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COMPREHENSIVE ORGANOMETALLIC CHEMISTRY

*The Synthesis, Reactions and Structures of
Organometallic Compounds*

Volume 2



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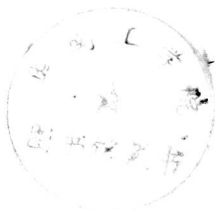
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COMPREHENSIVE ORGANOMETALLIC CHEMISTRY

Preface

Although the discovery of the platinum complex that we now know to be the first π -alkene complex, $K[PtCl_3(C_2H_4)]$, by Zeise in 1827 preceded Frankland's discovery (1849) of diethylzinc, it was the latter that initiated the rapidly developing interest during the latter half of the nineteenth century in compounds with organic groups bound to the elements. This era may be considered to have reached its apex in the discovery by Grignard of the magnesium reagents which occupy a special place because of their ease of synthesis and reactivity. With the exception of trimethylplatinum chloride discovered by Pope, Peachy and Gibson in 1907 by use of the Grignard reagent, attempts to make stable transition metal alkyls and aryls corresponding to those of main group elements met with little success, although it is worth recalling that even in 1919 Hein and his co-workers were describing the 'polyphenylchromium' compounds now known to be arene complexes.

The other major area of organometallic compounds, namely metal compounds of carbon monoxide, originated in the work starting in 1868 of Schützenberger and later of Mond and his co-workers and was subsequently developed especially by Hieber and his students. During the first half of this century, aided by the use of magnesium and, later, lithium reagents the development of main group organo chemistry was quite rapid, while from about 1920 metal carbonyl chemistry and catalytic reactions of carbon monoxide began to assume importance.

In 1937 Krause and von Grosse published their classic book 'Die Chemie der Metallorganischen Verbindungen'. Almost 1000 pages in length, it listed scores of compounds, mostly involving metals of the main groups of the periodic table. Compounds of the transition elements could be dismissed in 40 pages. Indeed, even in 1956 the stimulating 197-page monograph 'Organometallic Compounds' by Coates adequately reviewed organo transition metal complexes within 27 pages.

Although exceedingly important industrial processes in which transition metals were used for catalysis of organic reactions were developed in the 1930s, mainly in Germany by Reppe, Koch, Roelen, Fischer and Tropsch and others, the most dramatic growth in our knowledge of organometallic chemistry, particularly of transition metals, has stemmed from discoveries made in the middle years of this century. The introduction in the same period of physical methods of structure determination (infrared, nuclear magnetic resonance, and especially single-crystal X-ray diffraction) as routine techniques to be used by preparative chemists allowed increasingly sophisticated exploitation of discoveries. Following the recognition of the structure of ferrocene, other major advances quickly followed, including the isolation of a host of related π -complexes, the synthesis of a plethora of organometallic compounds containing metal-metal bonds, the characterization of low-valent metal species in which hydrocarbons are the only ligands, and the recognition from dynamic NMR spectra that ligand site exchange and tautomerism were common features in organometallic and metal carbonyl chemistry. The discovery of alkene polymerization using aluminium alkyl-titanium chloride systems by Ziegler and Natta and of the Wacker palladium-copper catalysed ethylene oxidation led to enormous developments in these areas.

In the last two decades, organometallic chemistry has grown more rapidly in scope than have the classical divisions of chemistry, leading to publications in journals of all national chemical societies, the appearance of primary journals specifically concerned with the topic, and the growth of annual review volumes designed to assist researchers to keep abreast of accelerating developments.

Organometallic chemistry has become a mature area of science which will obviously continue to grow. We believe that this is an appropriate time to produce a comprehensive review of the subject, treating organo derivatives in the widest sense of both main group and transition elements. Although advances in transition metal chemistry have appeared to dominate progress in recent years, spectacular progress has, nevertheless, also been made in our knowledge of organo compounds of main group elements such as aluminium, boron, lithium and silicon.

In these Volumes we have assembled a compendium of knowledge covering contemporary organometallic and carbon monoxide chemistry. In addition to reviewing the chemistry of the ele-

ments individually, two Volumes survey the use of organometallic species in organic synthesis and in catalysis, especially of industrial utility. Within the other Volumes are sections devoted to such diverse topics as the nature of carbon-metal bonds, the dynamic behaviour of organometallic compounds in solution, heteronuclear metal-metal bonded compounds, and the impact of organometallic compounds on the environment. The Volumes provide a unique record, especially of the intensive studies conducted during the past 25 years. The last Volume of indexes of various kinds will assist readers seeking information on the properties and synthesis of compounds and on earlier reviews.

As Editors, we are deeply indebted to all those who have given their time and effort to this project. Our Contributors are among the most active research workers in those areas of the subject that they have reviewed and they have well justified international reputations for their scholarship. We thank them sincerely for their cooperation.

Finally, we believe that 'Comprehensive Organometallic Chemistry', as well as providing a lasting source of information, will provide the stimulus for many new discoveries since we do not believe it possible to read any of the articles without generating ideas for further research.

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9.1

Organosilanes

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9.1.1 INTRODUCTION

9.1.1.1 Historical Survey

Silica and the silicates form the major component of the Earth's crust. The name comes from the Latin word *silex*, *silicis* for flint, which itself has been used since the dawn of Man as a weapon and tool, and is believed to have influenced the shape of his hand.¹

In 1771, Scheele obtained silicon tetrafluoride as a gas from silica using hydrogen fluoride. The element was isolated 40 years later as a powder when Gay-Lussac and Thenard reduced the tetrafluoride with potassium. Berzelius in 1823 prepared it similarly using potassium hexafluorosilicate and the same year made silicon tetrachloride. This was used by Ebelmen in 1846 to prepare ethyl orthosilicate $\text{Si}(\text{OEt})_4$. Then Wöhler discovered the volatile hydrides, trichlorosilane SiHCl_3 and silane SiH_4 around 1857, the year in which Sainte Claire Deville first obtained the element as steel grey pellets.

A superficial similarity in the chemistry of silicon and carbon was becoming apparent with the isolation of volatile chlorides and hydrides. This culminated in 1863 with the preparation of the first organosilicon compound, tetraethylsilane Et_4Si , by Friedel of France and Crafts of the U.S.A., working together in Germany. They obtained tetraethylsilane as a volatile liquid boiling between 152 and 154 °C by alkylating silicon tetrachloride with Frankland's diethylzinc.² During the next decade they extended this method to include other alkyl groups, and with Ladenburg found that aryl compounds of mercury were more effective than those of zinc for preparing arylsilanes.

In the meantime, the properties of tetraethylsilane and silicon tetrachloride and those of tetraethyltin, first prepared by Frankland in 1852, enabled Mendeleev in 1871 to predict those of ekasilicon. While the properties found by Winkler for germanium and its compounds were in general consistent with those predicted by Mendeleev, germanium is less metallic than at first anticipated. This has been rationalized in terms of the weak *d*-orbital screening of the outer electrons.³

The reaction of orthosilicates with zinc dialkyls was developed in the 1870s by Ladenburg⁴ then in 1884 Pape reacted trichlorosilane with dipropylzinc. Both tri- and tetra-propylsilane resulted, subsequent bromination yielding tripropylbromosilane and possibly allyltripropylsilane.⁵ The use of the Wurtz coupling reaction and of sodium alkyls in the preparation of tetraorganosilanes from silicon tetrachloride was introduced through the work of Polis at about the same time.⁶ However, control of the variety and yield of the products, particularly the partially substituted halides, resulted only when the Grignard reagents were discovered at the turn of the century.

This discovery opened up not only rapid developments in synthetic organic chemistry, but provided the platform from which organosilicon chemistry could expand. Within four years of Grignard's first paper on organomagnesium halides, published in 1900, Kipping in Nottingham and Diltthey in Zurich independently applied the Grignard reagent to the synthesis of organic derivatives of silicon. Diltthey reacted silicon tetrachloride with phenylmagnesium bromide, and the chlorides so obtained were hydrolysed to the silanols and siloxanes. Kipping had prepared ethylphenylsilicon dichloride and ethylphenylpropylsilicon chloride by stepwise substitution of chlorine. The dichloride he hydrolysed to an oil which he described as the silicoketone. Three years previously he had reported diphenylsilicium ketone Ph_2SiO to bear little resemblance to benzophenone, and possibly to be a polymer.⁷

Kipping's interest in this field developed mainly around the aryl and ethyl derivatives, and he is justifiably recognized as the father of classical organosilicon chemistry. During the ensuing 30 years he published some 50 papers on this topic. He reported to the Royal Society in his Bakerian lecture, delivered in 1936, that 'the prospect of any immediate and important advance in this section of organic chemistry does not seem to be very hopeful.'⁸

Meanwhile, the organic chemistry group of General Electric were seeking better electrical insulators. The proposal to use glass fibres necessitated the synthesis of a sympathetic polymer to bind the fibres and be non-porous and water resistant. Rochow developed this polymer at the invitation of Corning Glass. He had become interested in organometallic chemistry while at Cornell, where he heard Alfred Stock deliver the George Fisher Baker lectures on boranes and silanes. (Rochow provided the illustrations for the book subsequently published on these lectures.) General Electric then provided Rochow with a job in ceramics chemistry in 1935 and three years later he combined the two fields in an attempt to prepare this polymer.⁹

Compounds devoid of carbon-carbon bonds but containing a silicon-oxygen skeleton were suggested and subsequently prepared by hydrolysing a mixture of methyltrichlorosilane and dimethyldichlorosilane. The polymers resulting had high thermal stability, and the name silicones, subsequently used for these polymers, was brought into everyday use through wax polishes. The name silicone had been suggested as early as 1857 by Wöhler and was extensively used by Kipping.

Methylchlorosilanes are now prepared by the process developed originally in 1945 by Rochow and Patnode using the reaction of methyl chloride with silicon in the presence of a copper catalyst at 300–400 °C. The careful fractionation of the methylchlorosilanes so formed provides all the intermediates needed for the silicones industry. The history of organosilicon chemistry draws on many branches of chemistry and the interleaving of these aspects provides an interesting chapter in the history of science.¹⁰

The increasingly successful use of silyl derivatives as intermediates in organic synthesis is reflected in the twentyfold increase in the number of papers published in this area in the period from the early 1960s to 1976. Nevertheless the 270 or so papers published in 1976 in this particular area represented only just over 10% of the total published in organosilicon chemistry that year, and more than 400 papers have been published on the topic each year since. The European market for silylating agents in 1977 was more than twice the global market of 1973, and trimethylchlorosilane and dimethyldichlorosilane have become bulk chemicals.¹¹

The encyclopaedic compilation of organosilicon compounds also reflects this increased interest. Some 14 000 have been reported up to mid 1961. The 22 000 reported for the subsequent period up to the end of 1969 included some previously listed, while the ensuing six year period, 1970–1975, includes 24 000 new compounds.¹² All are cross-referenced with physical properties, so no extensive tabulations will be given in this chapter, though melting points and boiling points are mentioned in passing.

The early literature has been extensively surveyed¹³ and Eaborn's book 'Organosilicon Compounds' covers the subject up to 1960.¹⁴ This has been updated as part of Aylett's volume of the fourth edition of 'Organometallic Compounds',^{14a} and by annual surveys^{15,16} and specific reviews,¹⁷ and compared with the chemistry of organometallic compounds of the rest of the group.¹⁸ The synthesis and reactions of the silicon-carbon bond were extensively reviewed in 1968 and 1972.¹⁹ Particular reference is made to the use of organosilicon compounds in organic synthesis,²⁰ to organosilicon compounds with specific functional groups^{12,21,22} and to their structure and reactivity.^{23,24} Reviews and articles pertinent to organosilicon chemistry are included in the comprehensive main group organometallic bibliography, the topicality and breadth of the subject are admirably summarized in a pair of resource papers in the *Journal of Chemical Education*, and its appeal is reflected in the allocation of a complete volume of Houben-Weyl in which physical properties are extensively documented, following the publication of a short monograph for teachers on silicon chemistry and applications.²⁵

9.1.1.2 General Behaviour

The position of silicon in the upper centre of the Periodic Table classifies it as the gentlest of metals. It possesses few of the metallic features of the heavier elements of its group, with only the slightest of tendencies to form stable divalent derivatives and conform with the inert pair effect. While silicon dissolves in aqueous alkali giving orthosilicates, it also generates hydrogen from hydrofluoric acid, thereby indicating distinct amphoteric behaviour.

The similarity in behaviour of boron and silicon — their diagonal relationship — stems in the main from the stability of bonds of both elements to oxygen and to fluorine. Both elements have a tendency to form anionic derivatives with electropositive metals, these derivatives readily hydrolysing in acid to silanes and boranes.²⁶ The extensive studies of Sommer and then Eaborn, devoted to elucidating the mechanism of substitution at silicon, have now led to close comparisons being made with substitution in phosphorus and organophosphorus derivatives by Corriu.²⁷

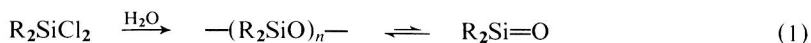
Much of the chemistry of silicon has therefore been considered in the light of elements only mildly metallic in character and the study of organosilicon compounds was the prerogative of organic chemists until Rochow introduced the inorganic silicate skeleton. The resurgence of organometallic chemistry with the discovery of ferrocene coincided with the commercial production of organochlorosilanes. Silicones were developed to supersede organic polymers, and inorganic chemists played an increasing role in developing the chemistry of substituted organosilicon compounds, *e.g.* R_3SiX and R_2SiX_2 where $X \neq C$. The gamut of these compounds is now being used extensively by organic chemists as synthetic intermediates.

In introducing general features of the chemistry of silicon, comparisons can conveniently be drawn with carbon, particularly in the areas of reactivity and multiple bond formation.

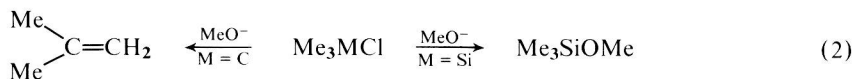
Substitution at silicon is much easier than that at carbon. Attack by protic bases and by organic nucleophiles makes chlorosilanes excellent synthetic intermediates. This stems from the high rate of bimolecular nucleophilic substitution which typifies a second period element,²⁸ and takes place with much poorer leaving groups than substitution at carbon. Thus the Si—F, Si—OR, Si—C and Si—H bonds can all be cleaved by the appropriate nucleophile. The mechanism of this substitution will be discussed in detail later (Section 9.1.2.3).

The facility of the above reactions, particularly hydrolysis, is in part due to the strength of bonds silicon forms with the electronegative elements. The bond strengths and bond lengths are given in Table 1. It should be emphasized that the bond strengths have been determined by a variety of techniques, but normally for homolysis, hence the spread of values. Heterolysis includes ionisation potential and electron affinity in the bond strength as well.¹⁴ The Si—F bond is one of the strongest encountered with the Si—O and Si—Cl bonds significantly stronger than the rest. It is easy to see from this how the silicones industry developed once methylchlorosilanes had been prepared. The extensive use of silicon compounds as synthetic intermediates in inorganic chemistry is based on the facile cleavage of Si—C, Si—N and Si—S bonds by chlorides of both main group and transition metals. Organic compounds silylated at carbon or oxygen can be readily regenerated using fluoride ion.

Kipping's attempts to isolate 'silicone', the silicon equivalent of ketone, failed partly because the silicon—oxygen single bond was so strong. The formation of two such bonds upon hydrolysing the dichlorosilane rendered the formation of a monomer with silicon—oxygen double bond energetically most unlikely (equation 1).



Multiple bonds to silicon involving $(p-p)\pi$ bonding have long been assumed to be weak, partly because of size disparity, but also because the Si—X bond is much longer than the C—X one, thereby decreasing π -overlap. The weakness of the silicon—carbon double bond precludes competitive elimination in methylchlorosilanes by methoxide, in sharp contrast to its reaction with *t*-butyl chloride (equation 2).



However, an increasing wealth of evidence is being amassed to support the transient existence of intermediates with multiple bonds to silicon from not only first period (carbon, nitrogen and oxygen) but also second period elements (silicon, phosphorus and sulphur). The silicon—carbon

Table 1 Bond Strengths and Bond Lengths of Some Silicon Compounds¹

| Bond | Compound | Dissociation energy (kJ mol ⁻¹) | Compound | Bond length (pm) |
|-------|---|--|---|--------------------------|
| Si—H | Me ₃ SiH | 376, ² 325, ³ 343 ⁴ | D ₃ SiH | 148 |
| Si—C | Me ₄ Si | 318, 271, ³ 286 ⁴ | Me ₄ Si | 189 |
| | | | (Ph ₂ Si) ₅ | 186.9–191.7 ⁸ |
| | | | PhSi(OCH ₂ CH ₂) ₃ N | 189.4 ⁹ |
| Si—Si | Me ₃ SiSiMe ₃ | 280, 337, ⁵ 284 ⁴ | H ₃ SiSiH ₂ F | 233 |
| | | | (Me ₃ Si) ₄ Si | 236 ¹⁰ |
| | | | (Ph ₂ Si) ₅ | 237–241 ⁸ |
| Si—N | Me ₃ SiNMeR (R = H, Me) (Me ₃ Si) ₂ NR | 305–330 ⁶ | (H ₃ Si) ₃ N | 174 |
| | (Me ₃ Si) ₃ N | | (Me ₃ Si) ₂ N ⁻ K(dioxan) [‡] | 164 ¹¹ |
| | | | Me ₃ SiN=NSiMe ₃ | 181 ¹² |
| | | | PhSi(OCH ₂ CH ₂) ₃ N | 213.4 ⁹ |
| Si—P | H ₃ SiPH ₂ | 370 | (Me ₃ Si) ₃ P ₇ | |
| | | | (Me ₂ Si) ₆ P ₄ | 225–229 ¹³ |
| | | | (Me ₂ Si) ₃ P ₄ Bu ₂ [‡] | |
| Si—O | Me ₃ SiOMe | 530 | (H ₃ Si) ₂ O | 163.1 ¹⁴ |
| | (Me ₃ Si) ₂ O | 445, ⁶ 443 ⁴ | (Me ₃ Si) ₂ O | 162.6 ¹⁴ |
| | Me ₃ SiOH | 430 ⁶ | cyclosiloxanes | 161–165 ¹⁵ |
| | | | Me ₃ SiOOSiMe ₃ | 168.1 ¹⁶ |
| | | | PhSi(OCH ₂ CH ₂) ₃ N | 165.6 ⁹ |
| Si—S | Me ₃ SiSBu ⁿ | 330 ⁶ | (MeSi) ₄ S ₆ | 212.9 ¹⁷ |
| | | | (MePhSiS) ₃ | 214.3 ¹⁸ |
| Si—F | Me ₃ SiF | 590 | H ₃ SiF | 159.5 |
| | | | SiF ₄ | 154 |
| Si—Cl | Me ₃ SiCl | 380, 426, ³ 410 ⁴ | H ₃ SiCl | 204.8 |
| | | | SiCl ₄ | 201 |
| Si—Br | Me ₃ SiBr | 310–320, 334 ⁶ | H ₃ SiBr | 220.9 |
| | | | SiBr ₄ | 215 |
| Si—I | Me ₃ SiI | 235–245 | H ₃ SiI | 243 |
| | | | SiI ₄ | 243 |
| Si—Hg | (Me ₃ Si) ₂ Hg | >200 ⁷ | (Me ₃ Si) ₂ Hg | 250 ¹⁹ |

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π -bond energy in 1,1-dimethylsilene is estimated to be about 120 kJ mol⁻¹ and supports the structure recently measured by electron diffraction.²⁹ Early attempts to synthesize silabenzene (**1**) were thwarted by the reactivity of the polar silicon–carbon double bond. It has now been isolated in an argon matrix at 10 K by the flash pyrolysis of the substituted silahexadienes (**2**) and