(30)	−0.1643(4)	0.9080(3)	0.3240(2)	4.4(2)
C(30)	−0.2150(5)	0.8610(4)	0.4119(3)	3.0(2)
O(40)	−0.1581(6)	0.9505(3)	0.6351(3)	6.3(2)
C(40)	−0.2147(7)	0.8864(4)	0.6014(4)	3.8(2)
C(51)	0.0869(7)	0.1554(5)	0.9356(4)	4.9(3)
C(52)	0.1571(6)	0.0671(4)	1.0081(5)	5.0(3)
C(53)	0.0871(7)	0.0835(6)	1.1048(5)	5.7(3)
C(54)	−0.0305(6)	0.1853(6)	1.1048(5)	5.7(3)
C(55)	−0.0295(6)	0.2322(4)	0.9931(5)	5.3(3)
C(61)	−0.4995(6)	0.6943(4)	0.5097(4)	3.6(2)
C(62)	−0.4161(5)	0.6302(4)	0.6046(4)	3.2(2)
C(63)	−0.4664(6)	0.7002(4)	0.6847(3)	3.5(2)
C(64)	−0.5585(6)	0.8102(4)	0.6383(4)	4.2(2)
C(65)	−0.5591(5)	0.8077(4)	0.5310(4)	4.0(2)

^{a} B_{iso} is the mean of the principal axes of the thermal ellipsoid.

1-(Dicarbonylcyclopentadienylferrio)-1-phenylsilacyclopent-3-ene **(6)**

By using the same procedure as above, 1.10 g (3.1 mmol) of [CpFe(CO)$_2$]$_2$ and 1.22 g (6.2 mmol) of **2** gave 1.40 g of a yellow powder of **6** (yield: 67%). Anal. Calcd. (Found) for C$_{17}$H$_{16}$FeO$_2$Si: C, 60.73 (60.07); H, 4.80 (4.83). IR (pentane): ν(CO), 1995 (vs), 1940 (vs) cm^{-1}. ^{1}H- and ^{13}C{^{1}H}-NMR: see Table 3.

2.2.3. 1-(Dicarbonylcyclopentadienylferrio)-1-methylsilacyclopent-3 -ene (4)

As above, 1.00 g (2.83 mmol) of [CpFe(CO)$_2$]$_2$ and 0.75 g (5.66 mmol) of **3** gave 0.93 g of **7** as a yellow powder (yield: 60%). Anal. Calcd. (Found) for C$_{12}$H$_{14}$FeO$_2$Si: C, 52.57 (52.18); H, 5.15 (5.21). IR (pentane): ν(CO), 2000 (vs), 1950 (vs) cm^{-1}. ^{1}H- and ^{13}C{^{1}H}-NMR: see Table 3.

*1-(Dicarbonylcyclopentadienyl-ferrio)-1-[4-(dicarbonylcyclopentadienyl-ferrio)but-1-oxy]silacyclopent-3-ene* **(8)**

Compound **1** (0.85 g, 5.51 mmol) in 15 ml THF was added dropwise to a cold solution (−40°C) of 2.02 g (11.02 mmol) of Na[CpFe(CO)$_2$] prepared as above from [CpFe(CO)$_2$]$_2$ (2.72 g, 5.51 mmol) and sodium amalgam (4 mL Hg/0.5 g Na). The mixture was stirred at this temperature for 1 h, then warmed up to r.t., and stirred again for 12 h. After removal of the solvent in vacuo and work up of the residue with ether, 1.8 g of a yellow crystalline powder was obtained (yield: 65%). Recrystallization in ether/pentane gave single crystals suitable for X-ray work. Anal. Calcd. (Found) for C$_{22}$H$_{24}$Fe$_2$O$_5$Si: C, 51.99 (52.05); H, 4.76 (4.80). IR (pentane): ν(CO), 1998 (vs), 1940 (vs) cm^{-1}. ^{1}H-NMR (d, ppm, CDCl$_3$) (see Table 3 for atom labelling): 1.47 (4H, m, CH$_A$H$_B$), 1.24, 1.74, 1.94, 3.58 (8H, m, THF CH$_2$); 4.71 (5H, s, Cp), 4.78 (5H, s, Cp); 5.98 (2H, s, =CH$_C$); ^{13}C{^{1}H}-NMR (d, ppm, CDCl$_3$): 24.24 (ring CH$_2$), 63.66, 37.69, 34.38, 3.46 (THF CH$_2$), 85.39, 83.53 (Cp), 131.31 (=CH), 214.22 (CO).

2.2.5. 1-(Tetracarbonylcobaltio)-1,3-dimethylsilacyclopent-3-ene (11)

In a flask equipped with a condenser were added 1.32 g (3.9 mmol) of Co$_2$(CO)$_8$ dissolved in pentane (30 mL) and 0.96 g (8.6 mmol) of 1,3-dimethylsilacyclopent-3-ene (**4**) in pentane (10 mL). This mixture was refluxed for 24 h until complete disappearance of Co$_2$(CO)$_8$. Concentration of the solution in vacuo and work up gave 0.87 g of **11** as a dark powder (yield: 40%). Anal. Calcd. (Found) for C$_{10}$H$_{11}$CoO$_4$Si: C, 42.56 (42.07); H, 3.93 (3.81). IR (pentane): ν(CO), 2008, 2034, 2052, 2096 cm^{-1}. ^{1}H-NMR (δ, ppm, CDCl$_3$, 80 MHz): 5.80, (m br, 1H, =CH); 1.62 (m br, 4H, CH$_2$); 1.44 (s, 3H, C–CH$_3$); 0.73 (s, 3H, Si–CH$_3$).

2.3. Crystallographic work on 8

Yellow crystals of **8** were grown from pentane at −20°C. The dimensions (mm) of the specimen used were 0.40 {001} × 0.45 {010} × 0.48 {100}. The X-ray work was carried out with an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized Cu–K$_\alpha$ radiation. The reduced cell was deduced from 25 reflections detected on an oscillation photograph. The Niggli parameters ruled out any symmetry higher than triclinic, leaving $P\bar{1}$ and $P1$ as possible space groups. The structure solved and refined normally in the centric $P\bar{1}$ space group. Crystal data and other relevant crystallographic information are summarized in Table 1.
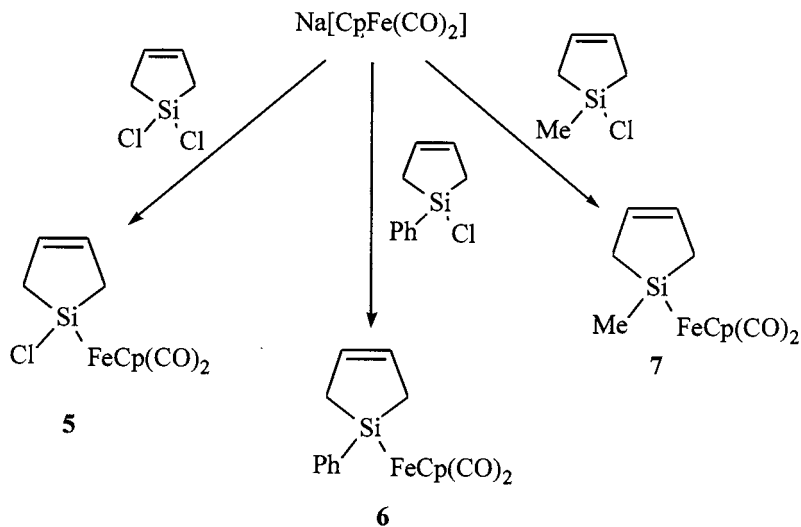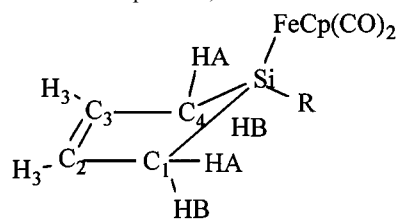
Scheme 2.

The intensity data were collected by the $\omega/2\theta$ scan technique, with a scan range $\Delta\omega$ of $(0.80 + 0.14 \tan\theta)°$ and a constant scan rate of $16.5°$ $\min^{-1}$. Orientation was monitored every 400 measurements, whereas intensity was checked every hour with five standard reflections. Intensity fluctuation remained within $\pm 3.4\%$. The whole sphere of data (8274 reflections) was collected. An absorption correction was applied (Gaussian

integration, transmission range: 0.02–0.17). Equivalent reflections were averaged and corrected for the Lorentz and polarization effects. The final data set consisted of 4205 independent reflections, of which 3348 with $I > 3.0$ $\sigma(I)$, were retained for structure determination.

The structure was solved by direct methods using SHELXS-86 [6] and difference Fourier syntheses using NCRVAX [7]. Least-squares refinement was based on F. All non-hydrogen atoms were refined anisotropically. Hydrogens were initially introduced at idealized positions and refined isotropically in the last cycles. Convergence was reached for R and Rw values of 0.040 and 0.045, respectively. The scattering curves were taken from standard sources [8]. The anomalous dispersion contributions df′ and df″ for Fe and Si were from Cromer and Liberman [9]. The final atomic positional parameters for the non-hydrogen atoms are listed in Table 2.

Table 3
^{1}H- and ^{13}C{^{1}H}-NMR data for the Cp(CO)$_2$Fe(RSiC$_4$H$_6$) compounds[a]

Compound	R = Cl (5)	R = Ph (6)	R = Me (7)
^{1}H	In CDCl$_3$	In CDCl$_3$	In CDCl$_3$
H$_A$, H$_B$	1.86, dd, 4H	1.47, dd, 4H	0.89, dd, 4H
	J$_{AB}$ = 17.2 Hz	J$_{AB}$ = 17.8 Hz	J$_{AB}$ = 15.3 Hz
H$_C$	6.06, s, 2H	5.98, s, 2H	5.92, s, 2H
R		7.59; 7.31, m, 5H (Ph)	0.3, s, 3H (Me)
Cp	4.06, s, 5H	4.63, s, 5H	4.72, s, 5H
^{13}C	In C$_6$D$_6$	In CDCl$_3$	In C$_6$D$_6$
C1, C4	29.14	23.34	25.50
C2, C3	130.98	128.06	129.75
R		127.71, 131.49, 132.97 (Ph)	4.60 (Me)
Cp	84.41	83.97	84.65
CO	213.22	213.60	213.20

[a] Room temperature, 80 MHz for ^{1}H, 50.32 MHz for ^{13}C.

3. Results and discussion

In THF at low temperature, metathesis reactions between the different silacyclopent-3-enes and the iron metallate anion [CpFe(CO)$_2$]$^-$ in a 1/1 ratio were observed to give good yields of the monosubstituted complexes 1-(dicarbonylcyclopentadienylferrio)-1-chlorosilacyclopent-3-ene) (5), 1-(dicarbonylcyclopentadienylferrio)-1-phenylsilacyclopent-3-ene (6) and 1-(dicarbonylcyclopentadienylferrio)-1-methylsilacyclopent-3-ene (7) (Scheme 2).

The three compounds gave satisfactory spectroscopic and elemental analysis data. The carbonyl stretches in the IR spectra were consistent with identical local symmetry around iron in all cases. In the ^{1}H-NMR spectra
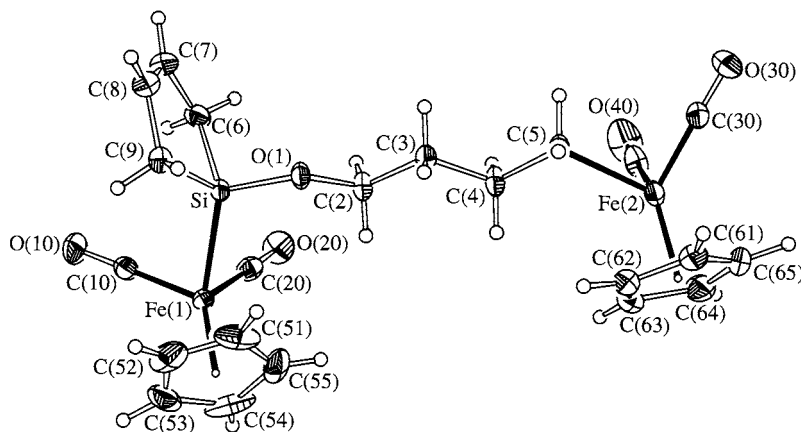
Fig. 1. ORTEP drawing of molecule **8**. Ellipsoids are drawn at 40% probability level. Hydrogens are shown as small spheres of arbitrary size.

(Table 3), the complexes exhibited a non-first order doublet of doublets at 0.9–1.9 ppm for the methylene protons H_A/H_B of the silacyclopent-3-ene ring, indicating the loss of ring planarity [10] upon metal coordination. Thus, the metal-bonded molecules adopt a puckered conformation, as observed for a related complex with a germacyclopentene derivative in the solid state [11]. However, it should be noted that the NMR

Table 4
Selected interatomic distances (Å) and bond angles (°) for **8**

Fe(1)–Si	2.2914(13)	Fe(2)–C(5)	2.077(4)
Fe(1)–C(10)	1.737(4)	Fe(2)–C(30)	1.755(4)
Fe(1)–C(20)	1.731(4)	Fe(2)–C(40)	1.738(5)
Fe(1)–C(51)	2.079(4)	Fe(2)–C(61)	2.115(4)
Fe(1)–C(52)	2.075(4)	Fe(2)–C(62)	2.113(4)
Fe(1)–C(53)	2.096(4)	Fe(2)–C(63)	2.098(4)
Fe(1)–C(54)	2.095(4)	Fe(2)–C(64)	2.108(4)
Fe(1)–C(55)	2.070(4)	Fe(2)–C(65)	2.107(4)
Si–O(1)	1.655(3)	C(3)–C(4)	1.532(5)
Si–C(6)	1.876(4)	C(4)–C(5)	1.521(5)
Si–C(9)	1.880(4)	C(6)–C(7)	1.506(7)
O(1)–C(2)	1.420(4)	C(7)–C(8)	1.300(7)
C(2)–C(3)	1.508(5)	C(8)–C(9)	1.491(6)
O(10)–C(10)	1.155(5)	O(30)–C(30)	1.136(5)
O(20)–C(20)	1.162(5)	O(40)–C(40)	1.148(6)
Si–Fe(1)–C(10)	86.4(1)	C(5)–Fe(2)–C(30)	88.9(2)
Si–Fe(1)–C(20)	84.7(1)	C(5)–Fe(2)–C(40)	86.8(2)
Si–Fe(1)–C(50*)[a]	119.1(2)	C(5)–Fe(2)–C(60*)[a]	120.9(2)
C(10)–Fe(1)–C(20)	93.6(2)	C(30)–Fe(2)–C(40)	93.4(2)
C(10)–Fe(1)–C(50*)[a]	127.5(2)	C(30)–Fe(2)–C(60*)[a]	124.9(2)
C(20)–Fe(1)–C(50*)[a]	130.9(2)	C(40)–Fe(2)–C(60*)[a]	129.8(2)
Fe(1)–Si–O(1)	114.4(1)	O(1)–Si–C(6)	107.6(2)
Fe(1)–Si–C(6)	117.5(1)	O(1)–Si–C(9)	102.8(2)
Fe(1)–Si–C(9)	117.6(1)	C(6)–Si–C(9)	94.4(1)
Si–O(1)–C(2)	125.2(2)	Si–C(6)–C(7)	101.9(3)
O(1)–C(2)–C(3)	109.8(3)	C(6)–C(7)–C(8)	118.8(4)
C(2)–C(3)–C(4)	112.9(3)	C(7)–C(8)–C(9)	119.4(4)
C(3)–C(4)–C(5)	111.7(3)	Si–C(9)–C(8)	102.1(3)
Fe(2)–C(5)–C(4)	115.6(3)		
Fe(1)–C(10)–O(10)	179.1(3)	Fe(2)–C(30)–O(30)	178.6(4)
Fe(1)–C(20)–O(20)	178.2(4)	Fe(2)–C(40)–O(40)	178.7(5)

[a] C(50*) and C(60*) are the centres of the Cp rings.

spectrum of the latter compound in solution showed only one singlet for these methylene protons, a result that was tentatively explained by fast exchange between the endo and exo isomeric forms. In contrast, our spectra indicate the presence of only one isomer in which the metal fragment is likely located at the exo position, as observed in complex **8** (vide infra).
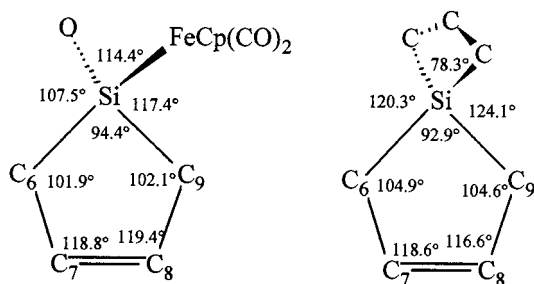
Reacting **1** with two equivalents of Na[CpFe(CO)$_2$] under the same experimental conditions gave compound **8** as an orange powder in 65% yield. Only two ν(CO) stretches appeared as strong and broad bands at 1998 and 1940 cm^{-1}, respectively, indicating that the two CpFe(CO)$_2$ fragments possess similar local environments. The ^{1}H-NMR spectra were consistent with the presence of a silacyclopentene ring and two non-equivalent Cp ligands in the compound. Although the existence of a THF unit was suggested from the microanalysis and the NMR signals for methylene groups at 1.24, 1.74, 1.94 and 3.58 ppm, an X-ray diffraction study was needed to definitively established the structure of this complex.

Single crystals suitable for X-ray work were obtained by slow crystallization from pentane. The structure of **8** is illustrated in Fig. 1. Selected interatomic distances and bond angles are listed in Table 4. The unit cell consists of discrete molecules containing two CpFe(CO)$_2$ fragments: one is bonded directly to the Si

Scheme 3.

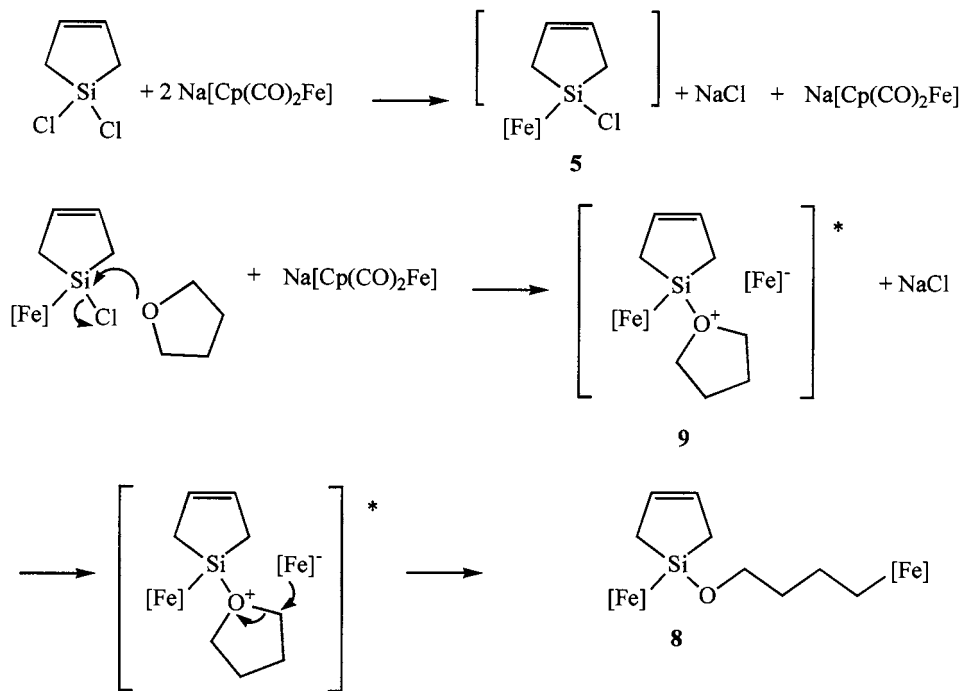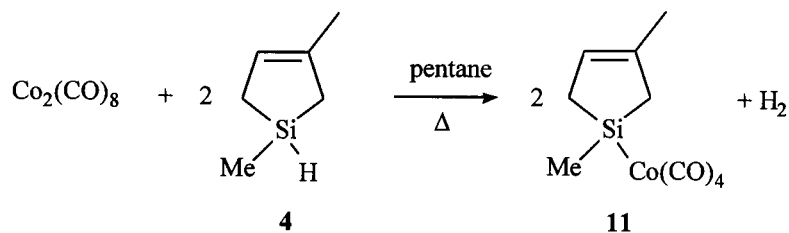Scheme 4.

atom of the silacyclopent-3-ene ring, whereas the other is at the carbon end of an opened THF molecule connected to the same Si atom by the oxygen end. Both metal centers are coordinatively saturated 18-electron systems. Their geometry is best described in terms of a distorted octahedral environment, in which five apices are occupied by the Cp ring (three sites) and two *cis* CO ligands. In the case of Fe(1), the sixth position is filled by a Si atom, whereas for Fe(2), it is occupied by a methylene group of the opened THF molecule acting as a bridging unit between Si and Fe(2).

Both Fe centres possess the environment typical of $CpFe(CO)_2L$ systems. The distances from Fe(1) to the Cp carbons (mean 2.084 Å) and CO ligands (mean 1.734 Å) are close to those found for complexes with other Si-donor groups [12–16]. The Fe–Si distance, however, is more sensitive the substituents: our distance of 2.291(1) Å is shorter than for various compounds with non-cyclic $SiMe_2R$ groups (2.328–2.350 Å), but greater than those observed when electron withdrawing groups are present ($-SiCl_3$, 2.216(1) Å; $-SiFPh_2$ 2.278(1) Å; SiMeF(OR), 2.267 Å). In the other $CpFe(CO)_2$ unit, the Fe(2)–CO and Fe–C(Cp) distances (mean values of 1.746 and 2.108 Å, respectively) seem to be slightly greater, whereas the CO–Fe–CO and Cp–Fe–CO angles are a few degrees smaller than those around Fe(1). This is consistent with the local steric requirement of the coordinated methylene group being greater than for the more distant Si-donor group. The $Fe–CH_2$ distance (2.077(4) Å) is similar to those of other $CpFe(CO)_2$(alkyl) systems [17].

The geometry of the silacyclopentene ring is very similar to that of the dimethylated five-membered ring in a disiladispirooctadecatetraene system [18]. The Si–C bond lengths (mean 1.878 Å) correspond to the value expected on the basis of covalent radii. The C=C (1.300 Å) and C–C distances (mean 1.498 Å) are also normal. The angles in the ring carbon atoms are remarkably close to those for sp^3 and sp^2 hybridizations. Therefore, the carbon part of the ring is not greatly affected by the presence of the long Si–C bonds, which simply reduce the C–Si–C angle to 94.4(2)°. This very small angle is not induced by the presence of the bulky $FeCp(CO)_2$ group, since it is not very different (95.2(1)°) in the dispiro compound. In fact, the five-membered ring geometry seems to be relatively insensitive to steric effects at the Si atom. X-ray results are available for a mono-spiro compound in which the other ring is a sustituted silabutylene [19]. Scheme 3 compares the angles in the five-membered rings in our complex **8** and in this spiro compounds. It is noteworthy that the Si atom can accommodate a very large angular variation from 78.3 to 114.4°, while producing only small changes in the ring from 94.4(2) to 92.9(3)°. Similar differences are found on the angles at the adjacent carbons, but the environment of the C=C bond is unaffected.

The planarity of the silacyclopent-3-ene ring is lost on coordination, which confirms the NMR data. The ring adopts an envelope conformation with a dihedral angle of 12° between the C–C=C–C and C–Si–C planes. This value is much lower than in the germacyclopent-3-ene analogue (30°), but the mono- and

Scheme 5.

dispiro compounds are much closer to planarity, with dihedral angles of 13.6 and 5.3°, respectively. As observed in solution, only one isomer is present in the solid state, the one with the Si-bonded CpFe(CO)$_2$ group occupying the least sterically hindered exo site, the all-*trans* conformation of the O(CH$_2$)$_4$FeCp(CO)$_2$ unit reducing the overall steric requirement of this group.

Insertion of a THF molecule into the Si–Fe(2) bond results from ring opening of the cyclic ether, a reaction for which there is few precedents in the literature [20,21]. A tentative mechanism can be proposed [22]. The first step corresponds to the σ coordination of the [CpFe(CO)$_2$]$^-$ anion to the Si atom via a SN$_2$ process giving **5** [23]. Presence of a second [CpFe(CO)$_2$]$^-$ anion generates the ion-pair intermediate **9** characterized by a strong silicon–oxygen bond [20,21,24]. Formation of **8** results then from the THF ring opening assisted by the nucleophilic attack of the [CpFe(CO)$_2$]$^{·}$ anion (Scheme 4). In agreement with this hypothesis is the fact that no THF insertion was observed when two reactants were in the 1/1 ratio, no matter the experimental conditions applied. No other iron species were present in the solution. Moreover, the reaction carried out with excess [CpFe(CO)$_2$]$^-$ in diethyl ether stopped at the monosubstitution stage, giving only complex **5** and in pentane, the mixture was heterogeneous and no reaction occurred.

3.1. Compounds with a σ silicon-cobalt bond

No reaction took place when **1**, **2** and **3** were reacted with [Co(CO)$_4$]$^-$ synthesized in-situ by reduction of the dimer using Na/Hg [4] or K[BH(*sec*-Bu)$_3$] [5] in THF. In this case, the solvent favored charge delocalization from the oxygen atom, giving polymers through Si–O–Si bond formation [21,25,26] and dimers of the metallate anions [26]. No better results were obtained by using pentane as solvent. However, the cobalt derivative **11** was successfuly prepared by hydrosilylation [2] (Scheme 5).

Complete loss of Co$_2$(CO)$_8$ (monitored by the disappearance of the bridging ν(CO) stretch at 1865 cm^{-1}) was observed after 24 h, and **11** precipitated as a dark powder. Its IR spectrum showed four ν(CO) bands at

2008, 2034, 2052 and 2096 cm^{-1}, respectively, in agreement with the IR data reported in the literature for R$_3$SiCo(CO)$_4$ complexes (2). Since this compound shows only one ^{1}H-NMR signal for the Si–CH$_3$ group, a single isomer is likely formed, as noticed above for the Fe systems.

4. Conclusion

Suitable experimental conditions of solvent, temperature and concentration allowed us to synthesize compounds containing silacyclopent-3-ene σ-bonded to iron complexes via the Si atom without opening of the silacyclopentene ring. These complexes are all stable. They are characterized by the presence of a puckered silacyclopentene ring and they illustrate the ability of the Si atom to undergo distortions far from the tetrahedral arrangement in order to accommodate substituents with a broad range of sizes.

5. Supplementary material available

Packing pattern, lists of temperature factors, hydrogen coordinates, bond lengths and angles, least-squares planes, torsion angles and structure factor amplitudes (35 pages) are available upon request from ALB.

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