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REACTIONS OF ALKALI-METAL DERIVATIVES OF METAL CARBONYLS
VIII*. PREPARATION AND PROPERTIES OF CYCLOPENTADIENYLIRON DICARBONYL DERIVATIVES CONTAINING SILICON–SILICON AND SILICON–HYDROGEN BONDS**

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SUMMARY

Reactions of $NaFe(CO)_2C_5H_5$ with the permethylpolysilanyl chlorides $(CH_3)_3Si[Si(CH_3)_2]_nCl$ in tetrahydrofuran solution give the yellow-orange (permethylpolysilanyl)iron derivatives $(CH_3)_3Si[Si(CH_3)_2]_nFe(CO)_2C_5H_5$ ($n=1, 2,$ and 3). Similarly, the reactions of $NaFe(CO)_2C_5H_5$ with the permethylpolysilanyl dichlorides $Cl[Si(CH_3)_2]_nCl$ give the yellow (permethylpolysilanyl)diiron derivatives $C_5H_5Fe(CO)_2[Si(CH_3)_2]_nFe(CO)_2C_5H_5$ ($n=2$ and 3). Reaction of $NaFe(CO)_2C_5H_5$ with dimethylchlorosilane gives orange volatile air-sensitive $(CH_3)_2Si(H)Fe(CO)_2C_5H_5$, which exhibits an unusually low ν(SiH) frequency at 2071 cm^{-1} and which undergoes facile chlorination with carbon tetrachloride at room temperature to give yellow-orange crystalline $(CH_3)_2Si(Cl)Fe(CO)_2C_5H_5$. Reactions of $NaFe(CO)_2C_5H_5$ with the halides $(CH_3)_3Si(CH_2)_nX$ ($n=1$, X=Br; $n=3$, X=Cl) give the orange liquids $(CH_3)_3Si(CH_2)_nFe(CO)_2C_5H_5$ ($n=1$ and 3). Triphenylphosphine reacts with $(CH_3)_3SiCH_2Fe(CO)_2C_5H_5$ to give the carbonyl insertion product $(CH_3)_3SiCH_2COFe(CO)[P(C_6H_5)_3](C_5H_5)$. Yellow crystalline $C_2H_4[Si(CH_3)_2Fe(CO)_2C_5H_5]_2$ was prepared from $NaFe(CO)_2C_5H_5$ and the corresponding silicon chloride.

Within the last few years numerous organosilyl derivatives of transition metals have been prepared[3-8]. However, when this work was started the only known silicon derivative of a transition metal containing a silicon–silicon bond was the (pentamethyldisilanyl)cobalt derivative $(CH_3)_3SiSi(CH_3)_2Co(CO)_4$[9]. This paper describes the preparation and properties of cyclopentadienyliron dicarbonyl derivatives of the general types $(CH_3)_3Si[Si(CH_3)_2]_nFe(CO)_2C_5H_5$ and $C_5H_5Fe(CO)_2[Si(CH_3)_2]_nFe(CO)_2C_5H_5$ with silicon–silicon bonds. This paper also describes the preparation and properties of the following complexes: (*a*) The derivatives $(CH_3)_3Si(CH_2)_n$-

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[*] For part VII see ref. 1.

[**] Presented in part at the Fourth International Symposium on Organometallic Chemistry, Bristol, England, July, 1969. For a preliminary communication of some of this work see ref. 2.

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$Fe(CO)_2C_5H_5$ without direct iron–silicon bonds*. (*b*) The compound $(CH_3)_2$-$Si(H)Fe(CO)_2C_5H_5$ containing both silicon–hydrogen and silicon–iron bonds. A variety of silyl (SiH_3) derivatives of manganese[10], iron[11], and cobalt[12] carbonyls are known, but the only reported transition metal derivative containing only one silicon–hydrogen bond is the cobalt derivative $(C_6H_5)_2Si(H)Co(CO)_4$[13].

EXPERIMENTAL

Microanalyses (Table 1) were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Infrared spectra were taken in the indicated media and recorded on a Perkin–Elmer Model 621 spectrometer with grating optics. Proton

TABLE 1

NEW CYCLOPENTADIENYLIRON DICARBONYL DERIVATIVES PREPARED IN THIS WORK

Compound color	M.p. or b.p.[a]	Yield (%)	Analyses, found (calcd.) (%)					ν(CO) freq.[b]
			C	H	O	Fe	Si	
$Me_5Si_2Fe(CO)_2C_5H_5$ orange	34–35° 84–90° (0.1)	52	47.1 (46.8)	6.3 (6.5)	10.2 (10.4)	18.2 (18.1)	18.0 (18.2)	1996 1952
$Me_7Si_3Fe(CO)_2C_5H_5$ orange	22–23° 135–145° (0.2)	~35	46.4 (45.9)	7.1 (7.1)	9.0 (8.7)	15.2 (15.3)	22.6 (22.9)	1994 1952
$Me_9Si_4Fe(CO)_2C_5H_5$ orange	Liquid	28	45.9 (45.3)	7.7 (7.6)	7.4 (7.6)	12.8 (13.2)	26.2 (26.4)	1995 1952
$Me_4Si_2[Fe(CO)_2C_5H_5]_2$ yellow	150°	40	46.1 (45.9)	4.7 (4.7)		23.8 (23.6)		1997 1949
$Me_6Si_3[Fe(CO)_2C_5H_5]_2$ yellow	172–173°	33	45.3 (45.5)	5.3 (5.3)		20.6 (21.0)		1990 1939
$Me_2Si(H)Fe(CO)_2C_5H_5$ orange	Liquid 59° (0.04)	58	44.2 (45.6)	5.1 (5.1)		23.2 (23.6)	11.9 (11.8)	1997 1948[d]
$Me_2Si(Cl)Fe(CO)_2C_5H_5$ yellow-orange	63–65°	50	40.3 (39.9)	4.4 (4.1)		20.6 (20.6)	[c]	2018 2000 1962 1947
$Me_3SiCH_2Fe(CO)_2C_5H_5$ orange	25° 94° (0.1) 73° (0.04)	54	49.6 (50.0)	6.1 (6.1)		21.2 (21.8)		2018 1960
$Me_3Si(CH_2)_3Fe(CO)_2C_5H_5$ orange	Liquid	25	54.7 (53.4)	7.5 (6.8)		17.5 (17.5)		1998 1956
$C_2H_4[SiMe_2Fe(CO)_2C_5H_5]_2$ yellow	155–156°	30	48.4 (48.2)	5.3 (5.2)		22.0 (22.5)		2005 1948

[a] The b.p. pressure in mm. is given in parentheses. [b] These frequencies were determined in cyclohexane solution on a Perkin–Elmer Model 621 spectrometer with grating optics. [c] Cl found 13.2%, calcd. 13.1%. [d] ν(SiH) 2071 cm^{-1}.

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* After this work was completed we were informed by B. M. Kingston (private communication, April, 1969) that he has independently studied $(CH_3)_3SiCH_2$ derivatives of iron, molybdenum, tungsten, manganese, and platinum in Dr. M. F. Lappert's group at the University of Sussex.

TABLE 2

PROTON NMR SPECTRA OF NEW COMPOUNDS PREPARED IN THIS WORK[a]

Compound	Solvent	Proton NMR chemical shift, τ[b]			
		π-C_5H_5	CH_2	CH_3SiFe[c]	CH_3SiSi[d]
$Me_5Si_2Fe(CO)_2C_5H_5$	$CDCl_3$	5.27 s		9.63 s	9.88 s
$Me_7Si_3Fe(CO)_2C_5H_5$	$CDCl_3$	5.22 s		9.46 s	9.77 s
$Me_9Si_4Fe(CO)_2C_5H_5$	$CDCl_3$	5.37 s		9.59 s	9.92 br
$Me_4Si_2[Fe(CO)_2C_5H_5]_2$	$CHCl_3$	5.21 s		9.55 s	
$Me_6Si_3[Fe(CO)_2C_5H_5]_2$	$CDCl_3$	5.22 s		9.48 s	9.70 s
$Me_2SiHFe(CO)_2C_5H_5$	Neat	5.51 s		9.55 d(4)	SiH:5.21m[e](4)
$Me_2Si(Cl)Fe(CO)_2C_5H_5$	$CDCl_3$	5.13 s		9.11 s	
$Me_3SiCH_2Fe(CO)_2C_5H_5$	$CDCl_3$	5.33 s	10.36 s		10.00 s
$Me_3SiCH_2COFe(CO)(PPh_3)C_5H_5$	$CDCl_3$	5.60 s	7.85 s		9.99 s
$Me_3Si(CH_2)_3Fe(CO)_2C_5H_5$	$CDCl_3$	5.56 s	8.57 s(br)		10.08 s
$C_2H_4[SiMe_2Fe(CO)_2C_5H_5]_2$	$CDCl_3$	5.50 s	9.14 s	9.68 s	

[a] These spectra were taken in the indicated solvents and recorded on a Varian A-60 or a Perkin–Elmer Hitachi R-20 spectrometer at 60 Mc or a Varian HA-100 spectrometer at 100 Mc. [b] The following abbreviations were used: s = singlet, d = doublet, m = multiplet, br = broad. Coupling constants in Hz are given in parentheses. [c] This column lists chemical shifts of protons of methyl groups bonded to a silicon atom which is bonded to one iron atom. [d] This column lists chemical shifts of protons of methyl groups bonded to silicon atoms which are bonded only to carbon and/or other silicon atoms. [e] This multiplet appeared to be the inner five lines of a 1/6/15/20/15/6/1 septet.

NMR spectra (Table 2) were taken in the indicated solvents and recorded on a Varian A-60 or HA-100 or a Perkin–Elmer Hitachi R-20 spectrometer. Mass spectra were taken at 70 eV electron energies on a Perkin–Elmer Hitachi RMU-6 mass spectrometer. Melting points were taken in capillaries and are uncorrected.

A nitrogen atmosphere was routinely provided for the following operations: (*a*) carrying out reactions; (*b*) handling filtered solutions of organoiron compounds; (*c*) admitting to evacuated vessels.

Reagents

Trimethylchlorosilane, dimethyldichlorosilane, and 1,2-bis(dimethylchlorosilyl) ethane were provided by Dr. William Atwell of the Dow-Corning Corporation. Hexamethyldisilane was prepared by coupling of trimethylchlorosilane using sodium–potassium alloy in xylene[14] in the early stages of this research but switching to the safer lithium in boiling tetrahydrofuran[15] for the later stages of this research. Octamethyltrisilane was prepared by coupling dimethyldichlorosilane with excess trimethylchlorosilane using lithium in tetrahydrofuran[16]. Decamethyltetrasilane was prepared by coupling pentamethylchlorodisilane using either sodium in boiling xylene[17] or lithium in tetrahydrofuran[18]. These polysilanes were converted to their monochlorides or dichlorides by chlorinative demethylation using acetyl chloride and aluminum chloride in stoichiometric quantities[19]. In our hands this method was found to be much more satisfactory than the older method[20] using concentrated sulfuric acid followed by addition of ammonium chloride. The (bromomethyl)trimethylsilane, (3-chloropropyl)trimethylsilane, and dimethylchlorosilane were purchased from Columbia Organic Chemicals (Columbia, South Carolina) and Peninsular Chem Research (Gainesville, Florida). The sodium salt $NaFe(CO)_2C_5H_5$ was prepared from $[C_5H_5Fe(CO)_2]_2$[21] by the standard procedure[22] using tetrahydrofuran redistilled over lithium aluminum hydride.

Preparation of the pentamethyldisilanyl derivative $(CH_3)_3SiSi(CH_3)_2Fe(CO)_2C_5H_5$ and related compounds

A tetrahydrofuran solution containing 54 mmoles of $NaFe(CO)_2C_5H_5$ was stirred with 9.0 g (54 mmoles) of pentamethylchlorodisilane (b.p. 133–135°, lit.[20] b.p. 134–135°) for 6 h. Solvent was removed at ~40°/40 mm. The residue was extracted with ~200 ml of hexane. Solvent was removed from the filtered hexane extract at ~25°/40 mm. The residue was distilled at 84–91°/0.1 mm to give 8.6 g (52% yield) of $(CH_3)_3SiSi(CH_3)_2Fe(CO)_2C_5H_5$, m.p. 34–35°.

The preparation of the heptamethyltrisilanyl derivative $(CH_3)_3Si[Si(CH_3)_2]_2$-$Fe(CO)_2C_5H_5$ was analogous to the preparation of the pentamethyldisilanyl derivative described above except that chromatography on an alumina column in hexane was also used to purify the product. The volatility of the nonamethyltetrasilanyl derivative $(CH_3)_3Si[Si(CH_3)_2]_3Fe(CO)_2C_5H_5$ was too low for this compound to be purified efficiently by vacuum distillation. It was therefore purified exclusively by chromatography on alumina in hexane solution.

Preparation of the tetramethyldisilanyl derivative $C_5H_5Fe(CO)_2[Si(CH_3)_2]_2Fe(CO)_2$-$C_5H_5$

A tetrahydrofuran solution containing 11.3 mmoles of $NaFe(CO)_2C_5H_5$ was stirred with 1.8 g (9.6 mmoles) of 1,2-dichlorotetramethyldisilane for 5 h. Solvent was then removed at ~25°/40 mm. A petroleum ether (30–60°) solution of the residue was chromatographed on a 2 × 40 cm alumina column. Elution of the column with petroleum ether first separated a yellow band of ferrocene. After removal of this ferrocene, the chromatogram was eluted with a 3/7 mixture of diethyl ether and petroleum ether to give a yellow eluate which upon evaporation gave a 40% yield of $C_5H_5Fe(CO)_2$-$[Si(CH_3)_2]_2Fe(CO)_2C_5H_5$, m.p. 150°.

A similar procedure was used to prepare the hexamethyltrisilanyl derivative $C_5H_5Fe(CO)_2[Si(CH_3)_2]_3Fe(CO)_2C_5H_5$ from $NaFe(CO)_2C_5H_5$ and 1,3-dichlorohexamethyltrisilane. In this case the chromatography was carried out in pentane solution.

Preparation of $(CH_3)_2Si(H)Fe(CO)_2C_5H_5$

A tetrahydrofuran solution containing 100 mmoles of $NaFe(CO)_2C_5H_5$ was stirred with 10.5 ml (9.45 g, 100 mmoles) of dimethylchlorosilane for about 12 h. Solvent was then removed at ~25°/40 mm. The residue was extracted with three 100 ml portions of 1/1 dichloromethane/pentane. Solvent was removed from the filtered extracts at ~25°/40 mm. Vacuum distillation of the residue gave ~13.6 g (58% yield) of orange liquid air-sensitive $(CH_3)_2Si(H)Fe(CO)_2C_5H_5$, b.p. 59°/0.4 mm.

A similarly carried out reaction between $NaFe(CO)_2C_5H_5$ and (bromomethyl)trimethylsilane gave a 52% yield of orange liquid $(CH_3)_3SiCH_2Fe(CO)_2C_5H_5$, m.p. ~25°, b.p. 73°/0.04 mm, 94°/0.1 mm.

Preparation of $(CH_3)_3Si(CH_2)_3Fe(CO)_2C_5H_5$

A tetrahydrofuran solution containing 11.3 mmoles of $NaFe(CO)_2C_5H_5$ was stirred with 2.5 g (16.6 mmoles) of (3-chloropropyl)trimethylsilane for 3 h at room temperature. Solvent was then removed from the reaction mixture at ~25°/40 mm. A petroleum ether solution of the residue was chromatographed on a 2 × 40 cm alumina column. Elution of the yellow band with petroleum ether followed by evaporation of the filtered eluate at ~25°/40 mm gave orange liquid $(CH_3)_3Si(CH_2)_3Fe(CO)_2C_5H_5$ in ~25% yield.

Preparation of $C_2H_4[Si(CH_3)_2Fe(CO)_2C_5H_5]_2$

A tetrahydrofuran solution containing 22.6 mmoles of $NaFe(CO)_2C_5H_5$ was stirred with 2.2 g (10.3 mmoles) of 1,2-bis(dimethylchlorosilyl)ethane for 16 h. Solvent was removed at ~25°/40 mm. A filtered diethyl ether solution of the residue was chromatographed on a 2 × 40 cm alumina column made up in hexane. The chromatogram was developed with hexane. The first yellow band was eluted with hexane; evaporation of this eluate gave ferrocene. The second yellow band was eluted with 1/1 hexane/diethyl ether. Evaporation of this eluate gave yellow crystals which were recrystallized twice from mixtures of diethyl ether and pentane to give a 30% yield of $C_2H_4[Si(CH_3)_2Fe(CO)_2C_5H_5]_2$, m.p. 155–156°.

Reaction of $(CH_3)_2Si(H)Fe(CO)_2C_5H_5$ *with carbon tetrachloride*

Carbon tetrachloride (~50 ml) was treated with 1.4 g (1 ml, 5.9 mmoles) of $(CH_3)_2Si(H)Fe(CO)_2C_5H_5$. While stirring overnight at room temperature solvent was removed in a stream of nitrogen. The resulting crystals were dissolved in ~15 ml of pentane and the filtered solution cooled in a −78° bath. Yellow-orange crystals of the chlorination product separated. The supernatant liquid was removed from these crystals by decantation at −78°. The crystals were then dried at 0.1 mm while warming slowly from −78° to room temperature to give 0.8 g (50% yield) of yellow-orange air-sensitive $(CH_3)_2Si(Cl)Fe(CO)_2C_5H_5$, m.p. 63–65°.

Reaction of $(CH_3)_3SiCH_2Fe(CO)_2C_5H_5$ *with triphenylphosphine*

A mixture of 0.57 g (2.16 mmoles) of $(CH_3)_3SiCH_2Fe(CO)_2C_5H_5$, 0.57 g (2.18 mmoles) of triphenylphosphine, and ~100 ml of tetrahydrofuran was boiled under reflux for 55 h. Solvent was removed from the reaction mixture at ~25°/40 mm. The red oil was treated with hexane. The resulting red crystals were washed several times with hexane to give 0.34 g (30% yield) of $(CH_3)_3SiCH_2COFe(CO)[P(C_6H_5)_3](C_5H_5)$, m.p. 138–139°. A cyclohexane solution of this product exhibited ν(CO) frequencies at 1922 and 1584 cm^{-1}. (Found: C, 66.1; H, 6.1; O, 4.9; P, 6.2. $C_{29}H_{31}FeO_2PSi$ calcd.: C, 67.3; H, 6.0; O, 6.2; P, 6.2%.)

Infrared spectra

Table 1 lists the ν(CO) frequencies in cyclohexane solution of the new compounds prepared in this work. Spectra of some of the new compounds in other media are listed below:

A. $C_5H_5Fe(CO)_2[Si(CH_3)_2]_2Fe(CO)_2C_5H_5$ *(KBr pellet)*. ν(CH) band at 2938 (w, br) cm^{-1}; ν(CO) frequencies at 1977 (vs) and 1929 (vs) cm^{-1}; other bands at 1430 (vw), 1408 (w), 1356 (vw), 1255 (vw), 1234 (m), 1100 (vw), 1056 (vw), 1010 (w), 995 (vw), 835 (m), 817 (m), 764 (m), 663 (w), 640 (m), and 629 (w, sh) cm^{-1}.

B. $C_5H_5Fe(CO)_2[Si(CH_3)_2]_3Fe(CO)_2C_5H_5$ *(KBr pellet)*. ν(CH) band at 2880 (w, vbr) cm^{-1}; ν(CO) frequencies at 1977 (vs) and 1913 (vs) cm^{-1}; other bands at 1399 (w), 1389 (w), 1254 (vw), 1237 (m), 995 (vw), 835 (w), 816 (m), 757 (m), 736 (w), 720 (w), 642 (w), and 622 (w) cm^{-1}.

C. $(CH_3)_2Si(H)Fe(CO)_2C_5H_5$ *(liquid film)*. ν(CH) bands at 3119 (vw), 2941 (w), and 2838 (w) cm^{-1}; ν(SiH) band at 2067 (s) cm^{-1}; ν(CO) bands at 2001 (vs) and 1938 (vs) cm^{-1}; other bands at 1427 (m), 1412 (m), 1362 (w), 1237 (s), 1160 (vw), 1110 (w), 1059 (w), 1031 (vw), 1010 (m), 997 (m), 865 (s), and 822 (s) cm^{-1}.

D. $(CH_3)_3SiCH_2Fe(CO)_2C_5H_5$ *(liquid film)*. ν(CH) bands at 3110 (w), 2960 (m), 2900 (m), and 2860 (m) cm^{-1}; ν(CO) frequencies at 2002 (vs) and 1947 (vs) cm^{-1}; other bands at 1433 (m), 1417 (m), 1369 (w), 1364 (w), 1357 (w), 1287 (vw), 1253 (m), 1242 (s), 1115 (w), 1095 (vw), 1061 (w), 1024 (w), 1016 (m), 1001 (m), 964 (m), 924 (w), 845 (s, br), 820 (s, br), 773 (w), 758 (w), 748 (w), 722 (w), 680 (m), and 634 (s) cm^{-1}.

E. $(CH_3)_3SiCH_2COFe(CO)[P(C_6H_5)_3](C_5H_5)$ *(KBr pellet)*. ν(CH) bands at 3047 (vw), 2950 (vw), 2869 (vw), and 2856 (vvw) cm^{-1}; ν(CO) frequencies at 1918 (s), 1571 (m), and 1565 (m) cm^{-1}; other bands at 1481 (w), 1431 (m), 1414 (vw), 1253 (w), 1246 (m), 1185 (vw), 1179 (vw), 1119 (w), 1089 (m), 1065 (vw), 1009 (w), 992 (w), 941 (m), 848 (m), 813 (m), 750 (w), 733 (w), 714 (vw), 689 (m), and 604 (w) cm^{-1}.

F. $(CH_3)_3Si(CH_2)_3Fe(CO)_2C_5H_5$ *(liquid film)*. ν(CH) bands at 2943 (m) and 2914 (m) cm^{-1}; ν(CO) frequencies at 1994 (vs) and 1944 (vs) cm^{-1}; other bands at 1444 (vw), 1430 (vw), 1414 (w), 1254 (w), 1244 (s), 1166 (m), 1117 (vw), 1099 (vw), 1087 (vw), 1009 (w), 993 (w), 970 (vw), 884 (w), 854 (s), 824 (s), 817 (s), 753 (w), 696 (w), 683 (w), and 629 (s) cm^{-1}.

G. $C_2H_4[Si(CH_3)_2Fe(CO)_2C_5H_5]_2$ *(KBr pellet)*. ν(CH) bands at 3100 (vw), 2950 (w), 2900 (w), and 2821 (w) cm^{-1}; ν(CO) frequencies at 1983 (vs) and 1925 (vs) cm^{-1}; other bands at 1430 (w), 1410 (m), 1401 (m, sh), 1356 (w), 1250 (s), 1238 (s), 1129 (s), 1108 (vw), 1061 (vw), 1050 (vw), 1010 (m), 993 (w), 856 (m), 822 (s), 791 (s), 750 (s), 740 (m), 686 (m), 670 (m), and 640 (s) cm^{-1}.

Mass spectra

These spectra were taken at 70 eV on a Perkin–Elmer Hitachi RMU-6 mass spectrometer. Relative intensities of the ions are given in parentheses. Only the major ions clearly discernible from the background are given.

A. $(CH_3)_2Si(H)Fe(CO)_2C_5H_5$. $\mathrm{C_5H_5Fe(CO)_2SiH(CH_3)_2^+}$ (3), $\mathrm{C_5H_5Fe(CO)_2Si(CH_3)_2^+}$ (1), $\mathrm{C_5H_5Fe(CO)_2SiHCH_3^+}$ (6), $\mathrm{C_5H_5FeCOSiH(CH_3)_2^+}$ (92), $\mathrm{C_5H_5FeCOSiHCH_3^+}$ (7), $\mathrm{(C_5H_5)_2Fe^+}$ (23), $\mathrm{C_5H_5FeSiH(CH_3)_2^+}$ (99), $\mathrm{C_5H_5FeCOSiH^+}$ (57), $\mathrm{C_5H_5FeSiCH_3^+}$ (100), $\mathrm{C_5H_5FeSiH^+}$ (6), $\mathrm{C_5H_5FeSi^+}$ (5), $\mathrm{C_5H_4FeSi^+}$ (6), $\mathrm{C_5H_5Fe^+}$ (46), $\mathrm{FeSi(CH_3)_2^+}$ (92), $\mathrm{C_6H_7Si^+}$ (16), $\mathrm{FeSiCH_2^+}$ (20), $\mathrm{C_3HFe^+}$ (61), $\mathrm{C_5H_6^+}$ (41), $\mathrm{C_5H_5^+}$ (18), $\mathrm{(CH_3)_2SiH^+}$ (14), $\mathrm{Fe^+}$ (39).

B. $(CH_3)_3SiFe(CO)_2C_5H_5$. $\mathrm{C_5H_5Fe(CO)_2Si(CH_3)_3^+}$ (47), $\mathrm{C_5H_5Fe(CO)_2Si(CH_3)_2^+}$ (11), $\mathrm{C_5H_5FeCOSi(CH_3)_3^+}$ (37), $\mathrm{C_5H_5FeCOSi(CH_3)_2^+}$ (8), $\mathrm{C_5H_5FeSi(CH_3)_3^+}$ (100), $\mathrm{C_5H_5FeCOSiCH_3^+}$ (24), $\mathrm{C_5H_5FeSi(CH_3)_2^+}$ (37), $\mathrm{C_5H_5FeSi(CH_3)(CH_2)^+}$ (66), $\mathrm{C_5H_5FeSiCH_3^+}$ (18), $\mathrm{C_5H_5FeSi^+}$ (5), $\mathrm{C_5H_4FeSi^+}$ (5), $\mathrm{C_6H_6Fe^+}$ (11), $\mathrm{FeSi(CH_2)(CH_3)_2^+}$ (45), $\mathrm{C_5H_5Fe^+}$ (61), $\mathrm{C_6H_7Si^+}$ (13), $\mathrm{HFeSiCH_3^+}$ (29), $\mathrm{FeSiCH_2^+}$ (18), $\mathrm{C_3H_3Fe^+}$ (16), $\mathrm{C_3HFe^+}$ (53), $\mathrm{FeSi^+}$ (16), $\mathrm{(CH_3)_3Si^+}$ (95), $\mathrm{Fe^+}$ (76), $\mathrm{CH_3Si^+}$ (24), $\mathrm{C_3H_3^+}$ (16).

C. $(CH_3)_5Si_2Fe(CO)_2C_5H_5$. $\mathrm{C_5H_5Fe(CO)_2Si_2(CH_3)_5^+}$ (11), $\mathrm{C_5H_5Fe(CO)_2Si_2(CH_3)_4^+}$ (2), $\mathrm{C_5H_5FeCOSi_2(CH_3)_5^+}$ (7), $\mathrm{C_5H_5FeCOSi_2(CH_3)_4^+}$ (6), $\mathrm{C_5H_5FeSi_2(CH_3)_5^+}$ (5), $\mathrm{C_5H_5Fe(CO)_2Si(CH_3)_3^+}$ (15), $\mathrm{C_5H_5Fe(CO)_2SiH(CH_3)_2^+}$ (20), $\mathrm{C_5H_5Fe(CO)_2Si}$-

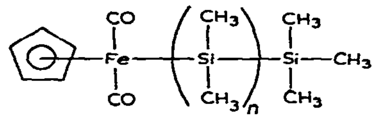
$(CH_3)_2^+$ (27), $C_5H_5Fe(CO)_2Si(CH_3)(CH_2)^+$ (22), $C_5H_5FeCOSi(CH_3)_3^+$ (6), $C_5H_5FeCOSi(CH_3)_2^+$ (9), $C_5H_5FeSi_2C_2H_4^+$?(10), $C_5H_5FeSi(CH_3)_3^+$ (11), $C_5H_5FeSi(CH_3)_2^+$ (12), $C_5H_5FeSi(CH_3)(CH_2)^+$ (14), $(CH_3)_5Si_2^+$ (100).

D. $(CH_3)_7Si_3Fe(CO)_2C_5H_5$. $C_5H_5Fe(CO)_2Si_3(CH_3)_7^+$ (11), $C_5H_5Fe(CO)_2Si_3(CH_3)_6^+$ (0.5), $C_5H_5FeCOSi_3(CH_3)_7^+$ (3), $C_5H_5FeCOSi_3(CH_3)_6^+$ (8), $C_5H_5FeSi_3(CH_3)_7^+$ (3), $C_5H_5Fe(CO)_2Si_2(CH_3)_4^+$ (3), $C_5H_5FeCOSi_2(CH_3)_4^+$ (27), $C_5H_5Fe(CO)_2Si(CH_3)_2^+$ (27), $C_5H_5FeCOSi(CH_3)_2^+$ (8), $(CH_3)_7Si_3^+$ (100), $C_5H_5FeSi(CH_3)_2^+$ (6), $(CH_3)_6Si_2H^+$ (14), $(CH_3)_5Si_2^+$ (57), $C_5H_5Fe^+$ (21), $(CH_3)_4Si_2^+$ (54), $(CH_3)_3Si_2CH_2^+$ (27), C_3HFe^+ (25), $(CH_3)_3Si^+$ (200), $CH_3SiCH_2^+$ (48), Fe^+ (16), $SiCH^+$?(37), $C_3H_3^+$ (25).

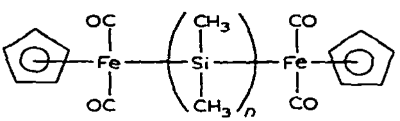
E. $(CH_3)_9Si_4Fe(CO)_2C_5H_5$. $C_5H_5Fe(CO)_2Si_4(CH_3)_9^+$ (6), $C_5H_5Fe(CO)_2Si_4(CH_3)_8^+$ (3), $C_5H_5FeCOSi_4(CH_3)_9^+$ (0.7), $C_5H_5FeCOSi_4(CH_3)_8^+$ (6), $C_5H_5FeCOSi_4(CH_3)_7^+$ (0.7), $C_5H_5FeSi_4(CH_3)_6^+$ (3), $(CH_3)_9Si_4^+$ (100), $C_5H_5Fe(CO)_2Si(CH_3)_2^+$ (40), $C_5H_5FeCOSi(CH_3)_2^+$ (10), $(CH_3)_7Si_3^+$ (8), $C_5H_5FeSi(CH_3)_2^+$ (11), $(CH_3)_5Si_3CH_2^+$ (138), $(CH_3)_5Si_2^+$ (22), $C_5H_5Fe^+$ (20), $(CH_3)_3Si_2CH_2^+$ (19), $(CH_3)_3Si^+$ (410).

DISCUSSION

The preparations of the polysilanyl derivatives of cyclopentadienyliron dicarbonyl from the corresponding polysilanyl halides and $NaFe(CO)_2C_5H_5$ are completely analogous to the preparation of $(CH_3)_3SiFe(CO)_2C_5H_5$ from trimethylchlorosilane and $NaFe(CO)_2C_5H_5$ reported in 1956[3]. Derivatives with a $C_5H_5Fe(CO)_2$ group at either one or both ends of a permethylpolysilanyl chain could be prepared. The compounds with one $C_5H_5Fe(CO)_2$ group $(CH_3)_3Si[Si(CH_3)_2]_nFe(CO)_2C_5H_5$ (I: $n=1, 2$, and 3) are yellow-orange liquids at or slightly above room temperature and possess sufficient, volatility for mass spectra to be obtained. The compounds with two $C_5H_5Fe(CO)_2$ groups $C_5H_5Fe(CO)_2[Si(CH_3)_2]_nFe(CO)_2C_5H_5$ (II: $n=2$ and 3) are much less volatile yellow solids melting at or above 150°. These compounds with both iron–silicon and silicon–silicon bonds appear to be at least as stable as the trimethylsilyl derivative $(CH_3)_3SiFe(CO)_2C_5H_5$ to both air oxidation and thermal decomposition. For example the tetrasilanyl derivative $(CH_3)_3Si[Si(CH_3)_2]_3Fe(CO)_2C_5H_5$ (I: $n=3$) survives heating to ~200°/0.5 mm. These observations suggest that the presence of the silicon–silicon bonds in polysilanyliron derivatives of the types (I) and (II) does not introduce additional instability.



(I)



(II)

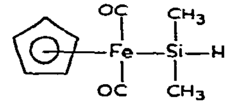
The infrared spectra of the new permethylpolysilanyl derivatives of types (I) and (II) exhibit the two ν(CO) frequencies characteristic of cyclopentadienyliron dicarbonyl derivatives. The proton NMR spectra of the permethylpolysilanyl derivatives (I) and (II) each exhibit a singlet resonance in the range τ 5.2–5.4 arising from the five equivalent protons of the π-cyclopentadienyl ring. The methyl protons attached to silicon atoms bonded directly to iron atoms exhibit a singlet resonance in the range τ 9.4–9.6 and significantly separated from the resonances of the methyl protons attached to silicon atoms only bonded to carbon atoms or other silicon atoms which appear in the range τ 9.7–10.0. Integration of the methyl resonances of these two types in the proton NMR spectra of the complexes (I) and (II) provided an excellent confirmation of the types of permethylpolysilanyl groups present in the complexes.

Attempts were made to prepare pentamethyldisilanyl derivatives of other transition metals by reactions of chloropentamethyldisilane with the sodium salts $NaM(CO)_5$ (M = Mn and Re) and $NaM(CO)_3C_5H_5$ (M = Mo and W). However, no pentamethyldisilanyl derivatives of any of these transition metals could be isolated from these reaction mixtures. The lower nucleophilicity of these anions[23] relative to the $[C_5H_5Fe(CO)_2]^-$ anion may account for the failure of these manganese, rhenium, molybdenum, and tungsten anions to form pentamethyldisilanyl derivatives upon reaction with chloropentamethyldisilane.

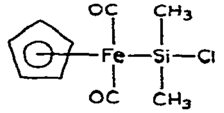
A compound of particular interest is the dimethylsilyl derivative $(CH_3)_2Si(H)Fe(CO)_2C_5H_5$ (III) since it contains both a silicon–iron bond and a silicon–hydrogen bond. This compound is readily obtained from the reaction between $NaFe(CO)_2C_5H_5$ and dimethylchlorosilane as an orange rather air-sensitive liquid which can be purified by vacuum distillation. The proton NMR spectrum of $(CH_3)_2Si(H)Fe(CO)_2C_5H_5$ supports its formulation as (III). The six methyl protons appear at τ 9.55 as a doublet ($J = 4$ Hz) owing to coupling with the SiH hydrogen atom. The single SiH proton appears at τ 5.21 as a multiplet ($J = 4$ Hz) owing to the coupling with the six methyl protons. Only the inner five lines of the expected 1/6/15/20/15/6/1 septet could be observed.

The infrared spectrum of the dimethylsilyl derivative (III) exhibits the usual two ν(CO) frequencies around 2000 cm^{-1}. In addition, however, a third strong band is observed at 2071 cm^{-1} which can be assigned to the ν(SiH) frequency. This value for the ν(SiH) frequency is an unusually low one, since ν(SiH) frequencies for ordinary silanes with chloro, alkyl, aryl, and alkoxy substituents fall in the range 2260–2090 cm^{-1}. However, the value of the ν(SiH) frequency is found to decrease as the electronegativity of the other substituents attached to the silicon atom is decreased[24]. The relatively low value of the ν(SiH) frequency in $(CH_3)_2Si(H)Fe(CO)_2C_5H_5$ (III) thus appears to be a consequence of the relative electropositivity of the iron atom in the $C_5H_5Fe(CO)_2$ group which is bonded to the silicon atom. Even lower ν(SiH) frequencies ($\sim$2055 cm^{-1}) are found in silanes of the type $(R_3Si)_3SiH$[25] where the silicon atom bonded to the hydrogen atom is bonded to three other relatively electropositive silicon atoms.

The low ν(SiH) frequencies in silanes of the types $(R_3Si)_3SiH$ as well as in the new iron compound $(CH_3)_2Si(H)Fe(CO)_2C_5H_5$ (III) indicate weak silicon–hydrogen bonds thereby suggesting unusual chemical reactivity for silanes of these types. Experimental data on $[(CH_3)_3Si]_3SiH$ indicate this silane to be unusually reactive[26]. Thus the silicon–hydrogen bond in $[(CH_3)_3Si]_3SiH$ is readily chlorinated by carbon



(III)



(IV)

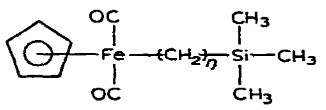
tetrachloride at room temperature to give the corresponding chloride $[(CH_3)_3Si]_3$-

SiCl[26]. Treatment of the new dimethylsilyliron derivative $(CH_3)_2Si(H)Fe(CO)_2C_5H_5$ (III) with carbon tetrachloride at room temperature likewise results in rapid chlorination giving $(CH_3)_2Si(Cl)Fe(CO)_2C_5H_5$ (IV) as an air-sensitive yellow-orange crystalline solid. Attempts to prepare $(CH_3)_2Si(Cl)Fe(CO)_2C_5H_5$ (IV) from $NaFe(CO)_2$-C_5H_5 and dimethyldichlorosilane were unsuccessful; such reactions failed to give identifiable quantities of silyliron derivatives. Reactions of $(CH_3)_2Si(Cl)Fe(CO)_2$-C_5H_5 (IV) with nucleophiles in attempts to prepare other types of silicon derivatives of the $C_5H_5Fe(CO)_2$ system are currently under investigation.

The infrared spectrum of $(CH_3)_2Si(Cl)Fe(CO)_2C_5H_5$ (IV) in cyclohexane solution exhibits four strong ν(CO) frequencies rather than the more usual two ν(CO) frequencies for $C_5H_5Fe(CO)_2$ derivatives. This indicates the presence of two conformational isomers in solution and represents a further example of a conformational effect on terminal ν(CO) frequencies first noted by Jetz and Graham[6] in the infrared spectrum of the closely related compound $CH_3SiCl_2Fe(CO)_2C_5H_5$.

The mass spectra of the silyl derivatives with one $C_5H_5Fe(CO)_2$ group were investigated. The molecular ion undergoes the usual stepwise loss of the two carbonyl groups. However, loss of methyl groups by cleavage of the silicon–methyl bond can compete effectively with this stepwise carbonyl loss. Cleavage of silicon–silicon bonds also competes with loss of carbonyl groups giving rise to ions of the type C_5H_5Fe-$(CO)_nSi(CH_3)_2^+$ ($n=0$, 1, and 2) in the mass spectra of the permethylpolysilanyl derivatives. Analogous cleavage of the methyl–tin bonds was found to be a facile process in the reported[27] mass spectrum of the trimethyltin derivative $(CH_3)_3SnMo$-$(CO)_3C_5H_5$. Tetramethyldisilanyl ions of the type $C_5H_5Fe(CO)_nSi_2(CH_3)_4^+$ ($n=2$ and 1) are also observed in the mass spectra of the heptamethyltrisilanyl derivative $(CH_3)_3Si[Si(CH_3)_2]_2Fe(CO)_2C_5H_5$ (I: $n=2$). The molecular ion of the dimethylsilyl derivative $(CH_3)_2Si(H)Fe(CO)_2C_5H_5$ (III) exhibits loss of a single hydrogen atom (presumably by cleavage of the silicon–hydrogen bond) to give the ion $C_5H_5Fe(CO)_2$-$Si(CH_3)_2^+$. All of these processes indicate that groups attached to a silicon atom also attached to an iron atom undergo facile cleavage under the conditions of mass spectrometry. This may relate to the relative weakness of the silicon–hydrogen bond in $(CH_3)_2Si(H)Fe(CO)_2C_5H_5$ (III) discussed above. The mass spectrum of the pentamethyldisilanyl derivative $(CH_3)_3SiSi(CH_3)_2Fe(CO)_2C_5H_5$ (I: $n=1$) also exhibits the series of ions $C_5H_5Fe(CO)_nSi(CH_3)_3^+$ ($n=2$, 1, and 0) apparently formed by shift of a methyl group from the silicon atom not bonded to the iron atom to the silicon atom bonded to the iron atom or by shift of a trimethylsilyl group from silicon to iron.

Organosilicon derivatives of cyclopentadienyliron dicarbonyl of the type $(CH_3)_3Si(CH_2)_nFe(CO)_2C_5H_5$ (V: $n=1$ and 3) not containing direct iron–silicon bonds were also prepared in this work for comparison with the derivatives containing direct iron–silicon bonds. The properties of these compounds resemble those of other alkyls of the type $RFe(CO)_2C_5H_5$ with iron–carbon bonds. Of particular interest is the derivative $(CH_3)_3SiCH_2Fe(CO)_2C_5H_5$ (V: $n=1$), apparently the first transition metal derivative of a silicon neopentane type system to be reported in the literature. Similar $(CH_3)_3SiCH_2$ derivatives have been prepared of main group elements such as phosphorus and tin by use of the organomagnesium reagent $(CH_3)_3SiCH_2MgCl$[28]. The iron compound $(CH_3)_3SiCH_2Fe(CO)_2C_5H_5$ (V: $n=1$) is obtained as an orange liquid freezing around room temperature and which can be purified by vacuum distil-



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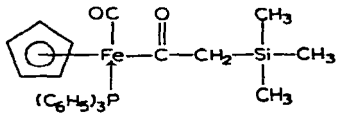
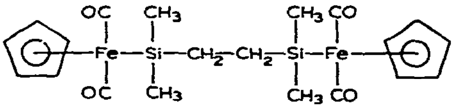


(VI)



(VII)

lation. The infrared and proton NMR spectra of $(CH_3)_3SiCH_2Fe(CO)_2C_5H_5$ support the proposed structure V ($n = 1$). However, almost complete pyrolysis to give ferrocene occurred during an attempt to obtain the mass spectrum of $(CH_3)_3SiCH_2Fe(CO)_2C_5H_5$ under conditions successful for observing the mass spectra of the silyl derivatives with one $C_5H_5Fe(CO)_2$ group discussed in this paper. This observation clearly indicates the lower stability of a derivative with an iron–carbon σ-bond than a similar derivative with an iron–silicon σ-bond. The reactions of $(CH_3)_3SiCH_2Fe(CO)_2C_5H_5$ (V : $n = 1$) with tertiary phosphines proceed in a manner analogous to the corresponding reactions of the methyl derivative $CH_3Fe(CO)_2C_5H_5$ with an iron–carbon σ-bond rather than those of the trimethylsilyl derivative $(CH_3)_3SiFe(CO)_2C_5H_5$ with an iron–silicon σ-bond. Thus the reaction of $(CH_3)_3SiCH_2Fe(CO)_2C_5H_5$ (V : $n = 1$) with triphenyl phosphine results in carbonyl insertion into the bond between the iron atom and the $(CH_3)_3SiCH_2$ group to give the acyl derivative $(CH_3)_3SiCH_2COFe(CO)[P(C_6H_5)_3](C_5H_5)$ (V) similar to the reported[29] reaction of $CH_3Fe(CO)_2C_5H_5$ with triphenylphosphine to give the acetyl derivative $CH_3COFe(CO)[P(C_6H_5)_3](C_5H_5)$. This differs from the reaction of the trimethylsilyliron derivative $(CH_3)_3SiFe(CO)_2C_5H_5$ with triphenylphosphine which gives the simple substitution product $(CH_3)_3SiFe(CO)[P(C_6H_5)_3](C_5H_5)$ without rupture of the iron–silicon bond[30]. The infrared spectrum of the acyl derivative $(CH_3)_3SiCH_2COFe(CO)[P(C_6H_5)_3](C_5H_5)$ (VI) in cyclohexane solution exhibits an acyl $\nu(CO)$ frequency at 1584 cm^{-1} in addition to the expected metal $\nu(CO)$ frequency at 1922 cm^{-1}. Furthermore the chemical shift of the methylene protons in the $(CH_3)_3SiCH_2$ group decreases from τ 10.36 in $(CH_3)_3SiCH_2Fe(CO)_2C_5H_5$ to τ 7.85 in $(CH_3)_3SiCH_2COFe(CO)[P(C_6H_5)_3](C_5H_5)$ because of the insertion of the carbonyl group between the $(CH_3)_3SiCH_2$ group and the iron atom. A similar effect is noted in the NMR spectra of methyl and acetyl derivatives of transition metals.

One objective of this research was the preparation of ring systems containing both iron–iron bonds and iron–silicon bonds. In an attempt to prepare a compound with a six-membered ring containing two iron atoms, two silicon atoms, and two carbon atoms, the compound $C_2H_4[Si(CH_3)_2Fe(CO)_2C_5H_5]_2$ (VII) was exposed to ultraviolet irradiation in benzene solution. Chromatography of the reaction mixture yielded only unchanged (VII) and $[C_5H_5Fe(CO)_2]_2$. The $C_2H_4[Si(CH_3)_2Fe(CO)_2C_5H_5]_2$ required for these studies was prepared by treatment of the corresponding silicon chloride derivative with $NaFe(CO)_2C_5H_5$.

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