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SOME FERROCENE-SUBSTITUTED CARBOSILANES

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Although the chemistry of ferrocenes has been the subject of considerable study, no interest has been shown in ferrocenes containing $SiCH_2Si$ groupings. We report here the preparation and properties of some of these and related compounds.

RESULTS AND DISCUSSION

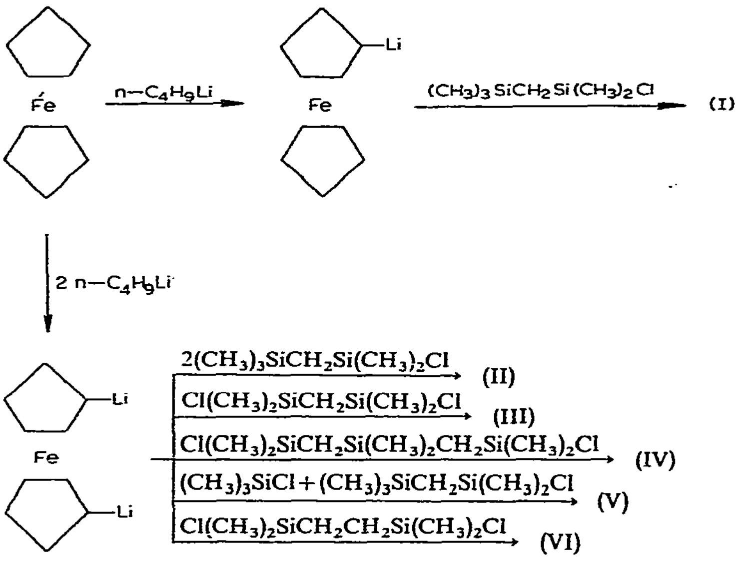
Structures and some physical properties for the ferrocenes prepared in this investigation are listed in Table 1 and their analytical data in Table 2.

Compounds (I), (II), (V) and (VI) are dark-red liquids, while compounds (III) and (IV) are crystalline solids like ferrocene in appearance. In accordance with the statement by Rosenblum and Woodward[1] that ferrocene derivatives, in which at least one ring remains unsubstituted, exhibit absorption in the IR spectrum near 9 and 10 μ, the IR spectrum of compound (I) did have bands at both 9 and 10 μ, while the spectra of compounds (II)–(VI) did not.

All of these compounds were synthesized by allowing appropriate chlorosilanes to react with metalated ferrocene. Thus, {[(trimethylsilyl)methyl]dimethylsilyl}ferrocene (I) and 1,1′-bis{[(trimethylsilyl)methyl]dimethylsilyl}ferrocene (II) were obtained from the reaction involving (trimethylsilyl)(dimethylchlorosilyl)-methane and a mixture of lithio- and 1,1′-dilithioferrocene. 2,4-(1,1′-Ferrocenylene)-2,4-dimethyl-2,4-disilapentane (III), 2,6-(1,1′-ferrocenylene)-2,4,4,6-tetramethyl-2,4,6-trisilaheptane (IV), and 2,5-(1,1′-ferrocenylene)-2,5-dimethyl-2,5-disilahexane (VI) were prepared from the reaction of bis(dimethylchlorosilyl)methane, bis[(dimethylchlorosilyl)methyl]dimethylsilane, and 1,2-bis(dimethylchlorosilyl)ethane, respectively, with 1,1′-dilithioferrocene. 1-(Trimethylsilyl)-1′-{[(trimethylsilyl)methyl]dimethylsilyl}ferrocene (V) was obtained along with other products by treating a mixture of trimethylchlorosilane and [(trimethylsilyl)methyl]dimethylchlorosilane with dilithioferrocene (see Reaction Chart 1).

Compound (II) was also synthesized by metalation of (cyclopentadienyldimethylsilyl)(trimethylsilyl)methane with n-butyllithium followed by treatment with ferrous chloride

$$C_5H_5(CH_3)_2SiCH_2Si(CH_3)_3 \xrightarrow[\text{2. }FeCl_2]{\text{1. n-}C_4H_9Li} \text{(II)}$$

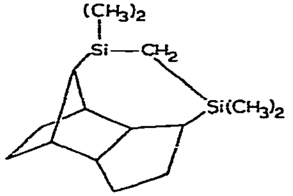


Reaction Chart 1.

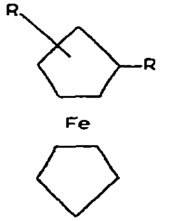
Attempts to prepare compound (III) in an analogous way, however, were unsuccessful, because bis(cyclopentadienyldimethylsilyl)methane did not undergo metalation with n-butyllithium appreciably.

In another work[2], it has been observed that the metalation of 1,3-dicyclopentadienylhexamethyltrisilane with n-butyllithium also does not proceed smoothly, whereas the metalation of 1,2-dicyclopentadienyltetramethyldisilane occurs with great ease to give, after treatment with ferrous chloride, 1,2-(1,1'-ferrocenylene)tetramethyldisilane in reasonable yield.

These facts suggest that the 1,3-dicyclopentadienyl-substituted silicon compounds would tend to exist in the form of an intramolecular adduct of Diels–Alder type. This is supported by the result of catalytic hydrogenation of bis(cyclopentadienyldimethylsilyl)methane; one mole of this compound absorbed only two moles of hydrogen to give a saturated product with the formula $C_{15}H_{28}Si_2$, its probable structure being depicted by (VII).



VII



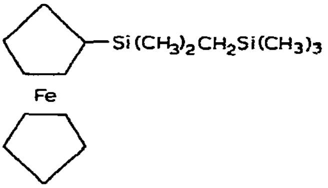
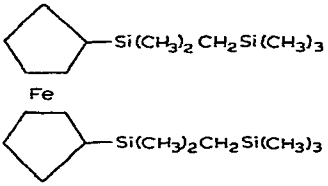
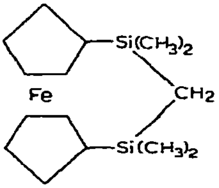
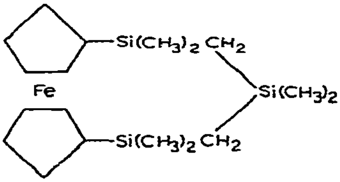
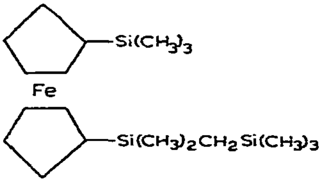
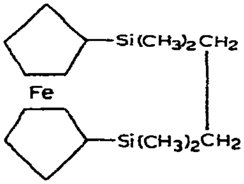
VIII

$R=(CH_3)_3SiCH_2Si(CH_3)_2—$

In their study on oligomethyleneferrocenes, Lüttringhaus and Kullick[3] prepared α,ω-dicyclopentadienylpropane, -butane and -pentane, and metalated each

TABLE 1

PHYSICAL PROPERTIES OF FERROCENE-SUBSTITUTED SILANES

No.	*Compound*	*B.p.* (°*C/mm*)	n_D^{20}	d_4^{20}
(I)		132/3	1.5530	1.1017
(II)		178/3	1.5279	1.0137
(III)		M.p. 69°		
(IV)		M.p. 61°		
(V)		145/3	1.5349	1.0456
(VI)		120–124/4		

of them without isolation because polymerization which occurred upon evaporation of solvent prevented isolation. They inferred the structure of the polymers obtained to be of intermolecular Diels–Alder type, but ruled out the possibility of formation of intramolecular Diels–Alder adducts for the steric reason.

TABLE 2

ANALYTICAL DATA FOR FERROCENE-SUBSTITUTED SILANES

No.	*Formula*	*C %* *Found* *(Calcd.)*	*H %* *Found* *(Calcd.)*	*Mol. wt.*[a] *Found* *(Calcd.)*
(I)	$C_{16}H_{26}FeSi_2$	58.36 (58.16)	8.06 (7.93)	336 (330)
(II)	$C_{22}H_{42}FeSi_4$	55.75 (55.66)	8.78 (8.92)	483 (475)
(III)	$C_{15}H_{22}FeSi_2$	57.53 (57.31)	6.82 (7.06)	322 (314)
(IV)	$C_{18}H_{30}FeSi_3$	56.35 (55.93)	8.01 (7.82)	330 .(387)
(V)	$C_{19}H_{34}FeSi_3$	56.91 (56.68)	8.60 (8.51)	388 (403)
(VI)	$C_{16}H_{24}FeSi_2$	58.75 (58.52)	7.56 (7.37)	328 (328)

[a] Cryoscopic in benzene.

Thermal behavior of the silicon-substituted ferrocenes was considered of interest and so examined. Compound (III) proved to be extraordinarily stable to heat; it was recovered unchanged after heating to 300° over an 80-h period in dry nitrogen atmosphere. In view of this high heat-stability of the bridged ferrocene (III) coupled with the fact that permethylated derivatives of certain metals and metalloids tend to undergo thermal condensation to cyclic compounds with the metal (or metalloid) to methylene linkages as a skeleton of molecule[4-6], we initially expected that thermolysis of compound (V) might give compound (III), while that of (II) might give (IV). Contrary to our expectation, thermolysis of compound (V), which occurred to some extent at 290–300° over a 25-h period, gave several products, among which ferrocene, (trimethylsilyl)ferrocene, and compound (I) were detected, but did not yield traces of expected compound (III). Also, thermolysis of compound (II) at 300° for 60 h gave neither expected (IV) nor another cyclic compound (VI). However, in this case, interestingly enough, we observed that a considerable amount of a new compound was formed, which had the same composition as the starting substance (II), and whose retention time in the gas chromatogram was close to, but distinctly different from, that of the latter. The IR spectrum of this product does display the characteristic peaks both at 9 and 10 μ indicative of the presence of an unsubstituted cyclopentadienyl ring. Its proton NMR spectrum exhibits signals due to three kinds of cyclopentadienyl ring protons at τ 5.85, 5.99, and 6.12 ppm with relative intensities in the ratio of approximately 2 : 5 : 1. These data suggest that the product should be a homoannularly substituted bis{[(trimethylsilyl)methyl]dimethylsilyl}ferrocene (VIII). The isomerization appears to be reversible: an increase in heating time did not give rise to a great change in the peak-area ratio of (VIII) to (II) in the gas chromatogram, and thermolysis of compound (VIII) at 300° for 60 h resulted in the formation of a mixture of (VIII) and (II) in essentially the same composition as that obtained from (II).

The relative positions of the two $(CH_3)_3SiCH_2Si(CH_3)_2-$ groups on the ring in compound (VIII) remain unclear, although 1,3- rather than 1,2-positions are probable for reasons of steric hindrance of the substituents. The mechanism of such isomerization has not yet been fully understood. In order to learn more about the definite structure of (VIII), the scope and limitation of this type of isomerization, and the reaction mechanisms, we are continuing further studies along various lines.

EXPERIMENTAL

Chlorosilanes

(Trimethylsilyl)(dimethylchlorosilyl)methane, b.p. 153.5–155° (reported[7]: 153°) was prepared by the action of 1 mole of (trimethylsilyl)methylmagnesium chloride on 2 moles of dimethyldichlorosilane in tetrahydrofuran. Yield was 55%.

Bis(dimethylchlorosilyl)methane, b.p. 174–175° (reported[8]: 174.5–175.8°), n_D^{20} 1.4490, d_4^{20} 1.0175, was prepared by two methods. One involved intramolecular rearrangement of 1-(chloromethyl)-2-chlorotetramethyldisilane with anhydrous aluminum chloride, following the techniques reported previously[7]. The other method consisted of a sequence of processes: preparation of (phenyldimethylsilyl)(dimethylchlorosilyl)methane, b.p. 94–95°/24 mm, n_D^{20} 1.5072, d_4^{20} 0.9905 (Found: Cl, 14.72. $C_{11}H_{19}ClSi_2$ calcd.: Cl, 14.59%.) by the reaction of (phenyldimethylsilyl)methylmagnesium chloride (1 mole) with dimethyldichlorosilane (2 moles) in tetrahydrofuran (yield, 85%); and chlorodephenylation of this product with dry hydrogen chloride in the presence of anhydrous aluminum chloride as catalyst (yield, 93%).

Bis[(dimethylchlorosilyl)methyl]dimethylsilane, b.p. 136–137°/34 mm (reported[9]: b.p. 114–116°/12 mm) (Found: Cl, 25.61. $C_8H_{22}Cl_2Si_3$ calcd.: Cl, 25.93%.) was prepared in 67% yield by the reaction of acetyl chloride with bis[(dimethylethoxysilyl)methyl]dimethylsilane, $[(CH_3)_2(C_2H_5O)SiCH_2]_2Si(CH_3)_2$, b.p. 124°/24 mm, n_D^{20} 1.4349, d_4^{20} 0.8712 (Found: C, 49.39; H, 10.94. $C_{12}H_{32}O_2Si_3$ calcd.: C, 49.25; H, 11.02%.) The latter compound was obtained in 41% yield from the reaction involving (chloromethyl)dimethylethoxysilane, dimethyldichlorosilane and magnesium in tetrahydrofuran.

1,2-Bis(dimethylchlorosilyl)ethane, b.p. 80°/13 mm (reported[10]: b.p. 198°/734 mm) was prepared in almost quantitative yield by chlorodemethylation of bis(trimethylsilyl)ethane with two equivalents of acetyl chloride and two equivalents of anhydrous aluminum chloride, after the techniques recently developed in our laboratories[11].

(Cyclopentadienyldimethylsilyl)(trimethylsilyl)methane

Cyclopentadienylmagnesium bromide was prepared in the usual way by treatment of 0.6 mole of ethylmagnesium bromide in 300 ml of an ether/benzene (1 : 1) mixture with 40 g (0.6 mole) of cyclopentadiene over a 13-h period. To this reagent was added in 30 min 83 g (0.5 mole) of (trimethylsilyl)(dimethylchlorosilyl)methane in 100 ml of benzene, and the mixture was heated to reflux over an 18-h period, during which considerable quantities of inorganic salts precipitated. After removal of the precipitates by filtration, the filtrate was fractionally distilled to give 54 g (56% yield) of (cyclopentadienyldimethylsilyl)(trimethylsilyl)methane, b.p. 58–59°/6 mm, n_D^{20} 1.4780, d_4^{20} 0.8569, MR_D 69.54 (calcd., 69.24). (Found: C, 62.99; H, 10.78. $C_{11}H_{22}Si_2$ calcd.: C, 62.77; H, 10.54%.)

Bis(cyclopentadienyldimethylsilyl)methane

This compound, b.p. 84–86°/0.4 mm, n_D^{20} 1.5245, d_4^{20} 0.9865, was prepared in 50% yield from the reaction of two equivalents of cyclopentadienylmagnesium bromide with one equivalent of bis(dimethylchlorosilyl)methane in a benzene/ether mixture. (Found: C, 68.70; H, 9.32; Si, 21.54; mol.wt. cryoscopic in benzene, 265. $C_{15}H_{24}Si_2$ calcd.: C, 69.15; H, 9.28; Si, 21.56%; mol.wt., 260.5.) The MR_D observed equals 80.74. The MR_D calculated for the linear structure, $(C_5H_5)(CH_3)_2SiCH_2Si(CH_3)_2(C_5H_5)$, is 84.80, while that for structure corresponding to the intramolecular Diels–Alder adduct is 80.07.

Hydrogenation of bis(cyclopentadienyldimethylsilyl)methane

In a standard hydrogenator, 0.5340 g (2.05 mmole) of bis(cyclopentadienyldimethylsilyl)methane was hydrogenated over 2 g of a catalyst (10% palladium on carbon) in 25 ml of absolute ethanol. The uptake of hydrogen was 97 cc (4.1 mmole), thus corresponding to only two molecules of hydrogen per one molecule of the substrate. In a preparative scale, hydrogenation of 3 g of bis(cyclopentadienyldimethyl)-methane gave 3 g of colorless crystals, which had m.p. 45° after recrystallization from petroleum ether and analyzed for $C_{15}H_{28}Si_2$. (Found: C, 68.30; H, 10.96. $C_{15}H_{28}Si_2$ calcd.: C, 68.10; H, 10.67%.) Its IR spectrum showed no absorptions characteristic of C=C bond.

{[(Trimethylsilyl)methyl]dimethylsilyl}ferrocene (I) and 1,1'-bis{[(trimethylsilyl)methyl]dimethylsilyl}ferrocene (II)

Ferrocene (38 g, 0.2 mole) in 300 ml of ether was metalated with 0.3 mole of n-butyllithium in 150 ml of ether at room temperature over a 40-h period[12]. To this solution was added gradually 41 g (0.23 mole) of (trimethylsilyl)(dimethylchlorosilyl)-methane, and the mixture was then heated to gentle reflux for 10 h. It was hydrolyzed and the resulting organic layer was separated. Evaporation of the solvent resulted in precipitation of unchanged ferrocene which was removed by filtration. Fractional distillation of the filtrate gave 15 g (23% yield) of (I) and 8.8 g (9.2% yield) of (II). The IR spectra of (I) and (II) are essentially the same except that two strong absorptions appear at 9 and 10 μ in the spectrum of (I) while there are no such absorptions in that of (II). In a second run, 21 g (0.1 mole) of (cyclopentadienyldimethylsilyl)(trimethylsilyl)methane in 100 ml of ether was treated with 0.1 mole of n-butyllithium in 72 ml of ether at −20° for 4 h. To the mixture was added ferrous chloride prepared from 5.4 g (0.033 mole) of anhydrous ferric chloride and 0.93 g (0.017 g-atom) of iron powder in tetrahydrofuran[13] at −20° over a 10-min period, and the mixture was then stirred for 12 h. Most of the solvents was distilled off, and the black residue was cautiously hydrolyzed with dilute hydrochloric acid. Products were extracted with petroleum ether. The extracts, after removal of solvent, were fractionally distilled to give 8.5 g (41%) of unchanged $C_5H_5(CH_3)_2SiCH_2Si(CH_3)_3$ and 10.5 g (44% yield) of compound (II), b.p. 152–154°/0.4 mm, n_D^{20} 1.5280.

2,4-(1,1'-Ferrocenylene)-2,4-dimethyl-2,4-disilapentane (III)

To 28 g (0.15 mole) of ferrocene in 300 ml of tetrahydrofuran was added with stirring at −20° an ether solution (300 ml) containing 0.45 mole of n-butyllithium[14]. The mixture was stirred at −10° for 55 h and then at room temperature for 5 h. To the resulting dark-brown solution was added 35 g (0.17 mole) of bis(dimethylchlorosilyl)methane diluted with 200 ml of ether over a 1-h period and the mixture was stirred at room temperature over an 88-h period, during which considerable amounts of inorganic salt formed. After removal of most of the solvents by distillation, initially under ordinary pressure and later *in vacuo*, products were extracted with petroleum ether (b.p. 35–75°) from the residue in a Soxhlet apparatus. The extract was, after evaporation of the solvent, distilled to give a red-brown oil, boiling over the range of 135–195°/8 mm, which in part crystallized on cooling. Recrystallization of the crystals from petroleum ether gave 4.0 g (8.5% yield) of a pure sample of compound (III). Its IR spectrum showed no absorptions at 9 and 10 μ.

Attempted preparation of (III) from bis(cyclopentadienyldimethylsilyl)methane

To a solution of 33.2 g (0.12 mole) of bis(cyclopentadienyldimethylsilyl)methane in 100 ml of ether was added 0.27 mole of n-butyllithium in 190 ml of ether at −20°. The mixture was stirred at 0° for 2 h and then refluxed for 16 h. During these periods, 2.8 g of a colorless liquid was collected in a Dry Ice/aceton trap connected to the top of the reflux condenser, but it proved to be mainly composed of ether. To the above mixture was added at 0° ferrous chloride prepared from 13.2 g (0.082 mole) of ferric chloride and 2.3 g (0.041 g-atom) of iron powder in 80 ml of tetrahydrofuran[13], and the resulting mixture was stirred at room temperature over a 20-h period. At this point most of the solvents was removed by distillation, and the residue was cautiously hydrolyzed with dilute hydrochloric acid. Products were extracted with ether. The extracts were, after removal of solvent, distilled to give 26.8 g (83.2%) of unchanged bis(cyclopentadienyldimethylsilyl)methane, b.p. 95–98°/4 mm, n_D^{20} 1.5244. Repeated runs led to substantially the same result.

2,6-(1,1'-*Ferrocenylene*)-2,4,4,6-*tetramethyl*-2,4,6-*trisilaheptane* (*IV*)

Ferrocene (18.5 g, 0.10 mole) in 150 ml of tetrahydrofuran was metalated in essentially the same manner as described above with 0.3 mole of n-butyllithium in 120 ml of petroleum ether. To the resulting lithioferrocene was added with stirring and cooling 30 g (0.11 mole) of bis[(dimethylchlorosilyl)methyl]dimethylsilane diluted with 100 ml of petroleum ether. Stirring was continued at room temperature over a 43-h period. Removal of the solvent by distillation from the mixture left a brown-black tar, from which products were extracted first with petroleum ether and then with benzene in a Soxhlet apparatus. The combined extracts were, after removal of solvents, distilled under reduced pressure to give 3 g of a forerun, 10 g of a fraction boiling mainly at 213–216°/0.2 mm, and 23 g of residue, in addition to 4 g of unchanged ferrocene. Preparative gas chromatography of the second fraction gave the desired compound (IV) as orange-yellow crystals. Its IR spectrum showed no absorptions at 9 and 10 μ.

2,5-(1,1'-*Ferrocenylene*)-2,5-*dimethyl*-2,5-*disilahexane* (*VI*)

Ferrocene (20 g, 0.11 mole) in 150 ml of tetrahydrofuran was metalated with 0.33 mole of n-butyllithium in 150 ml of ether at −20° over a 50-h period. To the resulting solution was added 20 g (0.09 mole) of 1,2-bis(dimethylchlorosilyl)ethane diluted with 100 ml of ether over a 30-min period. The mixture was stirred at room temperature for 120 h. After a similar work-up to that described above, 4 g (14%

yield) of slightly impure compound (VI) was obtained as a red-brown oil. An analytically pure sample was obtained by preparative gas chromatography. The IR spectrum displayed no absorptions at 9 and 10 μ.

1-(*Trimethylsilyl*)-1'-{[(*trimethylsilyl*)*methyl*]*dimethylsilyl*}*ferrocene* (*V*)

Ferrocene (18.6 g, 0.10 mole) in 100 ml of tetrahydrofuran was treated with 0.24 mole of n-butyllithium in 100 ml of petroleum ether at −20° for 20 h and then at room temperature for 5 h. To this solution was added gradually with cooling a mixture of 8.7 g (0.08 mole) of trimethylchlorosilane and 17 g (0.08 mole) of (trimethylsilyl)(dimethylchlorosilyl)methane in 100 ml of petroleum ether. The mixture was stirred at room temperature for 20 h and then heated to reflux for 2 h. After a work-up in a similar way to that described above, 1.5 g (4.4% yield) of compound (V) was isolated by fractional distillation, together with 3 g (16%) of unchanged ferrocene and 11 g of lower-boiling fractions containing monosubstituted ferrocenes. The IR spectrum had no absorptions at 9 and 10 μ.

Attempted thermolysis of compound (*III*)

A small sample (*ca.* 0.5 g) of compound (III) was heated in a 5 × 30 mm sealed glass tube in an air-bath kept at temperatures of 300 ± 10° over an 80-h period. The content in the tube was shown to be completely identical with the starting substance by its m.p. and mixed m.p. 68.5–69.0°, and by gas chromatography.

Thermolysis of compound (*V*)

In essentially the same manner, about 0.3 g of compound (V) was heated in a sealed glass tube at 290–300° for 25 h. Gas chromatography of the contents of the tube revealed that they were composed mainly of four compounds, *i.e.*, unchanged compound (V), compound (I), (trimethylsilyl)ferrocene, and ferrocene, with the peak-area ratio on the gas chromatogram being approximately 100 : 15 : 5 : 2, respectively. Although several other minor compounds that were unidentified were also produced, no traces of compound (III) were detected.

Thermolysis of compound (*II*)

In a small flask equipped with a thermometer, a gas inlet tube, and a reflux condenser 4 g of compound (II) was heated in nitrogen atmosphere at 300 ± 10° over a 60-h period. Gas chromatography of the thermolysis product revealed that it contained unchanged (II), a homoannularly substituted bis{[(trimethylsilyl)methyl]dimethylsilyl}ferrocene (VIII), and compound (I), with the peak-area ratio on the gas chromatogram being approximately 100 : 66 : 10, respectively, together with a trace of ferrocene. No traces of compound (IV) and (VI) were detected. The compound (VIII), m.p. 36°, was isolated by preparative gas chromatography, and its identity was established by elemental analysis (Found: C, 55.81; H, 8.81. $C_{22}H_{42}FeSi_4$ calcd.: C, 55.66; H, 8.92%), by its IR spectrum which distinctly showed the characteristic bands both at 9 and 10 μ, and by its proton NMR spectrum having τ 5.85, 5.99, and 6.12 ppm with relative intensities in the ratio of approximately 2 : 5 : 1.

Thermolysis over a 145-h period at 300 ± 10° gave substantially the same ratio of (II) to (VIII) as that obtained over a 60-h period, although the relative amount of compound (I) somewhat increased.

Thermolysis of compound (VIII)

In a sealed glass tube was heated a small sample (*ca.* 0.1 g) of compound (VIII) at 300±10° over a 50-h period. Gas chromatography revealed that the product contained compounds (II), (VIII), and (I), with the peak-area ratio on the gas chromatogram being approximately 100:103:3.5, respectively, in addition to a trace of ferrocene.

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SUMMARY

Six silicon-substituted ferrocenes were prepared and characterized: {[(trimethylsilyl)methyl]dimethylsilyl}ferrocene (I), 1,1'-bis{[(trimethylsilyl)methyl]-dimethylsilyl}ferrocene (II), 2,4-(1,1'-ferrocenylene)-2,4-dimethyl-2,4-disilapentane (III), 2,6-(1,1'-ferrocenylene)-2,4,4,6-tetramethyl-2,4,6-trisilaheptane (IV), 1-(trimethylsilyl)-1'-{[(trimethylsilyl)methyl]dimethylsilyl}ferrocene (V), and 2,5-(1,1'-ferrocenylene)-2,5-dimethyl-2,5-disilahexane (VI). Structures for bis(cyclopentadienyldimethylsilyl)methane and its hydrogenated product are proposed to be of intramolecular Diels–Alder adduct type, on the basis of observations on the metalation and catalytic hydrogenation. The ferrocene (III) was recovered unchanged after 80-h heating at 300°. Thermolysis of (II) at 300° over a 60-h period gave a homoannularly substituted bis{[(trimethylsilyl)methyl]dimethylsilyl}ferrocene as a major product, which was reconverted into (II) under similar conditions.

REFERENCES

1 M. Rosenblum and R. B. Woodward, *J. Am. Chem. Soc.*, 80 (1958) 5443.
2 M. Kumada, K. Mimura, H. Tsunemi and M. Ishikawa, to be published.
3 A. Lüttringhaus and W. Kullick, *Makromol. Chem.*, 44–46 (1961) 669.
4 J. Goubeau and R. Epple, *Chem. Ber.*, 90 (1957) 171.
5 G. Fritz, J. Grobe and D. Kummer, *Advan. Inorg. Chem. Radiochem.*, 7 (1965) 349.
6 K.Ziegler, K. Nagel and M. Patheiger, *Z. Anorg. Allgem. Chem.*, 282 (1955) 345.
7 M. Kumada, J. Nakajima, M. Ishikawa and Y. Yamamoto, *J. Org. Chem.*, 23 (1958) 292.
8 R. O. Sauer and E. M. Hadsell, *J. Am. Chem. Soc.*, 70 (1948) 3590.
9 G. Greber and G. Degler, *Makromol. Chem.*, 52 (1962) 174.
10 W. A. Piccoli, G. G. Haberland and R. L. Merker, *J. Am. Chem. Soc.*, 82 (1960) 1883.
11 H. Sakurai, K. Tominaga, T. Watanabe and M. Kumada, *Tetrahedron Letters*, (1966) 5493.
12 R. A. Benkeser, D. Goggin and G. Schroll, *J. Am. Chem. Soc.*, 76 (1954) 4025.
13 N. Rabjohn (Ed.), *Org. Syn.*, Collective Vol. 4 (1963) 473.
14 D. W. Mayo, P. D. Shaw and M. D. Rausch, *Chem. Ind. (London)*, (1957) 1388.