Invited review

Some aspects of organosilicon and ferrocene chemistry

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Abstract

This review deals with three topics selected from my researches carried out over a period of nearly 40 years up to my retirement in 1983, namely (1) methylpolysilane chemistry, (2) some chemical properties of ferrocene-substituted silicon compounds and (3) some organic syntheses catalyzed by ferrocenylphosphine–transition metal complexes.

Keywords: Silicon; Iron; Ferrocene; Catalysis

1. A brief historical survey of methylpolysilane chemistry

Several years after World War II, commercial production of methylchlorosilanes and phenylchlorosilanes based on the Rochow direct process was commenced in Japan, both at Toshiba Electric Co. and at Sin-etsu Chemical Industry. In 1950, as an instructor at Osaka City University, I was interested in the identification and utilization, if possible, of the higher boiling fraction or "still-pot residue" of methylchlorosilanes obtained from the Rochow process, this residue at that time being regarded as a waste product. To the best of my knowledge, little if any attention was focused upon this topic elsewhere at that time.

Time-consuming fractional distillation of the "still-pot residue" through a home-made long Fenske-type distillation column did not permit us to separate any substance in a pure state because the residue was a complex mixture of constituents having closely similar boiling points; so we treated a number of fractions with an excess of MeMgBr in order to replace all the chlorine atoms attached to silicon by methyl groups, so as to simplify the mixture and to make separation by distillation possible.

On a very cold winter morning in 1953, when performing fractional distillation of an exhaustively methylated product from the fraction boiling around 150°C, we found that a distillate boiling at about 112°C crystallized just at the exit of the distillation column, a result of the fact that the laboratory was not heated even in the depth of winter. We quickly identified this crystalline

substance, with a boiling point of 113°C and melting point of 13°C, as hexamethyldisilane [1]:

$$Me_nCl_{6-n}Si_2 + (6 - n)MeMgBr \xrightarrow[Et_2O]{} Me_3SiSiMe_3$$
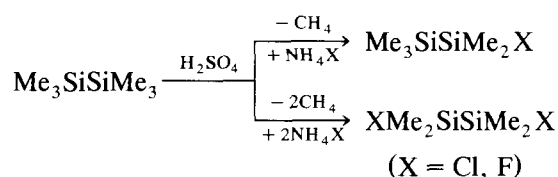
"distance fraction"

I remember clearly that I jumped with joy when I recognized this compound because, although it had been known since 1912 [2] and 1913 [3], very few studies, involving only very small quantities of this compound, had been reported, and now it had become possible to prepare this lowest member of the peralkylated polysilane family with great ease in large quantities by using the still-pot residue from the Rochow process as the starting material.

Similar exhaustive methylation of many fractions from the still-pot residue allowed us to conclude that the residue consists mainly of three types of compound, which we then named "disiloxane fraction", "disilane fraction" and "disilmethylene fraction", with the molecular framework and approximate boiling ranges as follows: disiloxane fraction, Si–O–Si, 100–150°C; disilane franction, Si–Si, 150–160°C; disilmethylene fraction, Si–CH$_2$–Si, 160–200°C. Of these three, we, of course, were most interested in the disilane franction. Soon after the isolation of hexamethyldisilane and some mixed methylalkyldisilanes, we observed that the Si–Si bonds in these species were extremely readily cleaved by halogens: in the case of chlorine it was necessary to pass the gas slowly into a dilute CCl$_4$ solution of the disilane with cooling, because otherwise the heat generated could cause a fire. The addition of bromine to neat

disilane had to be performed with careful cooling, but the reaction with iodine required reflux [4]. Each reaction gave the corresponding trialkylhalosilane quantitatively, and later the bromine-cleavage reaction often served as a test for the presence of the Si–Si bond in peralkylated silicon compounds. This is how my studies of organo (mostly methyl) polysilane chemistry began.

In order to enrich and develop the new area of aliphatic organopolysilane chemistry, we had, above all, to prepare a variety of silicon-functional disilanes and polysilanes of unambiguous structure as the building blocks for further synthesis. In 1956, we worked out two approaches particularly convenient for this purpose [5].

The first method involved chlorodemethylation or fluorodemethylation of hexamethyldisilane with concentrated sulfuric acid, followed by treatment with ammonium chloride or fluoride (or, better, ammonium hydrogenfluoride):

$$Me_3SiSiMe_3 \xrightarrow{H_2SO_4} \begin{cases} \xrightarrow[+NH_4X]{-CH_4} Me_3SiSiMe_2X \\ \xrightarrow[+2NH_4X]{-2CH_4} XMe_2SiSiMe_2X \end{cases}$$

$$(X = Cl, F)$$

This route was a combination of a reaction reported three years before (1953) by Sommer et al. [6] which involved the removal of one methyl group from silicon in 3-(trimethylsilyl)propionic acid and a reaction reported by Flood and Horvitz [7] involving conversion of $(R_3Si)_2O$ to R_3SiX which reaction had been known since 1933. Although hexamethyldisilane, just like liquid saturated hydrocarbons, is insoluble in, and seemingly unreactive towards, concentrated sulfuric acid under ambient conditions, we dared to stir a heterogeneous mixture of these two ingredients vigorously at room temperature in a flask connected to a gas collector. As evidenced by gas evolution, the demethylation took place smoothly in two distinct stages, with the first equivalent of methane being evolved rapidly and the second very slowly. Thus pure monohalodisilanes or 1,2-dihalodisilanes could be prepared with high yields.

The second method of making silicon-functional disilanes involved ethanolysis of the disilane fraction, to give a mixture consisting mainly of two compounds, readily separable by fractional distillation, namely 1,1,2-triethoxytrimethyldisilane and 1,1,2,2-tetraethoxydimethyldisilane:

$$Me_nCl_{6-n}Si_2 \xrightarrow[Et_2O]{EtOH-NH_3} (EtO)_2MeSiSiMe_2(OEt)$$

$$+ (EtO)_2MeSiSiMe(OEt)_2$$
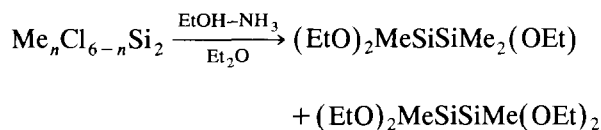
These results indicated that the disilane fraction consists mainly of two kinds of methylchlorodisilane: 1,1,2-tri-

chlorotrimethyldisilane and 1,1,2,2-tetrachlorodimethyldisilane. In later years, we worked out two even better methods of chlorodemethylation of methyldisilanes, involving reaction with acetyl chloride [8] or a large excess of trimethylchlorosilane [9] in the presence of anhydrous aluminum chloride.

One of the most interesting reactions discovered in the early days of our research on methylpolysilane chemistry was the thermal rearrangement of hexamethyldisilane to give pentamethyldisilmethylene which occurs when the former was passed through a quartz tube heated to about 600°C. We observed this in 1957 and reported it, together with a postulated radical chain mechanism involving initial production of the Me_3Si free radical, in 1958 [10]. Some years later, the same type of rearrangement was found to occur at a temperature as low as 450°C in a sealed tube [11]:

$$Me_3SiSiMe_3 \xrightarrow{\Delta} Me_3Si-Ch_2-\overset{\overset{\displaystyle H}{|}}{Si}Me_2 \ (+Me_3SiH)$$
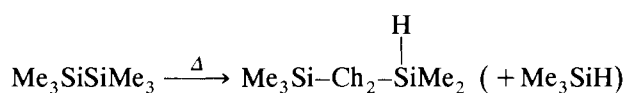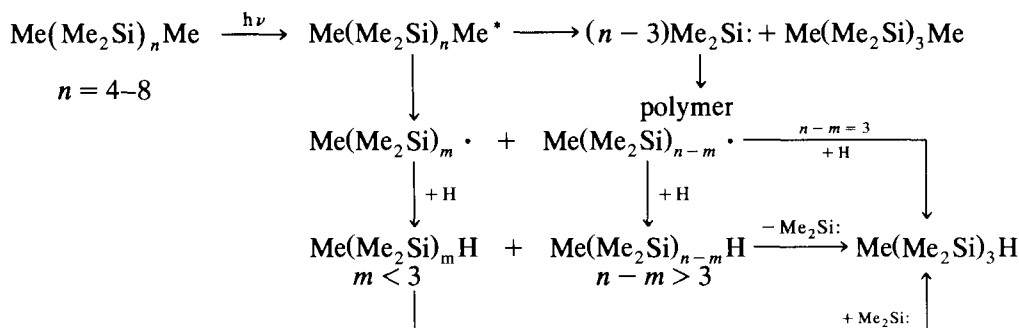
In later years, this type of thermal rearrangement aroused considerable interest of researchers engaged in gas-phase kinetics on the one hand and served as a model reaction underlying the first step of the process used by Yajima et al. [12] for β-silicon carbide fiber production on the other hand.

In the early 1960s, I moved to the newly founded Department of Synthetic Chemistry at Kyoto University and there we carried out the preparation of 11 lower members of a homologous series of permethylated polysilanes of the formula

$$Me \left(\begin{matrix} Me \\ | \\ Si \\ | \\ Me \end{matrix} \right)_n Me$$

$$(n = 2-12)$$
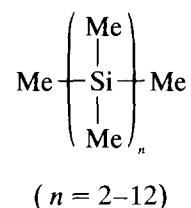
in a pure state by self- or co-condensation of appropriate chloro derivatives of monosilane, disilane, or trisilane by reaction with Na or Na–K alloy in hydrocarbon solvents [13].

In this context, it is appropriate to note that H. Gilman, in pursuit of a series of his studies on UV properties of organopolysilanes in 1964, asked me to send him small samples of all our permethylpolysilanes. He soon published a preliminary communication reporting that, except for the disilane, all the homologues of the polysilanes absorb in the near UV region, and the position λ_{max} of maximum absorption and the molar absorptivity ε increase regularly with increasing Si–Si chain length [14]. Since then the UV spectral properties of catenated compounds of Group 14 elements, in general, and of polysilanes, in particular, have been the

$$\text{Me}(\text{Me}_2\text{Si})_n\text{Me} \xrightarrow{h\nu} \text{Me}(\text{Me}_2\text{Si})_n\text{Me}^* \longrightarrow (n-3)\text{Me}_2\text{Si}: + \text{Me}(\text{Me}_2\text{Si})_3\text{Me}$$

$$n = 4\text{–}8$$

$$\text{Me}(\text{Me}_2\text{Si})_m\cdot \;+\; \text{Me}(\text{Me}_2\text{Si})_{n-m}\cdot \xrightarrow[+\text{H}]{n-m=3} \text{polymer}$$

$$\downarrow +\text{H} \qquad\qquad \downarrow +\text{H}$$

$$\text{Me}(\text{Me}_2\text{Si})_m\text{H} \;+\; \text{Me}(\text{Me}_2\text{Si})_{n-m}\text{H} \xrightarrow{-\text{Me}_2\text{Si}:} \text{Me}(\text{Me}_2\text{Si})_3\text{H}$$

$$m < 3 \qquad\qquad n-m > 3 \qquad\qquad\qquad\qquad + \text{Me}_2\text{Si}:$$

Scheme 1.

subject of many central theoretical and experimental studies.

Despite Gilman's striking discovery, surprisingly little interest had been shown in photochemical reactions of organopolysilanes before we started work along this line in 1969. Initially, we observed that dodecamethylcyclohexasilane in hydrocarbon solutions readily undergoes photolysis when irradiated with UV light (254 nm) at room temperature for 20–40 h, giving rise to two of the lower homologues of permethylated cyclopolysilanes, $(\text{Me}_2\text{Si})_5$ and $(\text{Me}_2\text{Si})_4$, together with relatively small amounts of 1,4-dihydrooctamethyltetrasilane and a polymeric material [15]:
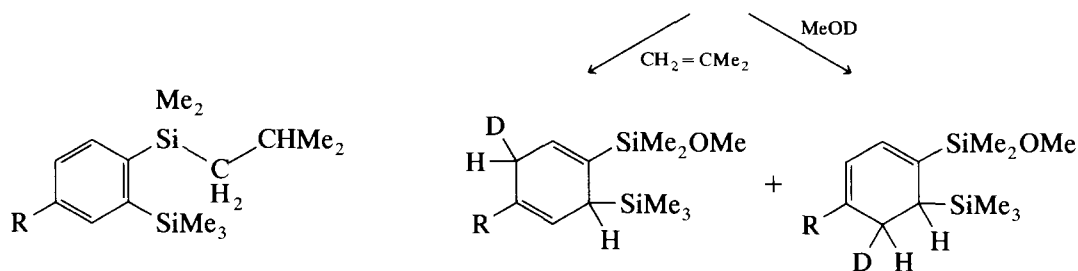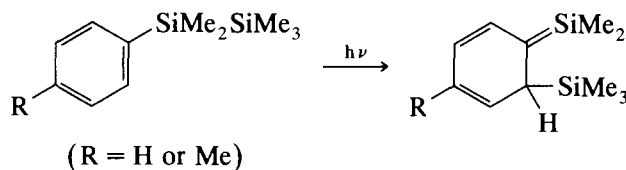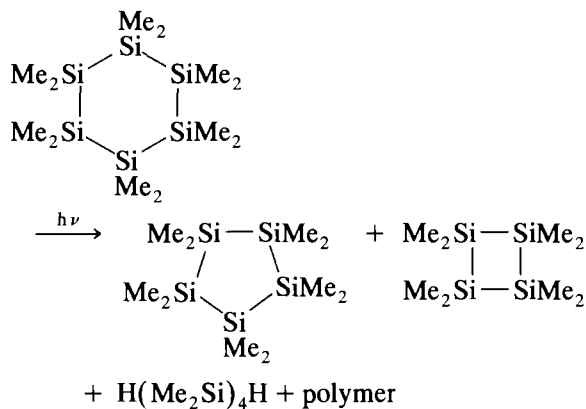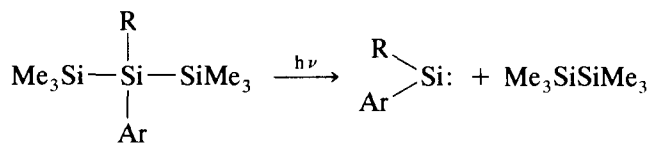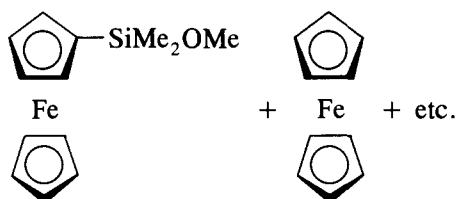
This photocatalysed ring contraction proceeds with generation of the Me_2Si: species. This was mainly established by trapping this species with, for example, Et_2MeSiH, to give the silylene insertion products $\text{Et}_2\text{MeSi}(\text{Me}_2\text{Si})_n\text{H}$ ($n = 1, 2$) with high yields. In contrast, the formation of the 1,4-dihydrotetrasilane must result from homolytic fission of the Si–Si bond in the cyclotetrasilane.

The permethylated linear polysilanes (tetrasilane and higher) were also found to undergo photolysis with generation of Me_2Si: and some homolytic cleavage of the Si–Si bond. The results are summarized in Scheme 1 [16]. This scheme has frequently been referred to recently in discussions of mechanisms of UV degradation of silane high polymers [17].

Permethylated trisilane is much less photoreactive than the higher homologues. However, replacement of at least one methyl group on the central silicon atom by an aryl made it photochemically labile, and the resulting trisilanes have been used as a good source of silylenes of the type RArSi:

Scheme 2.

The first synthesis of the thermally stable crystalline disilene $(Mes)_2Si=Si(Mes)_2$, by West et al. [18] in 1981 was based on an analogous photolysis of trisilane with R = mesityl (Mes).

In 1975, we observed that when a hydrocarbon solution of phenyl (or *p*-tolyl)pentamethyldisilane was irradiated with UV light an unprecedented type of silicon–carbon double-bonded intermediate was produced as a result of intramolecular migration of the trimethylsilyl group from silicon to an ortho position of the aryl group [19] (Scheme 2). These intermediates could efficiently be trapped with an appropriate reagent. For example, with isobutene as a trap an ene-type reaction occurred to give the expected product with 59% yield (for R = H), while with methanol-d_1 the expected 1,4- and 1,6-adducts were each isolated with about 27% yield (for R = Me). This study initiated further developments of UV photolysis of a wide range of π-electron system-substituted disilanes [19b].

In addition to the thermolysis and photolysis described above methylpolysilanes were found to undergo skeletal transformations very readily under various catalytic conditions, involving $AlCl_3$, or organosilyllithium compounds, or transition metal complexes [20]. Of these, the most interesting is the disproportionation of methylpolysilane hydrides such as pentamethyldisilane and *sym*-tetramethyldisilane catalyzed by certain late transition metal–phosphine complexes, to give, in each case an equilibrium mixture of several lower members of the corresponding homologous series [21]:

$$RMe_2SiSiMe_2H \xrightarrow[\substack{sealed\ tube \\ 90°C,\ 18\ h}]{cat.} \sum R(Me_2Si)_n H$$

$$(R = H, Me; n = 1, 2, \ldots, 6)$$

$$cat. = trans\text{-}[PtCl_2(PEt_3)_2],\ [NiCl_2(PEt_3)_2]\ etc.$$

Evidence that these disproportionations proceed via intermediate formation of dimethylsilylene species (probably not free but coordinated to the catalyst center) was provided by trapping the silylene with a suitable unsaturated hydrocarbon. Thus heating an equimolar mixture of the monohydrodisilane and diphenylacetylene in cyclohexane with the platinum catalyst at 90°C gave the 1,4-disilacyclohexadiene (5.3%), whereas treatment of an equimolar mixture of the dihydrodisilane and a disubstituted acetylene with the nickel catalyst under similar conditions gave the 1-silacyclopentadiene as the sole product with a good yield (30–95%):

$$2\ Me_3SiSiMe_2H + 2\ Ph\text{-}C{\equiv}C\text{-}Ph$$

$$(5.3\%)$$

$$HMe_2SiSiMe_2H + 2\ R\text{-}C{\equiv}C\text{-}R$$

$$(R = Me,\ Et,\ Ph,\ SiMe_3,\ etc.)$$

$$(30\text{–}95\%)$$

In both cases, none of the higher homologues of methylsilanes arising from disproportionation was formed [22].

Quite recently, many kinds of donor-stabilized silylene–transition metal compounds have been isolated and their X-ray crystal structures determined by several research groups [23].

2. Some unprecedented chemical properties of ferrocene-substituted silicon compounds

In the early 1960s at Osaka City University, we observed, very surprisingly, that repeated recrystallization of newly prepared 1,1'-bis(pentamethyldisilanyl)ferrocene from methanol caused the is melting point to approach the value reported for 1,3-(1,1'-ferrocenylene)-tetramethyldisiloxane:

mp 87–88°C

A few years later it occurred to us that the methanol might have been contaminated with a trace amount of hydrogen chloride possibly taken up from the atmosphere in the laboratory, which, to my shame, was often at that time polluted with chlorosilane vapors. Not only did we confirm this idea but also we established that the selective alcoholysis of the Si–Si bond in the 1,1'-bis(disilanyl)ferrocene, and also in pentamethyldisilanylferrocene, took place only when the HCl concentration was 0.05 M or less; at a higher concentration, complete desilylation to give ferrocene itself resulted [24]:

Several more years later at Kyoto University, we had an opportunity to revisit the methanolysis and observed that, all other conditions being kept constant, no cleavage of the Si–Si bond adjacent to a ferrocene nucleus occurred in a strictly oxygen-free sealed glass tube. Furthermore, we observed that, even under strictly oxygen-free conditions, if an oxidant such as $FeCl_3$ was present in a ratio of exactly two equivalents per Si–Si bond, the selective methanolysis of this bond went to completion [25]. The apparent stoichiometry for the reaction is shown below:
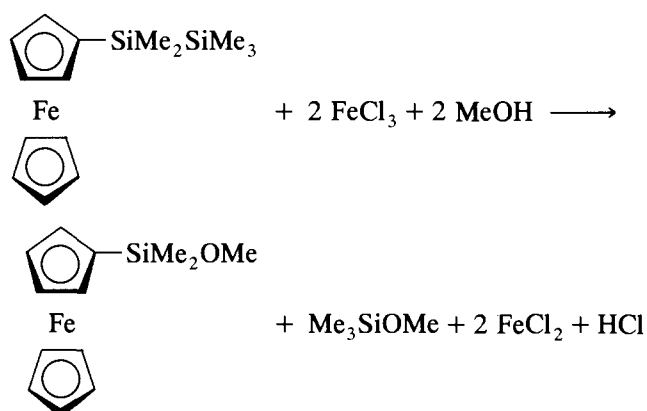
When the same reaction was carried out under ambient conditions, only a catalytic amount of the oxidant was needed, and this is because of the very ready participation of oxygen in the Fe(II) ⇌ Fe(III) redox process.

From extensive studies of related reactions, we concluded that the methanolysis proceeds in two stages, each of which involves formation of a ferricenium ion intermediate arising from a redox reaction. It is well known that, in contrast with an uncharged ferrocenyl group, a ferricenium cation moiety is electron withdrawing. As a result, the silicon atom β to the ferrocene ring becomes liable to nucleophilic attack even by the solvent methanol (Scheme 3).

As implied by the postulated mechanism, (ferrocenylmethyl)trimethylsilane ($Z = CH_2$) likewise underwent methanolysis under similar conditions to give ferrocenylmethyl methyl ether and trimethylmethoxysilane almost quantitatively [26].

Another interesting but not yet well-understood reaction that we observed about 30 years ago involves thermal isomerization of silicon- and germanium-substituted ferrocenes. Certain heteroannularly substituted bis(organosilyl)ferrocenes and bis(organogermyl)ferrocenes were found to undergo reversible isomerization to the corresponding homoannularly bis(probably 1,3)-substituted ferrocenes when heated to about 300°C in a strictly oxygen-free glass tube. The equilibrium lay slightly well over through the 1,1′ isomer [27]:

$Z = SiMe_3$, $SiMe_2SiMe_3$, $SiMe_2CH_2SiMe_3$, $GeMe_3$
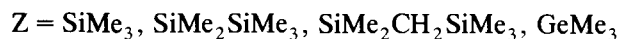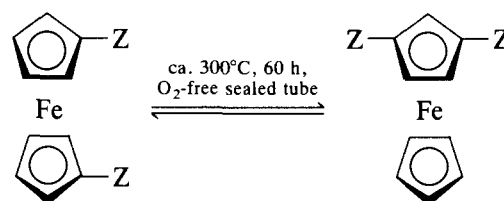
In seeking a clue to understanding of the mechanism of this unprecedented isomerization, we attempted to carry out a similar isomerization of the ferrocenes with $Z = Me_3C$, Me_3Sn or Me_2P, but they all decomposed extensively on heating. However, since we have been able to synthesize 1,1′-bis(dimethylphosphino)ferrocene only with great difficulty [28], we wanted to put the compound to some use. It was not long before we found that it could be used as a bidentate ligand and prepared some transition metal complexes of it. The only one known
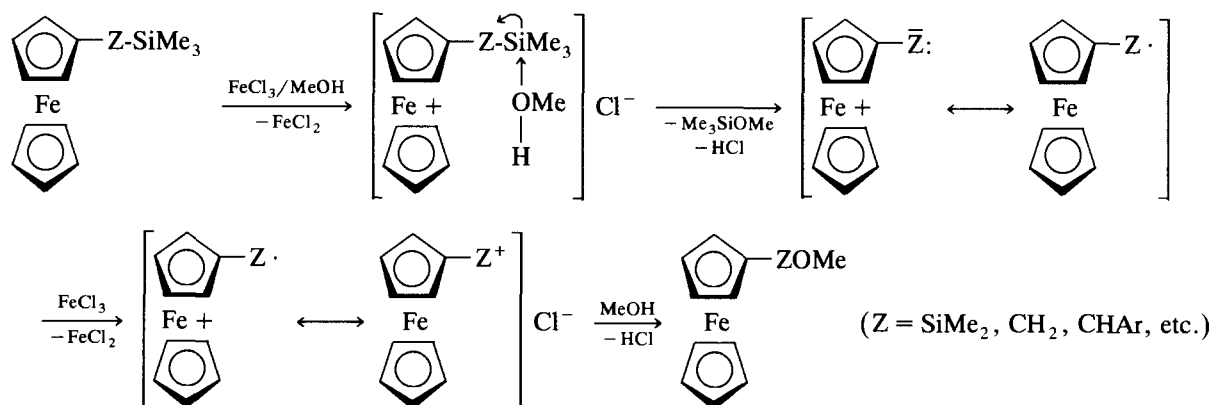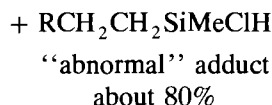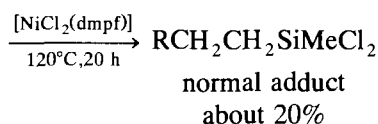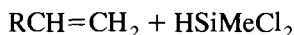

Scheme 3.

ligand of analogous structure at that time was 1,1'-bis(diphenylphosphino)ferrocene.

3. Some selective organic syntheses catalyzed by ferrocenylphosphine–transition metal complexes

We soon found (in 1970) that a nickel complex, [NiCl$_2$(dmpf)], where dmpf denotes 1,1'-bis(dimethylphosphino)ferrocene, exhibited catalytic activity in hydrosilylation of olefins that was interesting because it gave rise not only to the addition of silicon hydrides across the C=C bond but also to the interchange of hydrogen and chlorine on silicon. For example,

$$RCH=CH_2 + HSiMeCl_2$$

$$\xrightarrow[120°C,20\ h]{[NiCl_2(dmpf)]} RCH_2CH_2SiMeCl_2$$
$$\text{normal adduct}$$
$$\text{about } 20\%$$

$$+ RCH_2CH_2SiMeClH$$
$$\text{"abnormal" adduct}$$
$$\text{about } 80\%$$

where R = Pr or Bu. Although dmpf had given us the opportunity to enter into the new area of phosphinoferrocene chemistry, the great difficulty in obtaining dimethylchlorophosphine for synthesis of ligand dmpf directed our attention to other phosphinoferrocenes. Our efforts were successful in giving a wide range of optically active phosphinoferrocenes and led to a variety of asymmetric organic syntheses, mostly with high optical as well as chemical yields, as catalysts involving use of transition metal complexes bearing such ligands [29].

The representative chiral phosphinoferrocenes were readily prepared using optically resolved N,N-dimethyl-1-ferrocenylethylamine (FA) which had been reported by Ugi and coworkers [30] in 1970 by a highly stereospecific lithiation followed by treatment with diphenylchlorophosphine. Scheme 4 depicts the synthesis of $(+)$-(S)-(R)-PPFA and $(+)$-(S)-(R)-BPPFA, where the symbols (S) and (R) refer to the central chirality at carbon and the planar chirality due to 1,2-asymmetrically substituted ferrocene structure respectively. Similarly, $(-)$-(R)-(S)-PPFA and $(-)$-(R)-(S)-BPPFA were prepared from (R)-FA.

Catalytic asymmetric hydrosilylation of prochiral olefins and C–C bond-forming reaction between *sec*-alkylmagnesium bromide and vinylic halides catalyzed by PdCl$_2$[(R)-(S)-PPFA] ([Pd*]) are the typical examples:

(S)

50%ee

$(1R,2S,4S)$

50%ee

R = H: 95%ee

R = Me: 85%ee

R = Ph: 95%ee
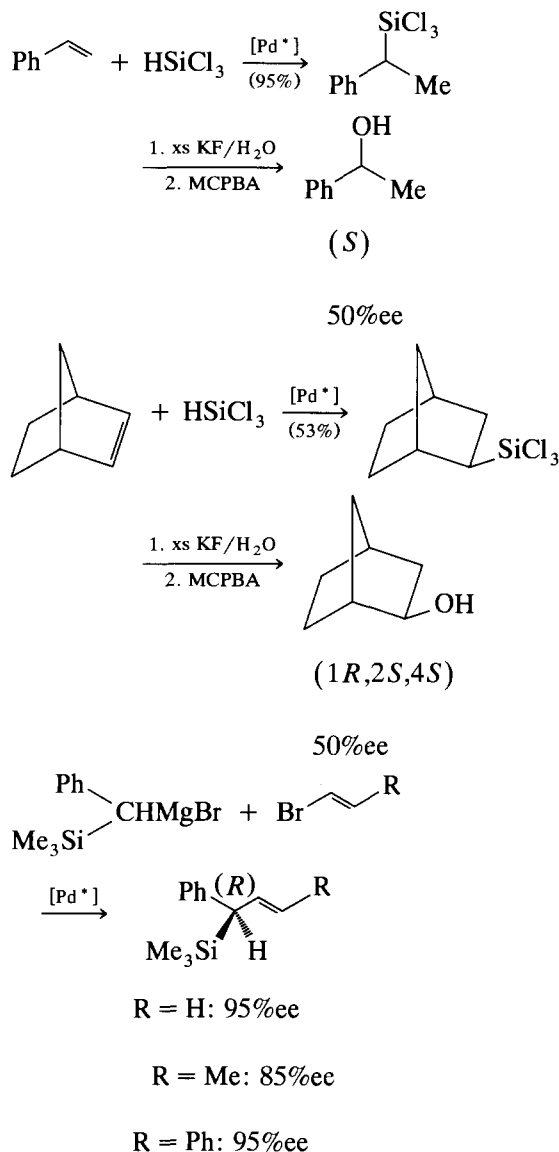
The second of these examples involves a successful application of the Grignard cross-coupling reaction discovered independently by Corriu and Masse [31] and by K. Tamao et al. [32] in our laboratory in 1972.
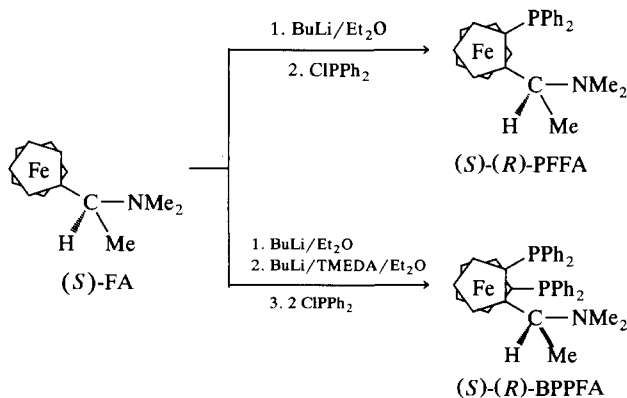
Scheme 4.

4. Conclusions

It will be apparent that the chance discovery that hexamethyldisilane could to be prepared conveniently and in large quantities from the "still-pot residue" of the Rochow process, together with a lucky observation of highly selective halodemethylation of the disilane, opened the way to a very fruitful field of organopolysilane chemistry. Furthermore, another accidental discovery, that of the unprecedented behavior of silicon-substituted ferrocenes, led luckily to the development of the use of phosphinoferrocene ligands, especially optically active ones, and to some highly selective organic syntheses involving use of metal complexes bearing such chiral ligands as catalysts.

Acknowledgements

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