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SYNTHESIS OF SILICON-FUNCTIONAL SILYLMETHYL TRANSITION METAL COMPLEXES

I. CYCLOPENTADIENYLIRON DICARBONYL DERIVATIVES

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Summary

The synthesis of $CH_2{=}CHSiMe_2CH_2Fe(CO)_2Cp$, $MeOSiMe_2CH_2Fe(CO)_2Cp$, $[Cp(CO)_2FeCH_2SiMe_2]_2O$, $Cp(CO)_2FeCH_2(Me)\overline{Si(OSiMe_2)_3O}$, $Et_2NSiMe_2CH_2$-$Fe(CO)_2Cp$, $[Cp(CO)_2FeCH_2SiMe_2]_2NH$, $Cp(CO)_2FeSiMe_2CH_2Fe(CO)_2Cp$ and $HSiMe_2CH_2Fe(CO)_2Cp$ has been achieved by the reaction of $NaFe(CO)_2Cp$ with an appropriate halomethyl silicon derivative. Reactions of the hydrosilylmethyl complex with Ph_3CCl, Ph_3CBF_4, and CH_3OH produce the corresponding silicon-functional chloro, fluoro and methoxy derivatives. The reaction of $Cp(CO)_2FeSiMe_2CH_2Fe(CO)_2Cp$ and the methoxy, disiloxy and disilazane derivatives with triphenylphosphine appears to produce the expected insertion products. Some properties of the new compounds prepared have been determined and are discussed.

Introduction

The investigation of silyl and silylmethyl transition metal complexes has been the subject of much recent work in organometallic chemistry [1]. In the case of the silyl derivatives, attention has been given to both the triorgano and certain other silicon-functional derivatives; however, practically all the work with silylmethyl complexes has involved studies of triorganosilylmethyl derivatives, particularly those which contain the Me_3SiCH_2 grouping. The properties of silicon-functional silylmethyl derivatives are of interest because the substituent is in a relatively reactive position β to the metal center. The novel and unexpected rearrangement of $HSiMe_2CH_2Fe(CO)_2Cp$ and $Me_3SiSiMe_2CH_2Fe(CO)_2Cp$ to form derivatives with silicon—iron bonds serves to illustrate the interesting chemistry that this class of compounds has to offer [2,3]. In the present work, we report the synthesis, characterization and some properties of a variety of new silicon-functional silylmethyl cyclopentadienyliron dicarbonyl complexes, most of which contain an electronegative substituent on silicon.

Experimental

All work with air-sensitive non-volatile compounds was carried out in a dry nitrogen atmosphere using conventional glove-bags. Apparatus and solvents were rigorously dried before use. Air-sensitive volatile compounds were handled in a vacuum system [4]. Infrared spectra were determined on a Perkin—Elmer Model 457 spectrometer. Proton NMR spectra were obtained on an Hitachi—Perkin—Elmer R-20 spectrometer, and mass spectra were obtained at 70 eV electron energies on a CEC MS-9 mass spectrometer. Microanalyses were performed by Schwarzkopf Microanalytical Laboratories or Geller Microanalytical Laboratory.

Materials

The sodium salt $NaFe(CO)_2Cp$ was prepared by the reaction of $[Cp(CO)_2Fe]_2$ with a sodium amalgam in tetrahydrofuran following the procedure reported by King [5]. Iodomethyldimethylsilane was prepared by first reducing $ClCH_2SiMe_2Cl$ to $ClCH_2SiMe_2H$ using $LiAlH_4$ followed by treating the $ClCH_2SiMe_2H$ with NaI in acetone in a manner similar to the procedure reported for the preparation of ICH_2SiH_3 [6]. Bromomethylmethoxydimethylsilane was prepared by the reaction of dry CH_3OH with $BrCH_2SiMe_2Cl$ at 0°C in anhydrous diethyl ether. The purity of the silicon compounds was checked by their NMR spectra. The following compounds used in this work were purchased from various commercial sources: $CH_2{=}CHSiMe_2CH_2Cl$, $(BrCH_2SiMe_2)_2O$, $ClCH_2SiMe_2Cl$, $Et_2NSiMe_2CH_2Cl$, $(ClCH_2SiMe_2)_2NH$, $\overline{O(SiMe_2O)_3Si}(Me)CH_2Cl$, $BrCH_2SiMe_2Cl$, $(ClSiMe_2)_2O$, Ph_3CCl, PPh_3, BCl_3, HCl, and HBr. The purity of the chemicals was checked by spectroscopic analyses.

Syntheses

The experimental procedures for the eight silicon-functional silylmethyl derivatives that were prepared by the reaction of $NaFe(CO)_2Cp$ with an appropriate halomethyl silicon derivative (see materials section) were essentially identical. The silicon compound was added to a tetrahydrofuran solution of the sodium salt and allowed to react with stirring at room temperature for 18-21 h (3.5 h for the $HSiMe_2CH_2$ derivative). The tetrahydrofuran was removed by vacuum evaporation and the residue was extracted with pentane. The pentane extract was centrifuged to remove the insoluble materials. Subsequent evaporation of the pentane yielded the desired product. Column chromatography, utilizing a 4.5 × 40 cm acid washed alumina column, was required for the complete purification of the vinyl, disiloxane and methoxy derivatives. A summary of the yields and analytical data obtained for the compounds is given in Table 1.

Reactions

(a) $HSiMe_2CH_2Fe(CO)_2Cp$ with CH_3OH

Approximately 1 ml of CH_3OH was condensed into a 10 ml tube on the

TABLE 1

YIELDS AND ANALYTICAL DATA FOR CERTAIN SILICON-FUNCTIONAL SILYLMETHYL CYCLOPENTADIENYLIRON DICARBONYL DERIVATIVES

Compound [a]	Yield (%)	Analysis found (calcd.) (%)		Mass measurement parent ion	
		C	H	found	(calcd.)
$CH_2{=}CHSiMe_2CH_2Fe(CO)_2Cp$	75	52.2(52,2)	6.1(5.8)	276.0274	(276.0269)
$[Cp(CO)_2FeCH_2SiMe_2]_2O$	43	46.4(46.7)	5.2(5.1)	514.0026	(514.0017)
$CH_3OSiMe_2CH_2Fe(CO)_2Cp$	77			280.0220	(280.0218)
$HSiMe_2CH_2Fe(CO)_2Cp$	58			250.0093	(250.0112)
$Et_2NSiMe_2CH_2Fe(CO)_2Cp$	75	52.6(52.3)	7.2(7.2)		
$[Cp(CO)_2FeCH_2SiMe_2]_2NH$ [b]	69	47.0(46.8)	5.4(5.3)		
$Cp(CO)_2FeCH_2SiMe_2Fe(CO)_2Cp$ [c]	48	48.5(47,9)	4.4(4.3)		
$Cp(CO)_2FeCH_2(Me)\overline{Si(OSiMe_2)_3O}$	89	38.6(38.1)	6.2(6.0)		

[a] Unless otherwise noted, the purified compounds were amber colored liquids. [b] Chocolate colored crystals melting at 49 ± 1°C. [c] Yellow solid, melts at 98-99°C with decomposition.

vacuum line containing $HSiMe_2CH_2Fe(CO)_2Cp$ (2.1 mmol) and the mixture was allowed to stand for 1.5 h at room temperature. The NMR spectrum of the amber liquid that remained after the non-condensible gas and excess methanol were pumped away was identical with that of $CH_3OSiMe_2CH_2Fe(CO)_2Cp$ prepared independently by the salt-elimination method.

(b) $HSiMe_2CH_2Fe(CO)_2Cp$ with Ph_3CCl

A 20 ml benzene solution of Ph_3CCl (2.9 mmol) was added dropwise over a 15 min period to a cooled (0°C) 25 ml benzene solution of $HSiMe_2CH_2$-$Fe(CO)_2Cp$. The white precipitate that appeared during the addition was identified as Ph_3CH by comparing its NMR spectrum with that of an authentic sample of Ph_3CH. The formation of $ClSiMe_2CH_2Fe(CO)_2Cp$ in the reaction was verified by the compound's proton NMR spectrum [7]. The reaction is quantitative.

(c) $ClSiMe_2CH_2Fe(CO)_2Cp$ with CH_3OH

Approximately 1 ml of CH_3OH was condensed into a tube on the vacuum line containing $ClSiMe_2CH_2Fe(CO)_2Cp$ (0.8 mmol). The reaction mixture was allowed to warm to room temperature and over a 3 h period a slow evolution of hydrogen chloride was observed. After all volatile materials were pumped out of the tube, an amber liquid remained, the NMR of which was identical with that of $CH_3OSiMe_2CH_2Fe(CO)_2Cp$ prepared by the salt-elimination reaction.

(d) $Et_2NSiMe_2CH_2Fe(CO)_2Cp$ and HBr

Hydrogen bromide (0.9 mmol) was condensed into a flask containing the $Et_2NSiMe_2CH_2$ derivative (0.9 mmol) dissolved in 15 ml of pentane. As the reactants slowly warmed to room temperature, the dark red solution turned yellow and the formation of a precipitate was noted. The reaction was allowed to proceed with stirring for 2 h. At this time, the solid material produced was separated from the pentane solution by centrifuging the mixture. Subsequent removal of the pentane by evaporation yielded a two component mixture identified by NMR spectroscopy as being mostly the disiloxane $[Cp(CO)_2FeCH_2SiMe_2]_2O$ with a small amount (approximately 10%) of $BrSiMe_2CH_2Fe(CO)_2Cp$ [7]. Other products of the reaction were not identified.

(e) $Cp(CO)_2FeCH_2SiMe_2Fe(CO)_2Cp$ and HCl

Hydrogen chloride (1.5 mmol) was condensed into a 35 ml heavy-walled flask containing $Cp(CO)_2FeCH_2SiMe_2Fe(CO)_2Cp$ (1.0 mmol). The vessel was allowed to warm to room temperature, but was occasionally cooled to −196° C to liquify the HCl. After a 6 h reaction period, the contents of the vessel were cooled to −196° C and a small amount of non-condensible material was pumped away. The products were then allowed to distill through a trap at −134° C. Hydrogen chloride passed through the trap while Me_3SiCl (0.9 mmol, identified by its infrared spectrum) condensed at −134° C. The major part of the residue in the flask was identified as being $[Cp(CO)_2Fe]_2$ by comparing its infrared (ν(CO) 2009, 1958, 1780) and proton NMR (τ(Cp) 5.21 ppm) spectra with the spectra of a pure sample of the dimer. The spectra also revealed the presence of a small amount (approximately 7% from NMR integration) of $Cp(CO)_2FeCl$ (ν(CO) 2016, 2057; τ(Cp) 4.89 ppm). The spectral data were identical with data obtained under identical conditions on a sample of pure $CpCO)_2FeCl$.

Attempts to identify any intermediates in the reaction, such as an initial cleavage product, were unsuccessful.

(f) Insertion reactions with triphenylphosphine

In the experiments described below, all solution transfers were carried out in a nitrogen-filled glove bag. Each reaction was carried out in a 35 ml flask equipped with a 3-way stopcock to aid in flushing the vessel with nitrogen and an 18/9 joint that was connected, after the solution transfer, to a short reflux condenser. A mercury bubbling device was connected to the end of the condenser.

The reactions were carried out in the following manner. A tetrahydrofuran solution of PPh_3 and the silylmethyl derivative was allowed to reflux for 13-19 h. About half of the solvent was stripped away by using a standard vacuum pump assembly and the vessel was filled with dry nitrogen. A 5 ml portion of pentane was added and the insertion product appeared as an orange precipitate. The orange solid was centrifuged out of the solution and washed with several 5 ml portions of pentane. The product was then dried in vacuo over a 3 h period. A modification of this procedure was to add pentane dropwise to the product mixture in tetrahydrofuran until the solution became cloudy. The solution was then placed in a refrigerator overnight, after which crystals of the insertion product appeared on the side of the vessel.

In a typical experiment, 2.4 mmol of PPh_3 and 2.4 mmol of $Cp(CO)_2FeCH_2SiMe_2OCH_3$ in 10 ml of tetrahydrofuran were allowed to reflux for 13 h. The insertion product $Cp(CO)(PPh_3)FeC(O)CH_2SiMe_2OCH_3$ was obtained in a 16% yield. Other systems studied included the reaction of PPh_3 with $[Cp(CO)_2FeCH_2SiMe_2]_2NH$ (1/1 and 2/1 ratios), $Cp(CO)_2FeCH_2SiMe_2Fe(CO)_2Cp$ (1/1 ratio) and $[Cp(CO)_2FeCH_2SiMe_2]_2O$ (2/1 ratio). The identification of the insertion products was made chiefly by examining their proton NMR and infrared spectra. Acyl ν(CO) stretches were examined in cases where the NMR data did not unequivocally establish the formation of the insertion products. (Analytical data obtained on the 2/1 silazane complex: Found: C, 64.5; H, 5.3. $C_{56}H_{57}O_4P_2Fe_2NSi$ calcd.: C, 64.8; H, 5.5%.) Spectroscopic data are given below.

Care had to be taken to rigorously exclude moisture from the solvents used in the preparation of the insertion product of the methoxy derivative. If moisture is present, the acyl derivative $Cp(CO)(PPh_3)FeC(O)CH_3$ (m.p. 141°C, lit. [8] 145°C) is obtained for this system. (Analysis found: C, 68.2; H, 5.1. $C_{26}H_{23}O_2PFe$ calcd.: C, 68.7; H, 5.1%.)

Results and discussion

Our goal to synthesize silicon-functional silylmethyl transition metal complexes led us to investigate the interaction of the cyclopentadienyliron dicarbonyl anion with various halomethyl silicon derivatives containing silicon—oxygen, silicon—nitrogen, silicon—hydrogen and silicon—carbon(vinyl) bonds. Although this reaction has been employed in the synthesis of Me_3SiCH_2— and $Me_3SiSiCH_2$—metal complexes [1,3], it had not been generally tested for cases in which potentially reactive substituents are bound to silicon. With these latter derivatives, there was a distinct possibility that the anion would preferentially attack at the silicon center rather than at the carbon—halogen bond. Indeed, it has been shown that the interaction of the anion with various chloro (or bromo) methyl chlorosilanes, $ClCH_2SiMe_{3-n}Cl_n$ ($n = 1$, 2 or 3) proceeds initially with substitution at silicon, rather than at carbon [7].

$$Cp(CO)_2Fe^- + ClCH_2SiMe_2Cl \rightarrow ClCH_2SiMe_2Fe(CO)_2Cp + Cl^- \qquad (1)$$

In our work we have found appropriate conditions where the main reaction of the anion with ICH_2SiMe_2H, $ClCH_2SiMe_2OMe$, $ClCH_2SiMe_2NEt_2$, $ClCH_2SiMe_2(CH{=}CH_2)$, $(ClCH_2SiMe_2)_2O$, $ClCH_2(Me)\overline{Si(OSiMe_2)_3O}$ and $(ClCH_2SiMe_2)_2NH$ proceeds at the carbon—halogen bond rather than at the silicon center and thus the general reaction results in a convenient synthesis of the corresponding silicon-functional silylmethyl cyclopentadienyliron dicarbonyl derivative.

$$RCH_2X + [Cp(CO)_2Fe]^- \xrightarrow{THF} RCH_2Fe(CO)_2Cp + X^- \qquad (2)$$

($R = CH_3OSiMe_2$, Et_2NSiMe_2, $CH_2 = CHSiMe_2$, $\overline{O(SiMe_2O)_3Si}Me$; $X = Cl$,
$R = HSiMe_2$, $X = I$)

$$(ClCH_2SiMe_2)_2Y + 2[Cp(CO)_2Fe]^- \rightarrow [Cp(CO)_2FeCH_2SiMe_2]_2Y + 2Cl^- \qquad (3)$$

($Y = O{<}, {>}NH$)

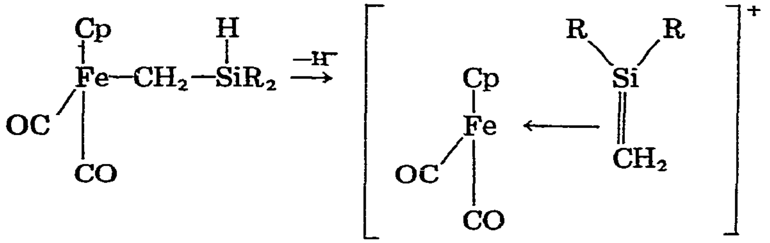
The synthesis of the hydride $HSiMe_2CH_2Fe(CO)_2Cp$ presented a challenge, owing to the presence of a very reactive Si—H bond in a position β to the iron atom. In fact, from the results of other investigations, it appeared that the synthesis of the Si—H derivative would not be successful. For example, the hydrosilylmethyl complex presumably produced in the reaction of $(Ph_3P)_3RhCl$ with the Grignard reagent prepared from $HSiMe_2CH_2Cl$ and magnesium in ether could not be isolated [9]. The products of this particular reaction were $(Ph_3P)_4RhH$, Rh metal, Me_3SiH and $Me_3SiCH_2SiMe_2H$. Likewise, it was not possible to isolate $(HSiMe_2CH_2)_4Ti$ from the reaction of the $HSiMe_2CH_2Cl/Mg$ reagent with $TiCl_4$ [9]. In a report closely related to the present study, the reaction of $NaFe(CO)_2Cp$ with $ClCH_2SiMe_2H$ was found to produce a very unstable red liquid which undergoes a reaction with Ph_3P under UV irradiation to produce $Me_3SiFe(CO)(PPh_3)Cp$ [2].

In our work we found that if ICH_2SiMe_2H was employed in the salt elimination reaction, $HSiMe_2CH_2Fe(CO)_2Cp$ could be obtained in about a 58% yield. The chief evidence for the formation of the $HSiMe_2CH_2$ derivative is found in the compound's proton NMR spectrum. The Si—H absorption is basically a 9 line pattern centered at τ 6.03 ppm. The CH_3 and CH_2 absorptions (6/2 overall intensity ratio) are both split into doublets by the Si—H proton ($J(CH_3SiH) = 3.5$, $J(CH_2SiH) = 3.9$ Hz). The hydride derivative decomposed appreciably in attempts to purify it by vacuum distillation, sublimation and chromatography on columns of either acid washed alumina or silica gel. The chief decomposition product was $Me_3SiFe(CO)_2Cp$ [10]. Reasonably pure (~95%) $HSiMe_2CH_2Fe(CO)_2Cp$ was obtained by its crystallization from pentane at —78° C; however, traces of $[Cp(CO)_2Fe]_2$ and $Me_3SiFe(CO)_2Cp$ could not be completely removed by this technique.

Although the hydrosilylmethyl complex is relatively unstable thermally, we found that it could be used as an intermediate in the synthesis of other silicon-functional derivatives. For example, its interaction with CH_3OH and the mild chlorinating reagent Ph_3CCl [11] led to the formation of the corresponding methoxy and chloro analogs, respectively.

$$HSiMe_2CH_2Fe(CO)_2Cp + CH_3OH \rightarrow CH_3OSiMe_2CH_2Fe(CO)_2Cp + H_2 \tag{4}$$
$$HSiMe_2CH_2Fe(CO)_2Cp + Ph_3CCl \rightarrow ClSiMe_2CH_2Fe(CO)_2Cp + Ph_3CH \tag{5}$$

It is interesting to note that if one could abstract the H^- from the hydrosilylmethyl complex by using an appropriate reagent, a transition metal stabilized $Me_2Si{=}CH_2$ species could possibly result (eqn. 6). This reasoning is based on the known formation of π complexes [12] when certain σ-bonded iron alkyls are treated with a hydride abstracting reagent (eqn. 7). We attempted this reaction with the hydrosilylmethyl derivative using Ph_3CBF_4 as the hydride abstracting reagent, but found that under the conditions used, (CH_2Cl_2 solvent at room temperature) the only reaction was that of fluorinating the Si—H bond



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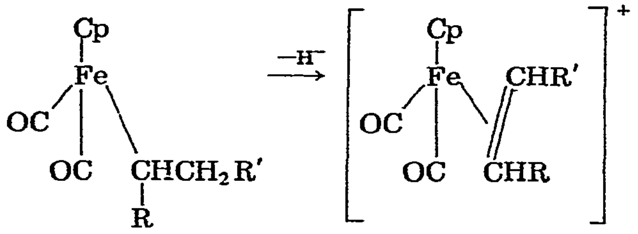

(7)

producing the new fluorosilylmethyl complex, $FSiMe_2CH_2Fe(CO)_2Cp$*.

$$HSiMe_2Fe(CO)_2Cp + Ph_3CBF_4 \rightarrow FSiMe_2CH_2Fe(CO)_2Cp + Ph_3CH + BF_3 \qquad (8)$$

Although the general hydride abstraction reaction certainly merits further study, the reaction observed in the present work points out the synthetic utility of the hydrosilylmethyl complex in preparing other silicon-functional silylmethyl cyclopentadienyliron dicarbonyl derivatives.

Several qualitative reactions were carried out with some of the silicon-functional silylmethyl complexes to see if the usual reactivity of the Si—X bond was altered by the presence of the metal complex. This is of particular interest if, as the reactions of the hydrosilylmethyl complex indicate, some of the derivatives are to be used to prepare other silicon-functional derivatives. The silicon—nitrogen bond of $Et_2NSiMe_2CH_2Fe(CO)_2Cp$ was found to be cleaved by anhydrous HBr, producing $BrSiMe_2CH_2Fe(CO)_2Cp$. The interaction of $[Cp(CO)_2FeCH_2SiMe_2]_2O$ with BCl_3 did not produce the chlorosilylmethyl derivative expected from the well-established boron halide cleavage of the Si—O—Si linkage [14]. Instead, an air-sensitive unidentified white solid was formed. The material appears to be a BCl_3 adduct and we are currently seeking more details about its composition and identity. Another interesting observation is that the vinyl derivative $CH_2{=}CHSiMe_2CH_2Fe(CO)_2Cp$ is not as thermally stable as we expected. The compound undergoes rapid decomposition at about 80° C (in vacuo) to form a brownish-black solid material. We have not yet been able to conclusively identify the decomposition products.

A totally different route to the chloro- and bromo-silylmethyl derivatives was reported during the course of our work. This alternate route is based on the surprising quantitative rearrangement of Cl(or Br)$CH_2SiMe_2Fe(CO)_2Cp$ [7].

$$XCH_2SiMe_2Fe(CO)_2Cp \rightarrow XSiMe_2CH_2Fe(CO)_2Cp \qquad (9)$$

(X = Cl, Br)

We also observed this reaction and utilized it in the preparation of a relatively simple silylmethyl complex that contained both an iron—carbon bond and an iron—silicon bond. Under relatively mild conditions, we were not able to obtain in any reasonable amounts the diiron derivative $Cp(CO)_2FeSiMe_2CH_2Fe(CO)_2Cp$ by the reaction of the cyclopentadienyliron dicarbonyl anion with the halomethyl derivative $ClCH_2SiMe_2Fe(CO)_2Cp$. However, by treating $ClSiMe_2CH_2$-$Fe(CO)_2Cp$ produced in the rearrangement of the $ClCH_2SiMe_2$ derivative with additional $NaFe(CO)_2Cp$, we were able to obtain the diiron complex $Cp(CO)_2$-$FeCH_2SiMe_2Fe(CO)_2Cp$ in about a 15% yield. An appreciable amount of the disiloxane $[Cp(CO)_2FeCH_2SiMe_2]_2O$ was also formed in this particular reaction and we noted that the best yield (48%) of $Cp(CO)_2FeSiMe_2CH_2Fe(CO)_2Cp$ was obtained when the reaction was carried out in a single step, using a 2/1 ratio of the cyclopentadienyliron dicarbonyl anion with $ClCH_2SiMe_2Cl$. Under these conditions, the rearrangement step presumably occurs in situ. Compounds that contain both carbon—iron and silicon—iron bonds are relatively rare. Prior to

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* We recognized that the particularly mild fluorination of the Si—H bond with Ph_3CBF_4 could have synthetic value for preparing certain organofluorosilanes. The results of a study of the interaction of Ph_3CBF_4 with various organosilanes are given in a separate publication [13].

our work, the cyclic derivative $(CO)_4\overline{FeSi(Me_2)CH_2CH_2CH_2}$ having these bonds had been prepared and studied [15]. Both the iron—silicon and iron—carbon bonds of this compound are cleaved by hydrogen chloride, producing $CH_3CH_2CH_2SiMe_2Cl$ [15]. Hydrogen chloride also cleaves both the iron—silicon and iron—carbon bonds of $Cp(CO)_2FeSiMe_2CH_2Fe(CO)_2Cp$, producing Me_3SiCl and $[Cp(CO)_2Fe]_2$ (eqn. 10). We were not able to characterize any intermedi-

$$Cp(CO)_2FeSiMe_2CH_2Fe(CO)_2Cp + HCl \rightarrow [Cp(CO)_2Fe]_2 + Me_3SiCl \qquad (10)$$

ates in the cleavage. The small amount of $Cp(CO)_2FeCl$ detected in the reaction was probably formed by the reaction of the dimer with hydrogen chloride, although it could have been formed as an intermediate*.

Spectral properties

A summary of the proton NMR and carbonyl infrared spectral data for $Me_3SiCH_2Fe(CO)_2Cp$ and the silicon-functional silylmethyl derivatives prepared in this work is given in Table 2. The CH_3(Si) protons in the substituted deri-

TABLE 2

PROTON NMR AND INFRARED DATA FOR SOME SILICON-FUNCTIONAL SILYLMETHYL DERIVATIVES OF CYCLOPENTADIENYLIRON DICARBONYL

Compound	Chemical shifts (τ ppm) [a]			ν(CO) (cm^{-1}) [b]
	CH_3	CH_2	Cp	
$Me_3SiCH_2Fe(CO)_2Cp$ [c]	9.96	10.32	5.24	2009, 1956
$Me_2Si(H)CH_2Fe(CO)_2Cp$ [d]	9.88	10.45	5.19	2011, 1958
$Me_2Si(F)CH_2Fe(CO)_2Cp$ [e]	9.76	10.46	5.21	2020, 1960
$Me_2Si(Cl)CH_2Fe(CO)_2Cp$ [f]	9.57	10.20	5.22	2018, 1959
$Me_2Si(Br)CH_2Fe(CO)_2Cp$ [g]	9.39	10.03	5.12	
$Me_2Si(vinyl)CH_2Fe(CO)_2Cp$ [h]	9.89	10.35	5.25	2015, 1956
$[Cp(CO)_2FeCH_2SiMe_2]_2O$	9.87	10.40	5.20	2014, 1955
$Me_2Si(OCH_3)CH_2Fe(CO)_2Cp$ [i]	9.85	10.43	5.10	2015, 1995
$[Cp(CO)_2FeCH_2SiMe_2]_2NH$	9.88	10.32	5.18	2020, 1958
$Me_2Si(NEt_2)CH_2Fe(CO)_2Cp$ [j]	9.90	10.30	5.17	2020, 1958
$Cp(CO)_2FeCH_2Si(Me)_2Fe(CO)_2Cp$	9.57	9.75	5.21	2016, 1953
			5.36 [k]	1986, 1936
$\overline{O(SiMe_2O)_3Si}(Me)CH_2Fe(CO)_2Cp$	9.90	10.58	5.15	2015, 1962

[a] Solvent was $DCCl_3$ with cyclohexane added as an internal standard. Peak areas were all approximately in the theoretical ratios expected. [b] Determined in pentane. [c] Previously reported values [16] (τ, ppm) CH_3 (10.00), CH_2 (10.36), Cp (5.33); ν(CO) (cm^{-1}) 2018, 1960. [d] τ(SiH) = 6.03 ppm (nine line pattern), $J(CH_3—SiH)$ = 3.5, $J(CH_2—SiH)$ = 3.9 Hz. [e] $J(CH_3—SiF)$ = 7.0, $J(CH_2—SiF)$ = 8.7 Hz. [f] Previously reported values (τ, ppm) CH_3 ([illegible]9), CH_2 (10.21), Cp 5.19 [7]. [g] Previously reported values (τ, ppm) CH_3 (9.45), CH_2 (10.02), Cp 5.20 [7]. [h] See discussion for an assignment of the vinyl protons. [i] τ(OCH_3) = 6.59 ppm. [j] For the Et grouping τ(CH_2) = 7.15, τ(CH_3) = 9.0 ppm, J(H—H) = 7.8 Hz. [k] Data for the $Cp(CO)_2FeSi$ part of the molecule.

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* A reasonable sequence for the cleavage is:

$$Cp(CO)_2FeSiMe_2CH_2Fe(CO)_2Cp + HCl \rightarrow Cp(CO)_2FeH + ClSiMe_2CH_2Fe(CO)_2Cp \qquad (a)$$

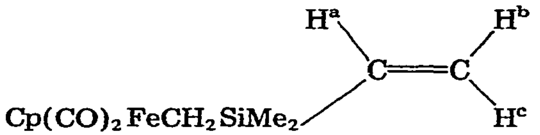
$$ClSiMe_2CH_2Fe(CO)_2Cp + HCl \rightarrow ClSiMe_3 + ClFe(CO)_2Cp \qquad (b)$$

$$Cp(CO)_2FeH + ClFe(CO)_2Cp \rightarrow [Cp(CO)_2Fe]_2 + HCl \qquad (c)$$

If some of the $Cp(CO)_2FeH$ decomposed to form the dimer $[Cp(CO)_2Fe]_2$ and H_2 before step (c) occurred (a non-condensable gas presumed to be H_2 was observed), the presence of $ClFe(CO)_2Cp$ in the reaction products is explained.

vatives prepared in this work all occur to the low field of the $CH_3(Si)$ protons in the unsubstituted Me_3Si derivative. The positon of the CH_2 proton in the substituted derivatives is less predictable and may occur at higher or lower fields than the CH_2 protons in $Me_3SiCH_2Fe(CO)_2Cp$.

The CH_2=CH protons in the vinyl silylmethyl complex produced a complex splitting pattern in the NMR spectrum at 60 MHz. At 250 MHz the spectrum was nearly first order and we were able to make the following assignments.



Chemical shift (τ ppm)		Coupling constant (Hz)	
H^a	3.75	$J_{a,b}$	14.5
H^b	4.11	$J_{a,c}$	20.0
H^c	4.28	$J_{b,c}$	3.1

The relative chemical shifts and the magnitude of the coupling constants of the vinyl group in the compound compare favorably with the corresponding data for Me_3SiCH=CH_2 [17] and $Cp(CO)_2FeSiMe_2CH$=CH_2 [18], the vinyl proton most sensitive to change at silicon being the one attached to the α-carbon [τ 3.89, 3.75 and 3.55 for $RSiMe_2CH$=CH_2, where R = CH_3, $Cp(CO)_2FeCH_2$, and $Cp(CO)_2Fe$, respectively].

The infrared spectra of the compounds showed the two terminal CO stretching vibrations that are characteristic of cyclopentadienyliron dicarbonyl derivatives [16]. Infrared spectra of the compounds also showed the characteristic C—H stretches of the alkyl—silicon grouping at 2850-3000 cm^{-1}, and the Si—CH_3 deformations at about 1400, 1260, and 800 cm^{-1}. The siloxy and methoxy derivatives had strong Si—O stretches at about 1070 cm^{-1}, the silazane derivatives had the Si—N stretch at about 1050 cm^{-1}. The hydrosilyl complex had ν(Si—H) at 2100 cm^{-1}.

Insertion reactions

The interaction of the silicon-functional silylmethyl derivatives with an equimolar quantity of PPh_3 in refluxing tetrahydrofuran appears to produce the expected iron—carbon insertion products in the cases that were studied.

$$\text{—}SiMe_2CH_2Fe(CO)_2Cp + PPh_3 \rightarrow \text{—}SiMe_2CH_2C(=O)Fe(CO)(PPh_3)(Cp) \qquad (11)$$

The infrared spectra of the insertion products showed a terminal ν(CO) frequency at about 1920 cm^{-1} and an acyl ν(CO) frequency at about 1590 cm^{-1} in the particular compounds that were examined.

By virtue of the asymmetric iron atom present in the insertion products, we expected to find a characteristic AB quartet for the non-equivalent methylene protons and two methyl silicon resonances for the $Cp(CO)(PPh_3)$-$FeC(O)CH_2SiMe_2$ portions of the complexes [19]. We observed this behavior in general for the insertion products of PPh_3 with $Cp(CO)_2FeSiMe_2CH_2$-$Fe(CO)_2Cp$, $CH_3OSiMe_2CH_2Fe(CO)_2Cp$, and the 1/1 product of PPh_3 with $[Cp(CO)_2FeCH_2SiMe_2]_2NH$. However, for the 2/1 ($PPh_3$/iron complex) ratio insertion products of the siloxane and silazane derivatives, the methylene and silicon—methyl absorption each appeared as single absorptions in a 1/3 ratio, respectively.

The PPh_3 insertion product of the silazane derivative deserves some additional comment. The NMR spectrum of the product taken at the end of the reaction with the silazane derivative (2/1 PPh_3/iron complex) before workup showed a multiplet of peaks in the τ 9.93-9.98 ppm region, a singlet at τ 7.66 ppm and a characteristic AB quartet with peak positions at τ 6.98, 7.21, 8.06 and 8.28 ppm. The solid sample was then warmed to 95° C in vacuo for 5 min and the product was washed with pentane. The NMR of the resulting solid material presumed to be the 2/1 insertion product (in $DCCl_3$) consisted of two single absorptions at τ 7.68 and 9.96 ppm in a 1/3 ratio. The AB quartet and other peaks in the τ 9.93 ppm region observed in the initial spectrum of the products were later identified as arising from the presence of some of the 1/1 PPh_3/silazane insertion product. Likewise, in the reaction of PPh_3 with the silazane derivative (1/1 ratio respectively), small impurity peaks at τ 7.68 and 9.96 ppm were assigned to the presence of some of the 2/1 insertion product.

These results prompted us to (*1*) obtain a chemical analysis of the 2/1 product and (*2*) redetermine the NMR of a freshly prepared sample of the material in CS_2 in case the $DCCl_3$ or possibly a trace amount of hydrogen chloride in the $DCCl_3$ caused or underwent a chemical reaction with the silazane insertion product. The analysis was consistent with the 2/1 complex and the NMR of the material in CS_2 showed the same singlet features that were observed in $DCCl_3$.

The spectral properties and melting points of the insertion products are summarized in Table 3.

The isolation of the insertion product derived from the $CH_3OSiMe_2CH_2$ derivative was particularly difficult and could not be done unless great care was taken to keep all traces of moisture out of the reaction flask and solvents. In order to see what the difficulty was, we purposely added a drop of water to a sample of $Cp(CO)(PPh_3)FeC(O)CH_2SiMe_2OMe$ that was used for the NMR analysis. A reaction immediately commenced and after 5 min, the solution was filtered and the NMR redetermined. Two absorptions at τ 9.84 ($SiMe_2$) and 6.46 ppm (OMe) in a 2/1 ratio were assigned to the siloxane $(MeOSiMe_2)_2O$. This was verified by the NMR spectrum of a sample of pure $(MeOSiMe_2)_2O$, prepared by the reaction of excess MeOH with $(ClSiMe_2)_2O$. The remaining absorptions at τ 2.56 (protons of coordinated PPh_3), 5.56 (Cp protons) and 7.68 ppm (CH_3 protons) in the ratio 15/5/3, led us to formulate a second product as being $Cp(CO)(PPh_3)FeC(O)CH_3$. A chemical analysis verified the identity of the acyl derivative. The products most likely arise from the hydrolytic cleavage of the silicon—carbon bond of the insertion product:

$$Cp(CO)(PPh_3)FeC(O)CH_2SiMe_2OMe + H_2O \rightarrow Cp(CO)(PPh_3)FeC(O)CH_3 + HOSiMe_2OMe \qquad (12)$$

The silanol given in equation 12 was not detected in the reaction, but presumably underwent condensation to form the observed disiloxane.

$$2\,MeOSiMe_2OH \rightarrow (MeOSiMe_2)_2O + H_2O \qquad (13)$$

TABLE 3

SOME PROPERTIES OF THE INSERTION PRODUCTS OBTAINED IN THE REACTION OF PPh_3 WITH SILICON-FUNCTIONAL SILYLMETHYL DERIVATIVES [a]

$Cp(CO)(PPh_3)FeC(O)CH_2X$ X =	M.p. (°C)	τ (PPh_3) (ppm)	τ(Cp) (ppm)	τ(CH_2) (ppm)	τ($SiMe_2$) (ppm)	ν(C≡O) (cm^{-1})	acyl ν(CO) (cm^{-1})
$SiMe_2OCH_3$ [b]	116 ± 0.5	2.58	5.53	[c]	9.96, 10.01	1920	1592
$SiMe_2Fe(CO)_2Cp$ [d]	142 [e]	2.53	5.49	7.08, 7.28 8.18, 8.38	9.39, 9.64	1920, 1939 1991	[g]
$SiMe_2\overset{H}{N}SiMe_2CH_2Fe(CO)_2Cp$ [f]		2.63	5.52	7.07, 7.12 8.19, 8.24	9.93, 9.98	1920, 1956, 2010	[g]
$SiMe_2\overset{H}{N}SiMe_2$	113 ± 0.5	2.54	5.51	7.66	9.96	1920	1585
$SiMe_2OSiMe_2$		2.55	5.53	7.69	9.93	1920	1592

[a] Melting points are uncorrected and were taken under nitrogen atmosphere. NMR data were obtained in $CDCl_3$ solution (~15% conc. by volume) with C_6H_{12} added as an internal solvent. Infrared data were obtained on samples dissolved in pentane. [b] $\tau(OCH_3) = 6.71$ ppm. [c] Not evaluated due to the presence of some impurity peaks in the expected region of the low intensity AB quartet. [d] τ(Cp) of the $\equiv SiFe(CO)_2Cp$ part of the molecule is at 5.37 ppm. [e] Sample appeared to melt and decompose at this temperature. The compound could be heated up to 135°C for 5 min without any change in its NMR spectrum: [f] τ of the Me, CH_2 and Cp protons of the $—SiMe_2CH_2Fe(CO)_2Cp$ part of the molecule at 9.72, 10.52 and 5.17 ppm, respectively. [g] Not measured.

The formation of $CH_3C(O)Fe(CO)_2Cp$ was also noted in the workup of the disiloxane · 2 PPh_3 insertion product when the solvents used were not scrupulously dry.

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