Introduction

Professor Makoto Kumada was born in 1920 in Obama, a small town facing the Sea of Japan, where he lived until 1937. In 1943 he graduated from the Department of Industrial Chemistry of Kyoto University. He received the degree of Doctor of Engineering from Osaka City University in 1953 for a thesis entitled (in Japanese) "Studies on Organosilicon Compounds". After a short period in the employ of Toshiba Electric Co., Ltd., he joined the faculty of Osaka City University, where he was appointed Professor of Chemistry in 1956. In 1962 he moved to the Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, from which he retired in 1984 upon reaching the age limit. He has since held the title of Professor Emeritus of Kyoto University. Professor Kumada is regarded as a "Grand Old Man" of the organosilicon fraternity; his own research reflects in itself the history of the rise and development of modern organosilicon chemistry.

Soon after he had moved to Osaka City University in 1950, two Japanese companies, Toshiba and Shin-etsu, began production of chlorosilanes based on Rochow's direct process. He was interested in the utilization of the distillation residue from the direct process, which formed more than 10 percent of all the products. Obviously the search for the main ingredients was the first step. Nothing other than distillation being available as a method of separation, his first job involved making a long Fenske column. Methylation of the distillates with methylmagnesium bromide was the only strategy for him, but it resulted in a very fruitful outcome. One cold winter morning, young Kumada found that a portion of the distillate from the methylated products solidified in the reservoir. He identified it as hexamethyldisilane (b.p. 113° C, m.p. 13° C), which was known in the literature but only as a compound difficult to prepare. He was able to obtain it in kilogram quantities! This provided just the opportunity for initiating organopolysilane chemistry.

$$Me_nSi_2Cl_{6-n} + (6-n)MeMgBr \rightarrow Me_3SiSiMe_3 + (6-n)MgClBr$$

Professor Kumada examined a variety of reactions of hexamethyldisilane, and some of the work was naturally directed to silicon-functionalized and carbon-functionalized disilanes as well as to permethylpolysilanes. His research developed rather slowly at first but explosively later. He published his first paper on disilane chemistry in 1954, as the 20th paper in his series on organosilicon compounds.

Professor Kumada's publications in the earlier period appeared mostly in local or domestic journals such as Memoirs Fac. Eng. Osaka City Univ. and Kogyo Kagaku Zasshi (J. Chem. Soc., Indus. Chem. Section), so that little attention seemed initially to be paid to his work. However, by June 1963, when he made the first lecture trip to the US and Europe, three important papers had been already appeared in J. Org. Chem.; these were on the synthesis of some methyldisilanes containing functional groups, the synthesis and intramolecular rearrangements of chloromethylpentamethyldisilane and 1-chloromethyl-2-chlorotetramethyldisilane, and the thermal rearrangement of hexamethyldisilane to trimethyl(dimethylsilylmethyl)silane. He included these three papers along with preprints of 13 other papers in a booklet which he made for his trip. This compilation and the subsequent appearance of the unpublished papers in the newly established J. Organometal. Chem., attracted much attention to his contributions to the chemistry of organopolysilanes. It was a breakthrough for both Kumada's chemistry and organosilicon chemistry itself.

In 1965, on the occasion of the First International Symposium on Organosilicon Chemistry, in Prague, he lectured by invitation on "Recent Research on Organopolysilanes", and in 1968, he wrote a successful review on "Aliphatic Organopolysilanes" in Adv. Organomet. Chem.

Professor Kumada received the Frederic Stanley Kipping Award in Organosilicon Chemistry from the American Chemical Society in 1967. The citation was "for his energetic and resourceful attack on research problems in the difficult areas of the polysilanes, the haloalkylsilanes and the rearrangements they undergo".

It is not exactly true, but probably close enough, to say that Professor Kumada's research in the 1960's was the result of his unrivaled enthusiasm for organosilicon chemistry. His efforts in cultivating the new field brought him an abundant crop in the 1970's.

Professor Kumada has published more than 280 original papers and 60 review articles. It is impossible to survey these works adequately in the limited space available, but if one dares to classify his contributions, the most important ones may be divided into the following five categories: (1) skeletal rearrangement of aliphatic polysilanes; (2) organopentafluorosilicates and organic synthesis; (3) silyl- and phosphino-substituted ferrocenes; (4) nickel complexes-catalyzed cross coupling of Grignard reagents with organic halides; and (5) stereochemical studies of important organosilicon reactions.

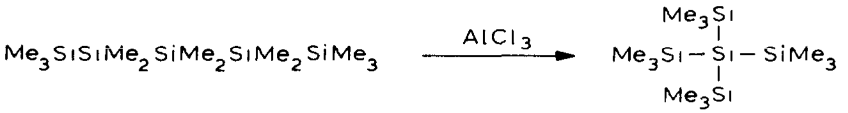
(1) Skeletal rearrangements of aliphatic polysilanes

The first paper on the skeletal rearrangement of polysilanes described the thermal rearrangement of hexamethyldisilane to pentamethyldisilmethylene, and was published in 1958.

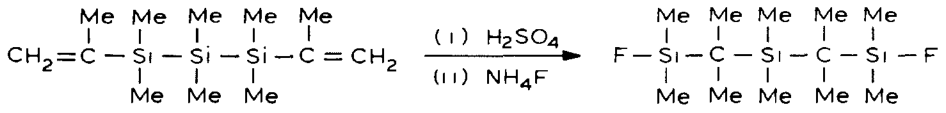
$$\mathrm{Me_3SiSiMe_3} \xrightarrow{600\,^\circ\mathrm{C}} \mathrm{Me_3SiCH_2SiMe_2H}\ (+\mathrm{Me_3SiH})$$

This reaction attracted much attention later and, indeed, constituted the basic reaction for the manufacture of β-SiC fibers from permethylpolysilane some 20 years later.

Aluminum chloride- and acid-catalyzed skeletal rearrangements of polysilanes are highlights of his work at this early stage.

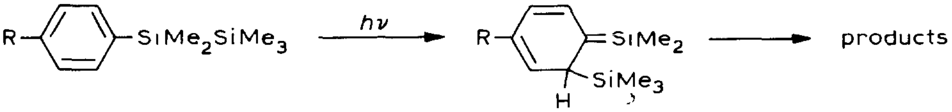


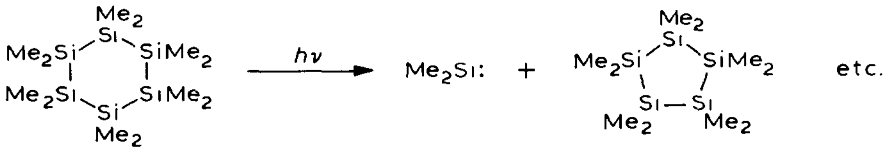
$$\mathrm{Me_3SiSiMe_2SiMe_2SiMe_2SiMe_3} \xrightarrow{\mathrm{AlCl_3}} \mathrm{Me_3Si{-}\underset{Me_3Si}{\overset{Me_3Si}{Si}}{-}SiMe_3}$$



$$\mathrm{CH_2{=}\overset{Me}{C}{-}\underset{Me}{\overset{Me}{Si}}{-}\underset{Me}{\overset{Me}{Si}}{-}\underset{Me}{\overset{Me}{Si}}{-}\overset{Me}{C}{=}CH_2} \xrightarrow[\text{(ii) }\mathrm{NH_4F}]{\text{(i) }\mathrm{H_2SO_4}} \mathrm{F{-}\underset{Me}{\overset{Me}{Si}}{-}\underset{Me}{\overset{Me}{C}}{-}\underset{Me}{\overset{Me}{Si}}{-}\underset{Me}{\overset{Me}{C}}{-}\underset{Me}{\overset{Me}{Si}}{-}F}$$

The photochemical rearrangement and degradation of permethyl and unsaturated polysilanes represent an important milestone in his chemistry. In particular, photochemical generation of dimethylsilylene from dodecamethylcyclohexasilane and acyclic polysilanes opened a fruitful field of silylene chemistry, and later provided the route to the first stable disilenes obtained by R. West.

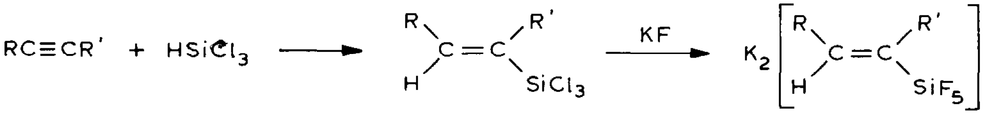


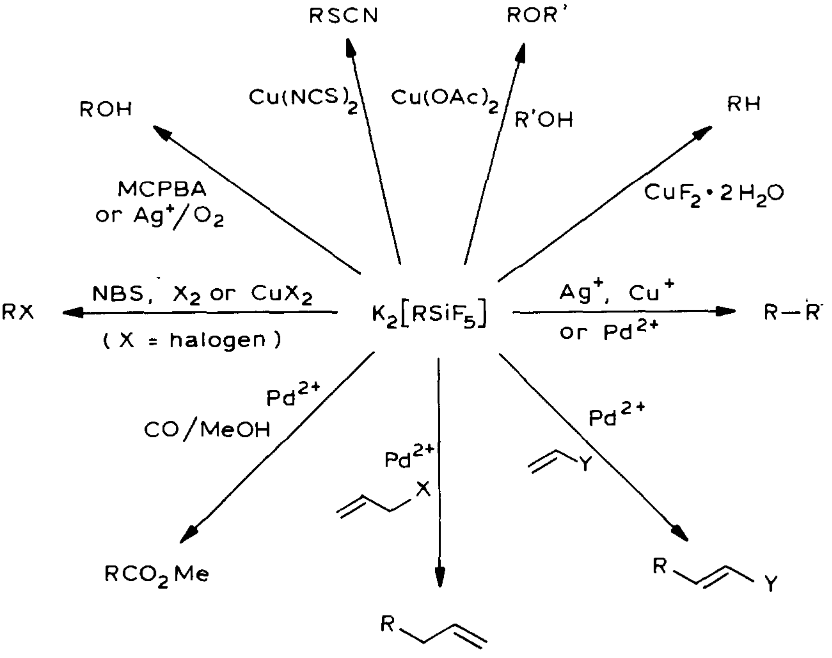


(2) Organopentafluorosilicate and organic synthesis

Professor Kumada developed a new methodology in organic synthesis based on hydrosilation/pentafluorosilicate strategy. The carbon–silicon bond (like the carbon–boron bonds produced by hydroboration) can be cleaved to give a variety of alkyl derivatives, as outlined below:

$$RCH{=}CH_2 \pm HSiCl_3 \longrightarrow RCH_2CH_2SiCl_3 \xrightarrow{KF} K_2[RCH_2CH_2SiF_5]$$

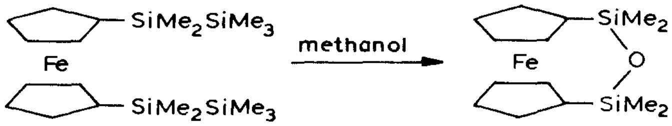




(3) Silyl- and phosphinyl-substituted ferrocenes

I suggest with some confidence that Professor Kumada has had a special affection for ferrocene. Of course, the preparation and identification of ferrocene was one of the most brilliant achievements in organometallic chemistry, and there is no doubt that he was deeply impressed by the discovery, like other young chemists at that time. However, without his special attachment it is difficult to explain how his long stroll in ferrocene chemistry led eventually to a beautiful garden.

His ferrocene chemistry obviously started with the simple motivation of preparing disilanyl-substituted ferrocenes, but he immediately observed a strange cleavage reaction.



He spent 10 years elucidating the mechanism of this reaction, and uncovered many other interesting reactions. One of the most important outcomes of his activity in this area was the introduction of a variety of phosphinylferrocenes which can be used as catalysts for useful reactions.

(4) Nickel complex-catalyzed cross-coupling of Grignard reagents with organic halides

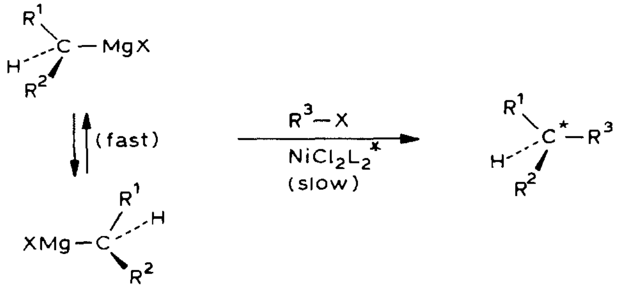
In 1972 Professors Kumada and Corriu independently observed that nickel phosphine complexes can catalyze cross coupling reaction between Grignard reagents and organic halides having $C(sp^2)$–X bonds.

$$RMgX + R'X \xrightarrow{NiCl_2L_2} R\text{–}R'$$

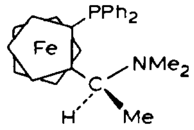
(R' = alkenyl, aryl, heteroaryl)

In these reactions, Kumada found that 1,1′-bis(diphenylphosphino)ferrocene (dppf) functions as a unique catalyst, preventing undesirable isomerization and reduction in the reaction with secondary or tertiary alkylmagnesium halides.

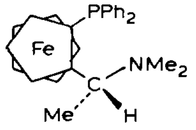
This unique behaviour of ferrocenophosphine-based catalysts was later employed in asymmetric Grignard cross-coupling reactions. Many new efficient chiral phosphine-nickel complexes were designed and prepared. Notable examples are as follows.



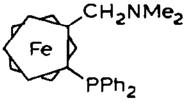
$$PhMeCHMgCl + CH_2{=}CHBr \xrightarrow{[Ni^*]} PhMeCH^*CH{=}CH_2$$



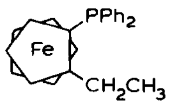
(*S*)-(*R*)-PPFA



(*R*)-(*R*)-PPFA

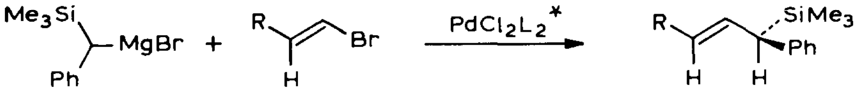


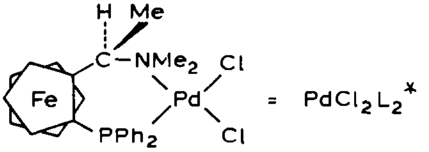
(*S*)-FcPN



(*R*)-PPEF

The optically active allylsilanes which he obtained in this way were especially useful in elucidation of the mechanisms of important reactions of allylsilanes.

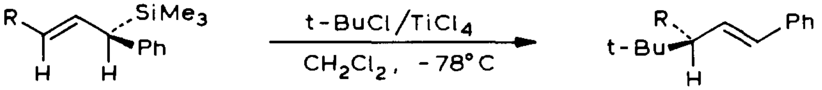




R = H 95% ee (R)
R = Ph 95% ee (R)
R = Me 85% ee (R)

(5) Stereochemical studies of important organosilicon reactions.

The optically active allylsilanes were found to undergo stereospecific reactions with carbon electrophiles. High *erythro* selectivity was observed for aldehydes.



In addition to these reactions, asymmetric hydrosilation of ketones catalyzed by chiral phosphine-platinum and -rhodium complexes must be mentioned as an important contribution in the field.

In addition to the F.S. Kipping Award, Professor Kumada received the Award of the Society of Synthetic Organic Chemistry of Japan in 1974. He has been a member of the Editorial Board of the Journal of Organometallic Chemistry since 1969, and one of its Regional Editors since 1981.

On a personal note I must say that it was my great pleasure and fortune to be a member of his group during 1962–1969 as an Associate Professor of Kyoto University. Those years were among the most fruitful of Professor Kumada's career.

Retirement from Kyoto University is compulsory at the age of 63. Professor Kumada remains young not only in appearance but in mind, and it is to be hoped that he will continue to lead and inspire all organosilicon chemists.

Professor Kumada will be the Chairman of the 7th International Symposium of Organosilicon Chemistry in Kyoto in September, 1984. The symposium will in a sense stand as a symbol of his long and successful career as organosilicon chemist and I heartily wish it every success.

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