Journal of Organometallic Chemistry, 110 (1976) 303—313

PREPARATION, REACTIONS AND STEREOCHEMISTRY AT SILICON OF (2,3,4,5-TETRAPHENYL-1-SILACYCLOPENTADIENE)IRON TRICARBONYLS *

HIDEKI SAKURAI, JOSABURO HAYASHI and TOSHIAKI KOBAYASHI
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980 (Japan)
(Received September 29th, 1975)

Summary

Twelve derivatives of (2,3,4,5-tetraphenyl-1-silacyclopentadiene)iron tricarbonyls were prepared. These complexes undergo a variety of substitution at silicon. The *exo* leaving groups showed enhanced reactivity in such reactions. The stereochemistry of substitution also differs significantly from that established for optically active silanes.

Introduction

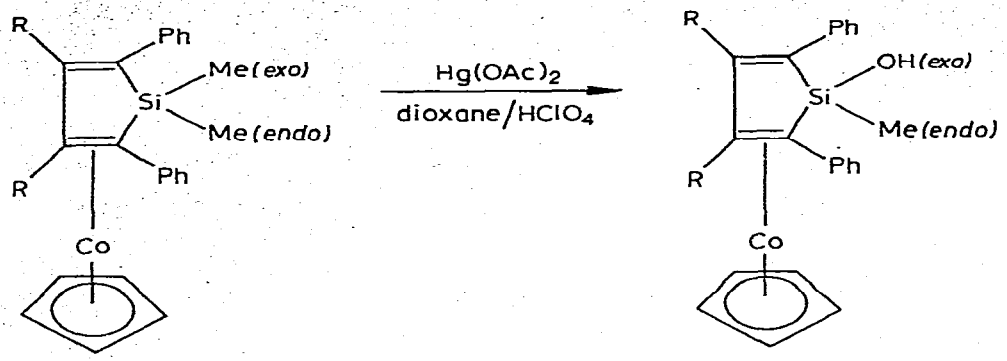
Some π ligands are known to undergo substitution at carbon with a remarkable reactivity when complexed to a transition metal. In a previous paper, we have reported the synthesis and some reactions of cobalt complexes of silacyclopentadiene [1]. We now describe a series of silacyclopentadiene complexes of iron tricarbonyl which undergo a variety of substitution reactions at silicon with enormously enhanced reactivity.

Brunet, Resibois, and Bertrand prepared several derivatives of (silacyclopentadiene)iron tricarbonyl [2]. Recently, Fink has reported the synthesis of some cobalt and iron complexes of 2,5-diphenyl-1-silacyclopentadiene [3]. However, these investigations were not extended beyond the preparation of alkyl and aryl derivatives of silicon. It is rather difficult to prepare other derivatives directly from the corresponding silacyclopentadiene and iron pentacarbonyl. For example, the reaction of 1-methyl-1-hydrido-2,3,4,5-tetraphenyl-1-silacyclopentadiene with iron pentacarbonyl does not give a corresponding complex but produces an uncharacterized mixture instead, since iron pentacarbonyl is a catalyst for hydrosilation. Accordingly, we have investigated substitution reactions at silicon of (1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene)iron tricarbonyl (I) in order to obtain silicon-functional derivatives of such a complex.

* Presented at the 21st Symposium on Organometallic Chemistry, Japan, Sendai, October 1973; Abstract, 201.

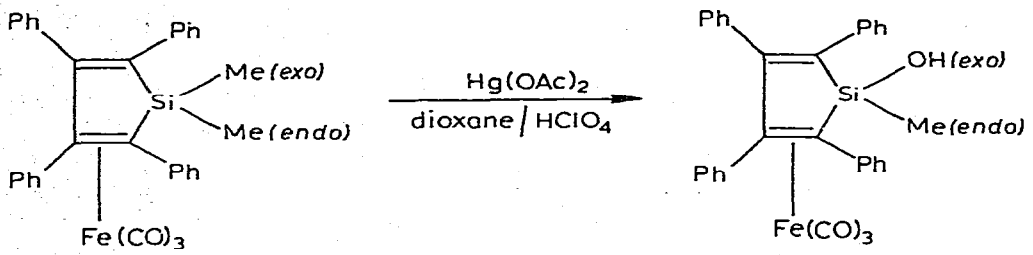
Results and discussion

We have reported that η-cyclopentadienylcobalt complexes of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene and 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene undergo a selective *exo* demethylation reaction with mercuric acetate [1]. The stereochemistry of these silanol complexes was determined unequivocally by NMR with lanthanide shift reagent [4].

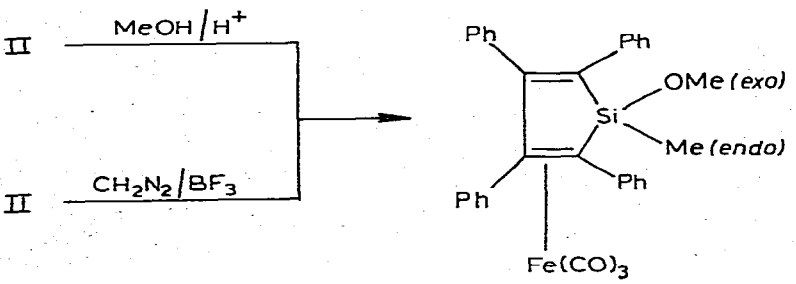


R = H , Ph

Analogously, the reaction of I with an equimolar amount of mercuric acetate in a mixture of dioxane and aqueous perchloric acid gave (1-*exo*-hydroxy-1-*endo*-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene)iron tricarbonyl (II) in 85% yield. The stereochemistry of II was assigned by relative chemical shifts of methyl protons (vide infra).



(I) (II)

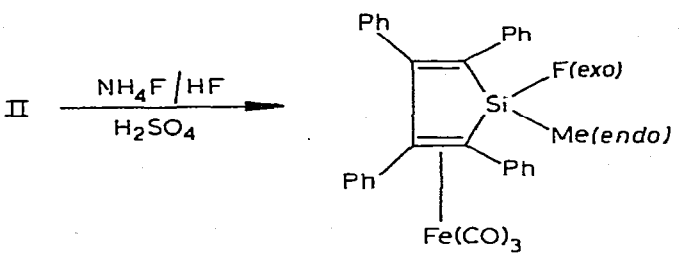


(III)

Although most silanols undergo acid-catalyzed condensation readily, exceptionally II was chemically stable under a variety of conditions. Even in acidic methanol, II can be converted to the methoxy derivative III in quantitative yield. That the stereochemistry of II was retained in III was shown by the fact that III also was obtained from II by the reaction with diazomethane. However, II underwent condensation to the corresponding disiloxane on heating.

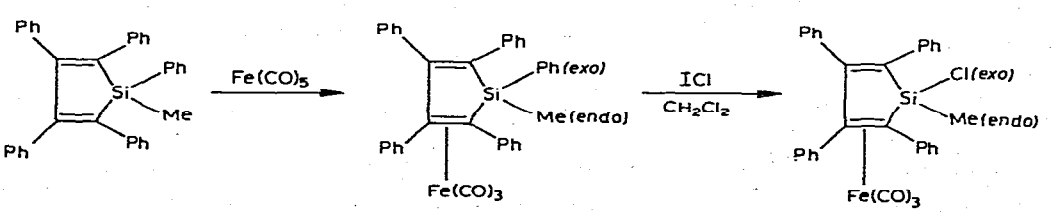
The NMR spectrum of I showed two sharp singlets at δ 0.25 and 0.80 ppm due to the *exo* and *endo* methyl protons. In both II and III, the high field signal at 0.25 ppm of I disappeared, leaving singlets at 0.68 and 0.70 ppm. The *exo*-methyl signals of substituted cyclopentadieneiron tricarbonyls appear at higher field than those of the corresponding *endo* isomer [5]. This relationship can be applied generally to the stereochemical assignment [3] and, in fact, the same relationship of methyl shifts was found for (η-cyclopentadienyl)cobalt complexes of silacyclopentadiene [1,4]. Therefore, the singlet appearing at high field in I was assigned to the signal of the *exo*-methyl group. NMR data of methyl protons of all derivatives are listed in Table 1. The assignment of the stereochemistry based on NMR data is consistent as seen in Table 1 and is well in accord with the chemical behavior described below.

Treatment of II with ammonium hydrogen fluoride in sulfuric acid gave the *exo*-fluoro-*endo*-methyl derivative (IV) stereospecifically.



(IV)

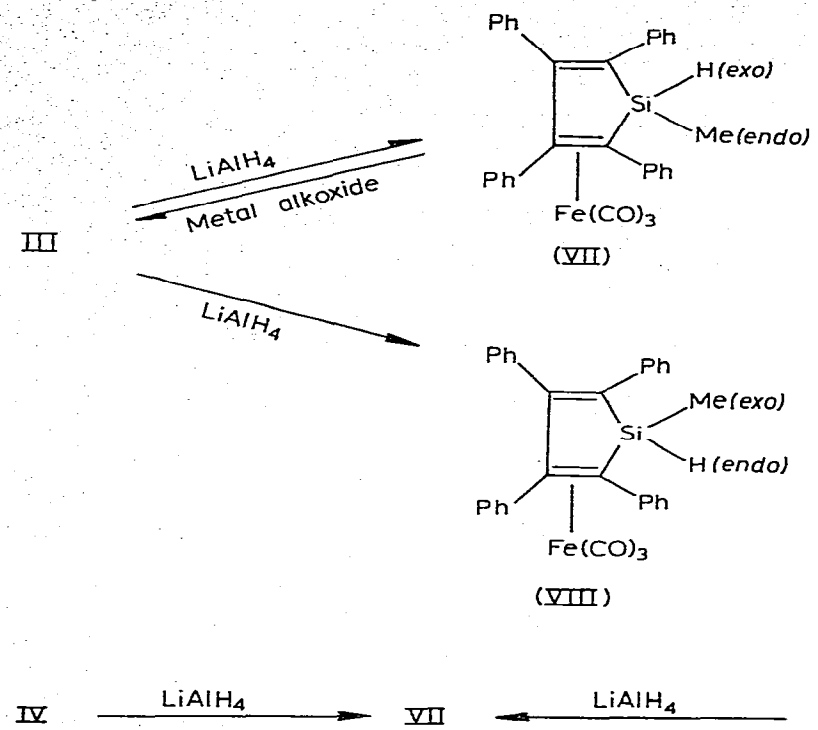
Reaction of the *exo*-phenyl-*endo*-methyl derivative (V), which was prepared directly from 1-phenyl-1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene and iron pentacarbonyl, with iodine monochloride in dichloromethane afforded exclusively the *exo*-chloro-*endo*-methyl derivative (VI).



(V) (VI)

Reduction of III, IV, and VI with lithium aluminum hydride produced interesting stereochemical results. Thus, reduction of III gave the *exo*-hydrido-*endo*-methyl isomer (VII) dominantly as a kinetically controlled product at an early stage of the reduction, but in the presence of a metal alkoxide, the *endo*-hy-

drido-*exo*-methyl isomer (VIII) was obtained finally (almost 100% yield) as a stable hydrosilane. Reduction of IV and VI afforded, on the other hand, VII exclusively.

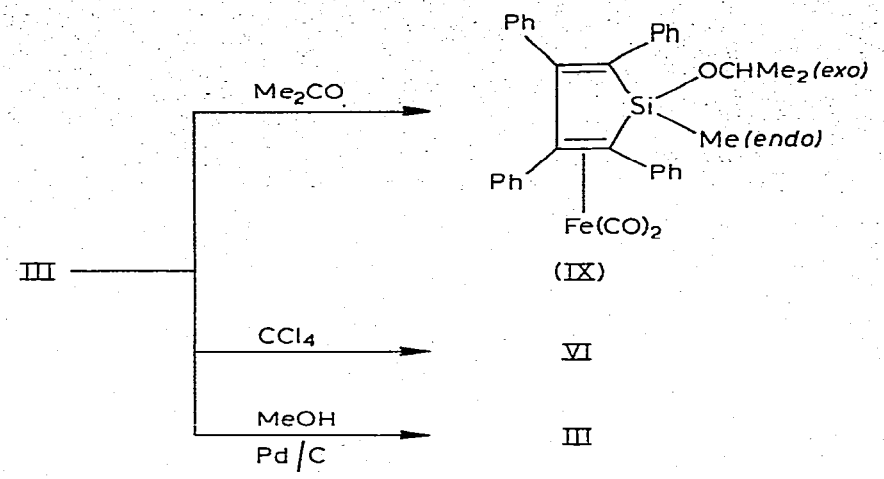


Both VII and VIII are thermally very stable in constrast to the known instability of the corresponding carbon analog, cyclopentadieneiron tricarbonyl [6], which decomposes thermally to a binuclear complex $[(\eta\text{-}C_5H_5)Fe(CO)_2]_2$ [7].

The pair of isomeric hydrosilanes (VII and VIII) showed remarkably different reactivity toward various reagents. The *exo*-hydrogen isomer (VII) was very reactive as evidenced by its facile reaction with acetone, which occurred readily at reflux for 1.5 h, to give the *exo*-isopropoxy derivative (IX). With carbon tetrachloride, VII gave VI in quantitative yield without any catalyst. However, VIII did not react with acetone nor carbon tetrachloride under the same conditions.

Since iron tricarbonyl complexes can not function as a catalyst of these reactions the high reactivity of the *exo*-hydrogen in complex VII, presumably as a hydride, can be considered to correspond to similar activation of *exo*-hydrogens of cyclopentadiene complexes of cobalt and iron [8]. Reaction of VII with methanol in the presence of 10% palladium/charcoal as a catalyst proceeded rapidly within 1 h at room temperature, giving the *exo*-methoxy derivative (III) in stereo-selective manner. On the other hand, VIII gave the same product (III) with inversion of configuration slowly after 25 h.

Alkylation of VI with a Grignard reagent resulted in the exclusive formation of the *exo*-alkyl derivative. Thus, with ethylmagnesium bromide, VI gave the



exo-ethyl-*endo*-methyl compound (X). An interesting example is the *exo*-CD_3-*endo*-methyl isomer (XI) which was prepared by the reaction of VI with trideuteriomethylmagnesium bromide. Demethylation of X with mercuric acetate afforted II, no deuterated silanol complex being detected by NMR and mass spectra. Therefore, the *exo*-methyl group of I was replaced specifically by a hydroxy group with retention of configuration in the reaction with mercuric acetate.

These stereochemical sequences can be explained in terms of the steric factor, since most of the reactions examined proceeded with retention of configuration (*exo* from *exo*). However, at the same time, it should be noted that the *exo* groups are activated significantly as seen in the case of the hydrosilanes VII and VIII.

In view of such an enhanced reactivity of the *exo*-hydrogen of VII, abstraction of a hydride ion from VII by triphenylmethyl tetrafluoroborate was examined in the expectation that VII would behave similarly to the corresponding carbon analog [8] to give a silicenium complex. However, the reaction actually gave the *exo*-fluoro derivative (IV) instead.

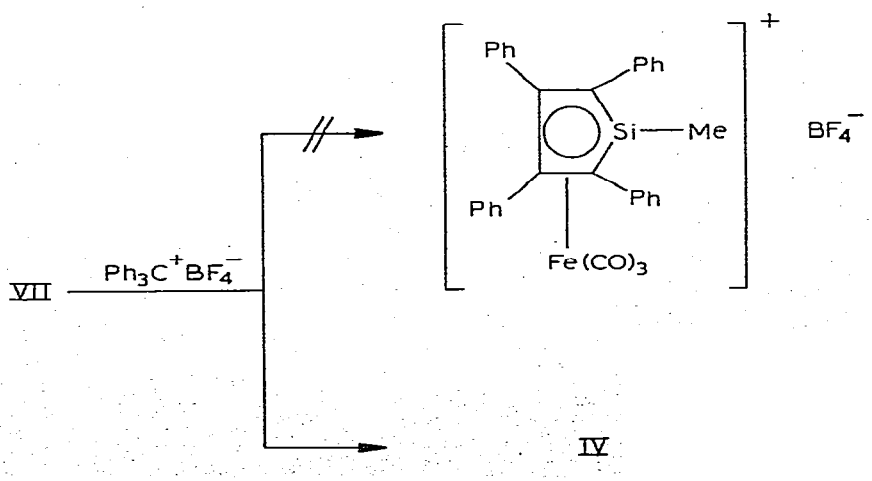


TABLE 1

PHYSICAL PROPERTIES OF NEW COMPLEXES

Compound	Substituent		M.p. [a] (°C)	NMR (δ) [b]		IR (cm^{-1}) [f] δ(Si—Me)
	exo	*endo*		*exo*	*endo*	
I	Me	Me	168	0.25	0.80	1260, 1245
II	OH	Me			0.68	1260
III	OMe	Me	141—142	3.45	0.70	1266
IV	F	Me	170—174		0.83d [c]	1270
V	Ph	Me	220		1.06	1263
VI	Cl	Me	178—180		1.13	1260
VII	H	Me	164—166	5.76q [d]	0.84d [d]	1260
VIII	Me	H	177—179	0.33d [d]	5.57q [d]	1240
IX	O-i-Pr	Me	162—163	1.10d [e]	0.76	1264
				4.11sep [e]		
X	Et	Me	145—157	0.5—1.1m	0.75	1260
XI	CD_3	Me			0.80	1260
XII	Siloxane				0.78	1265

[a] Uncorrected. [b] Cyclohexane (1.43) was used as the internal standard in CS_2. [c] J = 5.0 Hz. [d] J = 3.0 Hz. [e] J = 6.0 Hz. [f] In CCl_4.

Tables 1 and 2 list some characteristic physical properties and analytical data of the new complexes. Reactions of these complexes open a new interesting field in organosilicon chemistry. Related work is in progress in this laboratory.

Experimental

1,1-Dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene and its iron tricarbonyl complex (I) were prepared according to published procedures [9,2 resp.]. 1-Methyl-1,2,3,4,5-pentaphenyl-1-silacyclopentadiene (V) [10] was prepared by the known procedure [11,12]. The reaction was carried out with 3 to 4 times excess amount of methylphenyldichlorosilane to 1,4-dilithium-1,2,3,4-te-

TABLE 2

ANALYTICAL DATA OF NEW COMPLEXES

Compound [a]	Found (%)		Calcd. (%)	
	C	H	C	H
III	69.56	4.77	69.48	4.59
IV	68.92	4.30	68.82	4.15
V	74.08	4.57	74.03	4.58
VI	67.03	4.11	66.85	4.03
VII [b]	70.63	4.36	71.11	4.48
VIII	71.40	4.56	71.11	4.48
IX	70.28	5.19	70.30	5.05
X	72.04	5.11	71.83	4.96
XII	70.47	4.37	70.21	4.24

[a] II gave unsatisfactory results due to its unstability. [b] VII also gave less satisfactory data because of slight decomposition before analysis.

traphenylbutadiene in THF under nitrogen. Recrystalization from acetone gave pure V in 49.2% yield, m.p. 172—173°C (lit. [10] 173—175°C).

Preparation of (1-exo-hydroxy-1-endo-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene)iron tricarbonyl (II) by reaction of I with mercuric acetate

A mixture of I (100 mg, 0.18 mmol), mercuric acetate (61 mg, 0.18 mmol) and dioxane (10 ml) was placed in a 30 ml-flask under nitrogen and 70% aqueous perchloric acid (1 ml) was added at room temperature. After 20 min, the mixture was poured into a saturated solution of sodium bicarbonate, and subsequently extracted with ether. After evaporation of the solvent, the residual solid was purified by preparative TLC with petroleum ether and acetone (10/1) as eluent. The pure yellowish complex (II, 85 mg, 85% yield) was obtained. An analytical sample was purified further by sublimation (140°C/10^{-3} mmHg). The melting point could not be measured since condensation to the disiloxane (XII) took place on heating.

Preparation of (1-exo-methoxy-1-endo-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene)iron tricarbonyl (III) from II

In a 1 l round bottom flask equipped with a reflux condenser were placed 2 g (3.6 mmol) of II, 0.3 ml of conc. H_2SO_4 and absolute methanol. After the mixture had been refluxed for 25.5 h, under nitrogen, solid sodium bicarbonate was added. The reaction mixture was evaporated in vacuo, and the residual solid was extracted with ether. The ethereal solution was dried over anhydrous sodium sulfate and evaporated to dryness. Recrystallization of the residual solid from methanol afforded 1.83 g (89.5%) of pure III, m.p. 141—142°C; M^+ *m/e* 570.

Methylation of II

To 400 mg (0.72 mmol) of II dissolved in a small portion of dry diethyl ether was added one drop of 47% boron trifluoride in ethyl ether as a catalyst. The solution was cooled in a Dry Ice/methanol bath at —30 ~ —40°C, and an excess of ethereal diazomethane solution prepared from *N*-methylnitrosourea and dried over potassium hydroxide was added. After 1 h, the reaction mixture was filtered to remove polymethylene, and the filtrate was washed with aqueous saturated sodium bicarbonate and dried over anhydrous sodium sulfate. The residual oil was separated by preparative TLC with petroleum ether and acetone (15 : 1) as eluent to give 200 mg (50% yield) of pure yellowish III and 124 mg (31%) of recovered silanol complex (II). An analytical sample was recrystallized from methanol.

Preparation of (1-exo-fluoro-1-endo-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene)iron tricarbonyl (IV)

In a 200 ml three necked flask fitted with a mechanical stirrer, a reflux condenser and a dropping funnel were placed conc. sulfuric acid (40 ml) and III (1 g, 1.8 mmol). The mixture was cooled to —10 ~ —30°C with a Dry Ice/methanol bath under nitrogen. After vigorous stirring for ca. 2 h, ammonium hydrogen fluoride (1 g) and petroleum ether (50 ml) were added and stirred for additional 2 h. Then, the organic layer was extracted with petroleum ether several times and a small amount of sodium bicarbonate was added to the extract. The solu-

tion was filtered through anhydrous sodium sulfate, and the filtrate was evaporated under reduced pressure to give 0.66 g (66% yield) of crude IV. An analytical sample was sublimed at 160—180°C (10^{-3} mmHg), m.p. 170—174°C; M^+ *m/e* 558.

Reduction of (1-exo-fluoro-1-endo-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene)iron tricarbonyl (IV)

Several small pieces of $LiAlH_4$ were added portionwise to a solution of IV (0.170 g) in ether (10 ml) and the mixture was stirred with a magnetic stirrer at room temperature (ca. 2 h) under nitrogen. Then, 1 ml of water was added. Immediately, the reaction mixture was filtered through anhydrous sodium sulfate. The residual solid was washed several times with ether. The combined filtrate was evaporated to dryness in vacuo to give 0.14 g of crude 1-*exo*-hydrosilane complex (VII) (83.5%), almost pure for the purpose of synthetic use. An analytical sample was sublimed at 180°C (10^{-3} mmHg), m.p. 164—166°C; M^+ *m/e* 540.

Conversion of (1-endo-methyl-1,2,3,4,5-pentaphenyl-1-silacyclopentadiene)-iron tricarbonyl (V) to III through (1-exo-chloro-1-endo-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene)iron tricarbonyl (VI)

In a 30 ml-flask equipped with a reflux condenser were placed 100 mg (0.162 mmol) of V and 4 ml of dry methylene chloride. Iodine chloride was added dropwise to the solution and the mixture was stirred with a magnetic stirrer at room temperature under nitrogen (ca. 20 min). One ml of absolute methanol then was added, and the mixture was stirred for additional 3 h, and evaporated to dryness in vacuo. The NMR spectrum of the residual solid indicated the presence of pure III (80 mg, 86.5% yield).

Evaporation of the reaction mixture of V with iodine chloride gave the chlorosilane complex (VI) as a very hygroscopic solid, m.p. 178—180°C. Crude yields were around 95%. An analytical sample of VI was obtained by sublimation at 180°C (10^{-3} mmHg).

Reduction of (1-exo-methoxy-1-endo-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene)iron tricarbonyl (III)

In a 50 ml round-bottom flask equipped with a reflux condenser were placed 1 g (1.75 mmol) of III, and 40 ml of dry ether (distilled over sodium wire). The reaction system was flushed with nitrogen. Several small pieces of lithium aluminum hydride were added portionwise to the solution and the mixture was stirred (magnetic stirrer) at room temperature. Examination of the mixture by NMR revealed that VII was the main product, in addition to a large amount of unreacted III. However, the relative amount of the other hydrosilane, (1-*exo*-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene)iron tricarbonyl (VIII) increased steadily during the reaction. After starting material was consumed as checked by thin layer chromatography with petroleum ether/dry ether (20 : 1), 2 ml of water was added. Immediately, the reaction mixture was filtered through anhydrous sodium sulfate. The residual solid was washed several times with dry ether. The combined filtrate was evaporated to dryness in vacuo to give 917 mg (96.5% yield) of *endo*-hydrosilane complex (VIII). Recrystallization from dry ether gave pure VIII, m.p. 177—179°C.

In a similar way, VI (0.626 g) was reduced to VII (0.52 g, 85% yield).

Reaction of VII and VIII with acetone

In a 30 ml round-bottom flask equipped with a reflux condenser and a nitrogen inlet tube, a mixture of VII (100 mg, 0.185 mmol) and dry acetone (10 ml) was refluxed for 1.5 h with stirring (magnetic stirrer) under nitrogen. The reaction mixture was evaporated in vacuo. NMR investigation of the residual solid indicated that VII had been converted to (1-*exo*-isopropoxy-1-*endo*-methyl-2, 3,4,5-tetraphenyl-1-silacyclopentadiene)iron tricarbonyl (IV) stereoselectively in 100% yield.

The residual solid mass was separated with preparative TLC to give 77 mg (70% yield) of IX. An analytical sample was recrystallized from methanol, m.p. 162—163°C.

Reaction of VIII with acetone in the manner described above gave no isopropoxysilane complex. NMR indicated that VIII remained intact. After the mixture was refluxed for 24 h, only a small amount of IX was detected.

Reaction of VII and VIII with carbon tetrachloride

A mixture of VII (100 mg, 0.185 mmol) and anhydrous carbon tetrachloride (10 ml) was refluxed for an hour under nitrogen and then was evaporated in vacuo. NMR investigation of the residual solid demonstrated almost 100% conversion of VII to VI in a stereoselective manner. Evaporation of carbon tetrachloride from the mixture gave 89 mg (84% yield) of crude VI, which was converted to III with absolute methanol.

Reaction of VIII with carbon tetrachloride was effected under the same conditions, but no chlorinated derivative was obtained. NMR indicated that the *endo*-hydridosilane complex (VIII) was unchanged.

Reaction of VII and VIII with methanol in the presence of 10% palladium on charcoal

In a 30 ml flask were placed VII (200 mg, 0.37 mmol), absolute methanol (0.5 ml) and methylene chloride (5 ml). After a catalytic amount (ca. 10 mg) of 10% palladium on charcoal was added, the reaction mixture was stirred (magnetic stirrer) at room temperature for 1 h. After removal of the catalyst and solvent, examination of the mixture by NMR indicated almost 100% stereoselective conversion of VII to III. The product was separated by preparative TLC using a mixture of petroleum ether and ether (20 : 1) as eluent (169 mg, 80.5% yield).

Similarly, VIII (100 mg, 0.185 mmol), absolute methanol (0.25 mg), dry methylene chloride (2.5 ml), and a catalytic amount (ca. 10 mg) of 10% palladium on charcoal were stirred at room temperature for 25 h. After removal of the catalyst and solvent, NMR indicated ca. 80% conversion of VIII to III. Work-up gave 74 mg of methoxysilane complex III (70.5% yield).

Reaction of VII with aqueous acetone

A mixture of VIII (200 mg, 0.37 mmol), water (1 ml) and dry acetone (10 ml) was stirred with a magnetic stirrer at room temperature for 6.5 h. The solvent was evaporated under reduced pressure. After work-up, 182 mg of II was obtained (89.5% yield).

Reaction of VII with triphenylmethyl tetrafluoroborate

Triphenylmethyl tetrafluoroborate (33 mg) was added to VII (50 mg, 0.1 mmol) dissolved in 3 ml of anhydrous methylene chloride under nitrogen and the mixture was stirred at room temperature for 4 h. After addition of anhydrous ether, the solvent was evaporated under reduced pressure. NMR spectrum of the residual solid was identical to that of the fluorosilane complex (IV). Triphenylmethane was identified by comparison with the authentic sample.

Reaction of VI with ethylmagnesium bromide; preparation of (1-exo-ethyl-1-endo-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene)iron tricarbonyl (X)

To a solution of VI (0.5 g, 0.87 mmol) in 10 ml of anhydrous ether was added ethereal ethylmagnesium bromide. The solution was stirred under nitrogen at room temperature for ca. 0.5 h. After addition of water, the mixture was treated with saturated sodium chloride solution and dried over anhydrous sodium sulfate. The ethereal extract was evaporated under reduced pressure to give X (0.457 g, 92.5% yield). An analytical sample was purified by TLC followed by recrystallization from methanol, m.p. 145—147°C.

Reaction of VI with trideuteriomethylmagnesium iodide

To a solution of VI (0.9 g) in 10 ml of anhydrous ether was added ethereal trideuteriomethylmagnesium iodide prepared from 400 mg of magnesium metal. The solution was stirred under nitrogen at room temperature for ca. 3 h. After addition of water, the mixture was extracted with ether. The ethereal extract was washed with aqueous sodium bicarbonate and succesively with saturated sodium chloride and dried over anhydrous sodium sulfate. The filtrate was evaporated under reduced pressure. The residual solid was purified by TLC to give 0.5 g (57.5%) of trideuteriomethyl derivative (XI), which contained a small amount of tetraphenyl-1-silacyclopentadiene. Recrystallization of the sample from acetone afforded pure (1-*exo*-trideuteriomethyl-1-*endo*-methyl)iron tricarbonyl (XI). The NMR spectrum of XI showed the *endo*-methyl protons at δ 0.80 ppm, but no signal at high field due to *exo*-methyl proton was observed, M^+ *m/e* 557.

Demethylation of XI with mercuric acetate

Into a 30 ml-flask were charged XI (100 mg, 0.18 mmol), mercuric acetate (61 mg, 0.18 mmol), and 10 ml of dioxane under nitrogen, and 1 ml of 70% aqueous perchloric acid was added at room temperature. After 20 min, the reaction mixture was poured into aqueous sodium bicarbonate, and subsequently was extracted with ether. After removal of the solvent, the residual solid was purified by TLC. The NMR spectrum of the product was identical to that of an authentic sample of II. The mass spectrum of the product indicated no trideuteriomethyl group.

Acknowledgments

We thank Dr. Y. Nakadaira for helpful discussion. We are also grateful to Toshiba Silicone Co., Ltd., for a gift of chlorosilanes.

References

1 H. Sakurai and J. Hayashi, J. Organometal. Chem., 63 (1973) C10.
2 J.C. Brunet, B. Resibois and J. Bertrand, Bull. Soc. Chim. France, (1969) 3424.
3 W. Fink, Helv. Chim. Acta, 57 (1974) 167.
4 H. Sakurai and J. Hayashi, J. Organometal. Chem., 63 (1973) C7.
5 I.U. Khand, P.L. Pauson and W.E. Watts, J. Chem. Soc. C, (1969) 2024.
6 A. Davidson, M.L.H. Green and G. Wilkinson, J. Chem. Soc., (1961) 3172.
7 T.S. Piper, F.A. Cotton and G. Wilkinson, Inorg. Nucl. Chem., 1 (1955) 165.
8 D.W. Slocum and T.R. Engelmann, J. Amer. Chem. Soc., 94 (1972) 8596.
9 H. Gilman, S.G. Cottis and W.H. Atwell, J. Amer. Chem. Soc., 86 (1964) 1596.
10 W.H. Atwell and D.R. Weyenberg, J. Org. Chem., 32 (1967) 885.
11 E.H. Braye, W. Hübel and I. Caplier, J. Amer. Chem. Soc., 83 (1961) 4406.
12 K. Ruehlmann, Z. Chem., 5 (1965) 354.