Organosilanes in Radical Chemistry

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DEDICATION

To my parents Χρήστος and Πηνελόπη

CONTENTS

PREFACE

A large number of papers dealing with silyl radicals, dating back to the late 1940s, have been published. To my knowledge, there are no books on this subject. Several reviews and book chapters on silyl radicals have appeared from time to time on specific aspects. This book focuses on the recent literature of silyl radicals in the liquid phase. However, some related gas-phase data of pivotal species such as the $H_3Si\bullet$ and $Me_3Si\bullet$ radicals are taken into consideration when necessary. In the last decade, silyl radicals have thoroughly penetrated areas as diverse as organic synthesis and material sciences, and the eight chapters in this book survey the most exciting aspects of their chemistry.

Fundamental aspects of silyl radicals such as methods of formation, structural characteristics and thermodynamic data are discussed in Chapters 1 and 2. We will see that α-substituents have a profound influence on the geometry of silyl radicals as well as on the homolytic bond dissociation energies of silicon–silicon and silicon–heteroatom bonds. Gas-phase data are essential in order to understand the thermochemistry of organosilanes. Chapter 3 considers the elementary reaction steps, which play an essential role in the majority of radical chain reactions involving organosilanes. Research over the last two decades has indeed revealed the factors governing the reactivity of silicon hydrides towards a variety of radicals. In Chapters 4, 5 and 7, the concepts and guidelines for using silicon hydrides as radical-based reducing agents and as mediators for consecutive radical reactions will be illustrated. Nowadays radical chain reactions are of considerable importance in the development of synthetic methodologies and have allowed the synthesis of complicated polyfunctional molecules to be afforded in recent years. The art of synthesizing complex molecules from relatively simple starting materials in one-pot reactions driven by the radical reactivity is really impressive and will be illustrated by numerous examples. In Chapter 6 the various unimolecular reactions involving silyl radicals are considered, which have enabled synthetic organic chemists to explore reactivities and strategies incorporating these processes. In Chapter 8 silyl radicals in polymers and materials are contemplated. A unified mechanism for understanding the oxidation of poly(hydrosilane)s and hydrogen-terminated silicon surfaces has been proposed. In Chapter 8, a general discussion of how silicon surfaces are used to obtain monolayers is also presented. As mentioned above, it is not my purpose to consider the entire chemistry of silyl radicals or to discuss their applications. For example, I have taken into consideration the radical chemistry dealing with the monolayer formation of the silicon surfaces, but I have not entered into the field of silicon-containing ceramics obtained by chemical vapour deposition techniques, although gaseous silyl radicals are thought to be essential.

Since this book mainly deals with the literature on silyl radicals after the 1980s, the references quoted for the early work are not always the seminal ones but the available reviews. I hope that early experts in the field will forgive me if they find their pet paper uncited. I have tried to maintain an essential simplicity and readability of the text, and hope that I have succeeded so that the book is easily consulted also by nonexperts. I also hope that this book serves as an important link between the various areas of chemistry.

Chryssostomos Chatgilialoglu
Bologna, July 2003

ACKNOWLEDGEMENTS

I thank Keith U. Ingold for having introduced me to this subject. When I arrived in Ottawa at the National Research Council of Canada in 1979 for three years' postdoctoral work with him, very little was known on the reactivity of silyl radicals. At that time, several papers dealing with kinetics of silyl radicals were published, which allowed the reactivity of silyl radical to be translated into a quantitative base. Special thanks go to David Griller for his collaboration on the initial work on hydrogen donor abilities of silicon hydrides during the late 1980s.

Many thanks to Fluka Chemie AG for the Prize of 'Reagent of the Year 1990'. The discovery of tris(trimethylsilyl)silane as a good radical-based reducing agent stimulated our research during the 1990s. I am grateful to the colleagues who have worked with me over these years on this subject for the privilege of their collaboration and friendship. I am especially grateful to Carla Ferreri for her longstanding collaboration during these years as well as her continuing support and encouragement for completing this book.

Finally, I thank Hanns Fischer, Philippe Renaud, Vitaliy I. Timokhin and Andreas A. Zavitsas, for having critically read some of the chapters and for their valuable suggestions.

1 Formation and Structures of Silyl Radicals

1.1 METHODS OF GENERATION OF SILYL RADICALS

The reaction of atoms, radicals or excited triplet states of some molecules with silicon hydrides is the most important way for generating silyl radicals [1,2]. Indeed, Reaction (1.1) in solution has been used for different applications. Usually radicals X• are centred at carbon, nitrogen, oxygen, or sulfur atoms depending on the objective.

$$R_3SiH + X\bullet \longrightarrow R_3Si\bullet + XH \tag{1.1}$$

For example, photochemically produced *t*-BuO• radicals have been mainly used for the generation of silyl radicals to be studied by spectroscopic techniques (see Chapters 1 and 2). Carbon-centred X• radicals are of great importance in chemical transformations under reducing conditions, where an appropriate silane is either the reducing agent or the mediator for the formation of new bonds (see Chapters 4, 5 and 7). Chapter 3 is entirely dedicated to the hydrogen donor abilities of silicon hydrides towards a variety of radicals. In particular, a large number of available kinetic data are collected and analysed in terms of the substituent influence on the Si—H moiety and on the attacking radical.

Several methods for generating of silyl radicals exist using direct interaction of silanes with light (Reaction 1.2). However, none of them is of general applicability, being limited to some specific application [3].

$$R_3Si{-}Y \xrightarrow{h\nu} R_3Si\bullet + Y\bullet \tag{1.2}$$

The best example is the photochemistry of aryldisilanes, which undergo essentially three principal photoprocesses [4–6]. These include the silylene extru-

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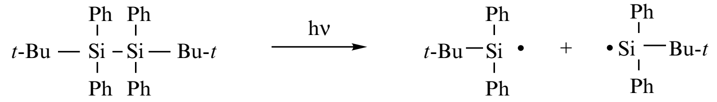
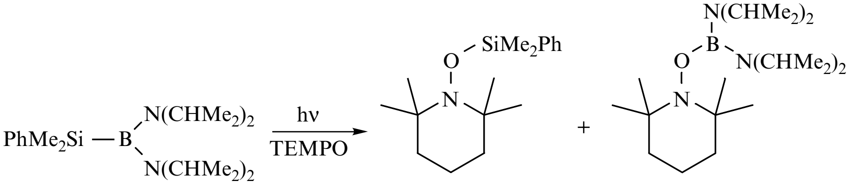
sion, 1,3-Si shift to the *ortho* position of the aryl group to afford silatrienes and homolytic cleavage of Si—Si bond to give silyl radicals. Silenic products are derived from the lowest excited singlet state and are the major products in nonpolar solvents, while silyl radicals are derived from the lowest excited triplet state and are the major products in polar solvents such as acetonitrile [5]. The homolytic cleavage can also be promoted when the 1,3-Si migration is sterically hindered as shown in Reaction (1.3) [7]. Regarding the alkyl substituted oligo- and polysilanes, the silylene extrusion is the principal photoprocess in the far-UV photochemistry whereas reductive elimination of silylsilylene and homolytic Si—Si scission is also detected [8,9].



$$t\text{-Bu}-\text{SiPh}_2-\text{SiPh}_2-\text{Bu-}t \xrightarrow{h\nu} t\text{-Bu}-\text{SiPh}_2\bullet + \bullet\text{SiPh}_2-\text{Bu-}t \qquad (1.3)$$

Organosiliconboranes having bulky substituents on the boron, e.g. $R_3SiB[N(CHMe)_2]_2$, exhibit UV absorption at wavelengths longer than 300 nm. Photolysis of this band afforded a pair of silyl and boryl radicals that can be trapped quantitatively by nitroxide (TEMPO) as shown in Reaction (1.4) [10].



(1.4)

Silyl radicals have been produced by one-electron oxidation of silyl metals [11]. This is found to be the method of choice for the generation of persistent silyl radicals and allowed the preparation of the first isolable silyl radical (see later in this chapter). Reactions (1.5) and (1.6) show two sterically hindered silyl anions with Na^+ as the counter-cation, and their oxidation by the nitrosyl cation [12] and the complex $GeCl_2$/dioxane [13], respectively.

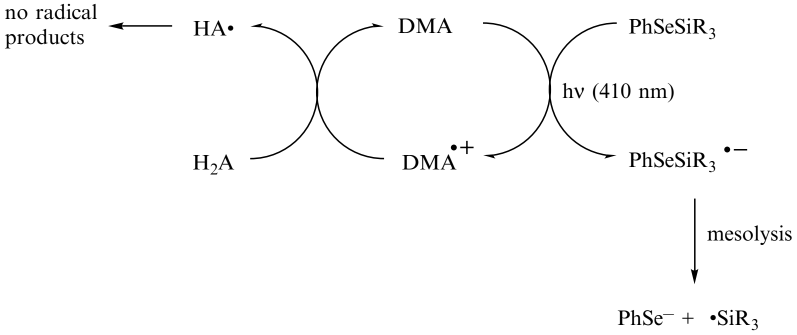
$$(t\text{-BuMe}_2\text{Si})_3\text{SiNa} \xrightarrow[n\text{-heptane}]{\text{NO}^+\text{BF}_4^-} (t\text{-BuMe}_2\text{Si})_3\text{Si}\bullet \qquad (1.5)$$

$$(t\text{-Bu}_2\text{MeSi})_3\text{SiNa} \xrightarrow[\text{Et}_2\text{O}]{\text{GeCl}_2/\text{dioxane}} (t\text{-Bu}_2\text{MeSi})_3\text{Si}\bullet \qquad (1.6)$$

Silyl radicals are also involved as the reactive intermediates during one-electron reduction of bromosilanes. As an example, Reaction (1.7) shows the reduction by sodium of a silyl bromide to produce a persistent radical, which has been characterized by EPR spectroscopy [12].

$$(t\text{-BuMe}_2\text{Si})_3\text{SiBr} \xrightarrow[n\text{-heptane}]{\text{Na}} (t\text{-BuMe}_2\text{Si})_3\text{Si}^\bullet \tag{1.7}$$

Processes involving photoinduced electron transfer of organosilanes [3,14,15] have not been covered in this book with the exception of the following method that was successfully applied to various radical reactions, such as cyclizations, intermolecular additions and tandem annulations (see Chapters 4, 5 and 7). Silyl radicals have been obtained by a complex but efficient method using $PhSeSiR_3$ as the reagent. The strategy is based on the mesolysis of $PhSeSiR_3^{-\bullet}$ to give $R_3Si^\bullet$ radical and $PhSe^-$ [16–18]. Indeed, the selective formation of $PhSeSiR_3^{-\bullet}$ is accomplished by visible-light irradiation (410 nm) of solutions containing $PhSeSiR_3$, 9,10-dimethoxyanthracene (DMA) as the electron donor, and ascorbic acid (H_2A) as the co-oxidant. Scheme 1.1 shows the photoinduced electron transfer with the formation of $PhSeSiR_3^{-\bullet}$ and $DMA^{+\bullet}$, together with the regeneration of DMA at the expense of ascorbic acid. The choice of the substituents is limited by their stabilities. Trialkyl substituted derivatives are highly sensitive to air and prone to hydrolysis, whereas the t-$BuPh_2Si$ derivative was found to be the most stable.



Scheme 1.1 Generation of silyl radicals by a photoinduced electron transfer method

$PhSeSiR_3$ reacts with Bu_3SnH under free radical conditions and affords the corresponding silicon hydride (Reaction 1.8) [19,20]. This method of generating $R_3Si^\bullet$ radicals has been successfully applied to hydrosilylation of carbonyl groups, which is generally a sluggish reaction (see Chapter 5).

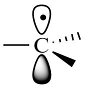
$$\text{PhSeSiEt}_3 + \text{Bu}_3\text{SnH} \xrightarrow[\text{benzene}]{\text{AIBN, 80 °C}} \text{PhSeSnBu}_3 + \text{Et}_3\text{SiH} \tag{1.8}$$

Although a detailed mechanistic study is still lacking, it is reasonable to assume that the formation of $R_3Si^\bullet$ radicals occurs by means of the mesolysis of reactive intermediate $PhSeSiR_3^{-\bullet}$, by analogy with the mechanistic information reported above. Indeed, an electron transfer between the initially formed stannyl radical and the silyl selenide is more plausible (Reaction 1.9), than a bimolecular homolytic substitution at the seleno moiety.

$$\mathrm{PhSeSiEt_3 + Bu_3Sn\bullet \longrightarrow PhSeSiEt_3^{\bullet -} + Bu_3Si^+} \qquad (1.9)$$

1.2 STRUCTURAL PROPERTIES OF SILYL RADICALS

Trisubstituted carbon-centred radicals chemically appear planar as depicted in the π-type structure **1**. However, spectroscopic studies have shown that planarity holds only for methyl, which has a very shallow well for inversion with a planar energy minimum, and for delocalized radical centres like allyl or benzyl. Ethyl, isopropyl, *tert*-butyl and all the like have double minima for inversion but the barrier is only about 300–500 cal, so that inversion is very fast even at low temperatures. Moreover, carbon-centred radicals with electronegative substituents like alkoxyl or fluorine reinforce the non-planarity, the effect being accumulative for multi-substitutions. This is ascribed to $n\sigma^*$ bonds between n electrons on the heteroatom and the bond to another substituent. The degree of bending is also increased by ring strain like in cyclopropyl and oxiranyl radicals, whereas the disubstituted carbon-centred species like vinyl or acyl are ‘bent’ σ radicals [21].



1

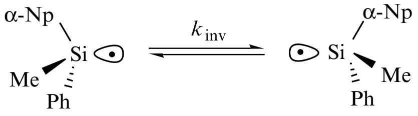
2

For a long time, this knowledge on carbon-centred radicals has driven the analysis of spectroscopic data obtained for silicon-centred (or silyl) radicals, often erroneously. The principal difference between carbon-centred and silyl radicals arises from the fact that the former can use only 2s and 2p atomic orbitals to accommodate the valence electrons, whereas silyl radicals can use 3s, 3p and 3d. The topic of this section deals mainly with the shape of silyl radicals, which are normally considered to be strongly bent out of the plane (σ-type structure **2**) [1]. In recent years, it has been shown that α-substituents have had a profound influence on the geometry of silyl radicals and the rationalization of the experimental data is not at all an extrapolation of the knowledge on alkyl radicals. Structural information may be deduced by using chemical, physical or theoretical methods. For better comprehension, this section is divided in subsections describing the results of these methods.

1.2.1 CHEMICAL STUDIES

The pyramidal structure of triorganosilyl radicals ($R_3Si\bullet$) was first indicated by chirality studies on optically active compounds containing asymmetric silicon.

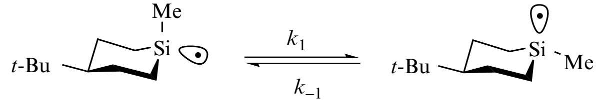
For example, the α-naphthylphenylmethylsilyl radical (**3**) generated by hydrogen abstraction from the corresponding chiral silane reacts with CCl_4 to give optically active chlorosilane that has retained, at least in part, the configuration of the starting material [22]. Thus, the silyl radical is chiral and exists in a pyramidal form with considerable configurational stability, and it abstracts a chlorine atom from CCl_4 faster than its inversion (Reaction 1.10). Moreover, it was observed that the α-naphthylphenylmethylsilyl radical gave varying degrees of optical purity in the products as the concentration of CCl_4 was progressively diluted with benzene or cyclohexane. Analysis of these results by using a Stern–Volmer type of approach, yielded $k_{inv}/k = 1.30$ M at 80 °C, where k_{inv} is the rate constant for inversion at the silicon centre (Reaction 1.10) and k is the rate constant for the reaction of silyl radical with CCl_4 [23]. From these data, $k_{inv} = 6.8 \times 10^9\ s^{-1}$ at 80 °C is obtained which corresponds to an activation barrier of ca 23.4 kJ/mol if a normal preexponential factor of inversion is assumed, i.e., $\log(A/s^{-1}) = 13.3$. A number of other optically active organosilanes behave similarly, when the α-naphthyl group in α-NpSi*(Ph)(Me)H, is replaced by neo-C_5H_{11}, C_6F_5or Ph_2CH [22]. Under the same conditions, however, $Ph_3SiSi^*(Ph)(Me)H$ gave a chloride that was racemic indicating either that the inversion rate of the disilyl radical is much faster than its rate of reaction with CCl_4, or that the radical centre is planar.



3

(1.10)

Analogous competitive kinetic studies have been reported for the inversion of silyl radicals **4** and **5** generated from corresponding silanes (Reaction 1.11) [24]. Rate constants for the interconversion of the two isomer radicals were estimated to be $k_1 \approx 9 \times 10^9\ s^{-1}$ and $k_{-1} \approx 4 \times 10^9\ s^{-1}$ at 0°C [23]. The equilibrium is slightly shifted to the right ($K \approx 2.3$) which suggests that radical **5** is a few hundred calories more stable than radical **4**. Activation energies for the forward and reverse inversion processes can be estimated to be ca 17–21 kJ/mol by assuming $\log(A/s^{-1}) = 13.3$.



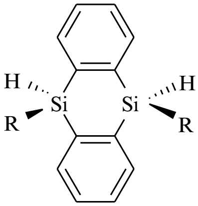
4 **5**

(1.11)

For comparison, it is worth mentioning that in the gas phase $H_3Si\bullet$ is bent out of the plane by (16.0 ± 2.0)°, corresponding to an H—Si—H bond angle of (112.5 ± 2.0)° and with an inversion barrier of 22.6 kJ/mol [25].

Structural information on silyl radicals has also been obtained from the isomerization of 9,10-dihydro-9,10-disilaanthracene derivatives **6** and **7** [26,27].

Indeed, irradiation of a pentane solution of either the *cis* isomer **6** or the corresponding *trans* isomer **7** in the presence of di-*tert*-butyl peroxide as radical initiator affords the same *cis*/*trans* mixture. For R = Me or Ph, a ratio of 47/53 is observed whereas for the more sterically hindered R = *t*-Bu a ratio of 81/19 is obtained. It was proposed that the radicals **9** and **10** generated by hydrogen abstraction from **6** and **7**, respectively, undergo inversion of the radical centre (Reaction 1.12) followed by hydrogen abstraction from the parent silanes (an identity reaction, see Chapter 3) [27]. Interestingly, the analogous 9-silaanthracene derivative **8** does not isomerize under identical conditions [8], suggesting that the disilaanthracene skeleton plays an important role either in lowering the activation energy of the identity reaction or fastening the inversion of silyl radical in Reaction (1.12).



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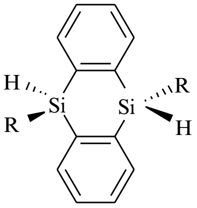

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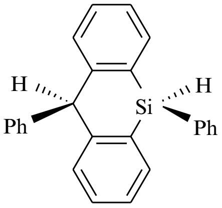

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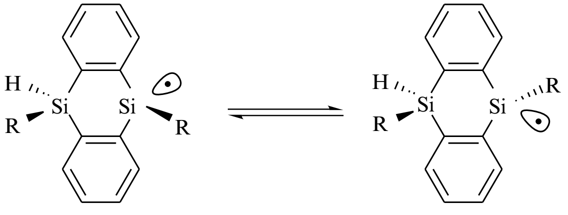

9 **10**

(1.12)

1.2.2 ELECTRON PARAMAGNETIC RESONANCE (EPR) SPECTRA

EPR spectroscopy is the most important method for determining the structures of transient radicals. Information obtained from the EPR spectra of organic radicals in solution are: (i) the centre position of the spectra associated with g factors, (ii) the number and spacing of the spectral lines related to hyperfine splitting (hfs) constants, (iii) the total absorption intensity which corresponds to the radical concentration, and (iv) the line widths which can offer kinetic information such as rotational or conformational barriers. The basic principles as well as extensive treatments of EPR spectroscopy have been described in a number of books and reviews and the reader is referred to this literature for a general discussion [28–30].

Generally, the EPR spectra of silyl radicals show a central set of lines due to ^{1}H hfs constants and weaker satellites due to the coupling with ^{29}Si($I = 1/2, 4.7$ %). The data for silyl radicals, presented in Table 1.1, have

Table 1.1 EPR data for a variety of α-substituted silyl radicals[a]

Silyl radical	$a(^{29}\text{Si})^{b}$(G)	a(others) (G)	g factor
H_3Si•	189	7.96 (3 H)[c]	2.0032
H_2MeSi•	181	11.82 (2 H)[c] 7.98 (3 H)	2.0032
HMe_2Si•	183	16.99 (1 H)[c] 7.19 (6 H)	2.0031
Me_3Si•	181	6.28 (9 H)	2.0031
Et_3Si•	170	5.69 (6 H) 0.16 (9 H)	2.0030
t-Bu_3Si•	163	0.43 (3^{13}C)	
Ph_3Si•[d]	150		
Mes_3Si•[e]	135	0.70 (33 H)	2.0027
$(MeO)_3Si$•	339		2.0012
$(t\text{-}BuO)_3Si$•	331	0.23 (27 H)	2.0014
F_3Si•	498	136.6 (3 F)	2.0003
$MeCl_2Si$•	295	10.5 (2^{35}Cl)	2.0035
Cl_3Si•	416	12.4 (3^{35}Cl)	2.0035
$(Me_3Si)Me_2Si$•	137	8.21 (6 H) 0.47 (9 H)	2.0037
$(Me_3Si)_2MeSi$•	90	9.28 (3 H) 0.44 (18 H)	2.0045
$(Me_3Si)_3Si$•	64	7.1 (3^{29}Si) 0.43 (27 H)	2.0053

[a] See Reference [1] for the original citations.

[b] Because the magnetogyric ratio of ^{29}Si is negative, the signs of $a(^{29}\text{Si})$ will also be negative.

[c] The sign is found to be positive by *ab initio* calculations [34].

[d] Phenyls are perdeuterated.

[e] Mes=2,4,6-trimethylphenyl.

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been chosen in order to include a variety of different substituents. In addition, isotropic hyperfine splitting and g factors are reported and most were obtained directly from solution spectra, although a few were taken from solid-state experiments. As an example, Figure 1.1 shows the EPR spectrum of $(Me_3Si)_2Si(\bullet)Me$ radical obtained at −40 °C by reaction of photogenerated t-BuO• radical with the parent silane [31]. The central quartet of relative intensity 1:3:3:1 with $a_H = 9.28$ G is caused by hyperfine coupling with the α-methyl protons. Each of these lines exhibits an additional hyperfine structure from 18 equivalent protons (six β-methyl groups) with $a_H = 0.44$ G (inset). The ^{29}Si-satellite regions were recorded with a 10-fold increase of the gain and are associated with $a(\alpha\text{-}^{29}\text{Si}) = 90.3$ G.

Table 1.1 shows that the nature of the α-substituent in the radical centre enormously influences the ^{29}Si hfs constants. These constants, which can be used as a guide to the distribution of unpaired electron density, were initially correlated to changes in geometry at the radical centre by analogy with ^{13}C hfs constants of α-substituted alkyl radicals. Indeed, it was suggested that by

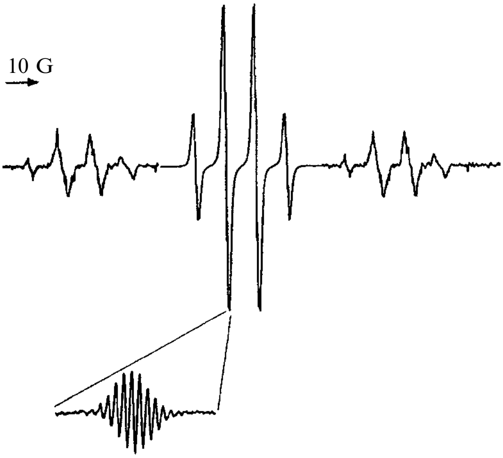
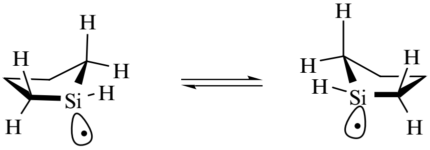


Figure 1.1 EPR spectrum of $(Me_3Si)_2Si(\bullet)Me$ recorded at 223 K. The satellite regions were recorded with a 10-fold increase of the gain. The inset shows an enlargement of the second spectral line recorded at lower modulation amplitude revealing hyperfine structure from 18 equivalent protons. Reprinted with permission from Reference [31]. Copyright 1992 American Chemical Society.

increasing the electronegativity of the α-substituents, the pyramidality of the silyl radical would increase, which would also mean a higher percentage of 3s character in the single occupied molecular orbital (SOMO), and therefore an increase in the ^{29}Si hfs, as well [32]. However, a theoretical study at the UMP2/DZP level reported that for a variety of α-substituted silyl radicals ($X_3Si\bullet$, where $X = H$, CH_3 NH_2, OH, F, SiH_3, PH_2, SH, Cl) the arrangement of atoms around silicon is essentially tetrahedral except for $X = SiH_3$ and that the large variation of the ^{29}Si hfs constants are due to the different distribution of the spin population at the Si center among 3s, 3p and 3d orbitals rather than to a change of geometry at the radical centre (see Section 1.2.5) [33,34]. The *g* factor of silyl radicals decreases along the series of substituents alkyl > alkoxyl > fluorine and silyl > chlorine (Table 1.1) while the spin–orbit coupling constant increases along the series $C < O < F$ and $Si < Cl$ [28]. Generally the *g* factor is larger than the free electron value of 2.00229 if spin–orbit coupling mixes the SOMO with low lying LUMOs and smaller if the mixing is with high lying doubly occupied orbitals. Moreover, the extent of the odd electron delocalization onto the atoms or groups attached to silicon is also expected to have an important influence on the *g* factor trend. Another factor affecting the magnitude of the *g* value is the geometry of the radical centre. Readers should refer to a general text on EPR for a more detailed discussion on the interpretation of hfs constants and *g* factors [29,30].

α-Aryl-substituted silyl radicals have been a subject of attraction in order to evaluate the extent to which a silicon centre radical can conjugate with an adjacent aromatic system. However, the high reactivity of the silyl radical towards aromatic substitution (see Section 5.1.1), limited the detection of this type of transients by EPR spectroscopy. For example, $PhH_2Si•$, $Ph_2HSi•$ and $Ph_3Si•$ radicals have not been observed in solution whereas the corresponding perdeuterated silyl radicals have been detected in a solid matrix [35]. Two sterically hindered analogous radicals, trimesitylsilyl and tris(3,5-di-*tert*-butylphenyl)silyl have been observed by EPR in solution and appear to be partially delocalized species according to the ring proton hfs constants [36,37]. Similar considerations and analogous experiments have been extended to α-vinyl substituted silyl radicals and the results are in line with the α-phenyl substituted case [38]. The spectra of Me_3Si-substituted silyl radicals are of particular interest. Thus, when Me_3Si groups progressively replace methyl groups, the ^{29}Si hfs constants decrease from 181 G in the $Me_3Si•$ radical to 64 G in the $(Me_3Si)_3Si•$ radical (Table 1.1). This trend is due mainly to the spin delocalization onto the Si—C β-bond and in part to the decrease in the degree of pyramidalization at the radical centre caused by the electron-releasing Me_3Si group [39].

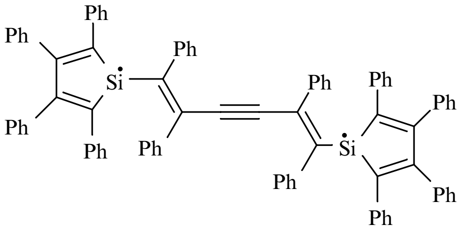
Kinetic information from the line width alterations of EPR spectra by changing the temperature has been obtained for a number of silacycloalkyl radicals [40,41]. For example, silacyclopentyl radical exists at low temperature (−119 °C) in two equivalent twist conformations (**11** and **12**), which interconvert at higher temperature (15 °C). The Arrhenius parameters for such interconversion are $\log A/s^{-1} = 12.0$ and $E_a = 21.3$ kJ/mol.



11 **12**

(1.13)

Persistent and stable silyl radicals have attracted considerable attention [42]. Bulky aryl or alkyl groups that generally make carbon-centred radicals persistent [43,44] have a much weaker effect on the silyl radicals. The high reactivity of the $Ph_3Si•$ radical contrary to the stable $Ph_3C•$ radical is mentioned above. The decay of the trimesitylsilyl radical at −63°C follows a first-order kinetics with a half-life of 20 s [37]. Tri-*tert*-butylsilyl radical is also not markedly persistent showing the modest tendency of *tert*-butyl groups to decrease pyramidalization [45]. The most persistent trialkyl-substituted silyl radical is $[(Me_3Si)_2CH]_3Si•$, which at 20 °C follows a first-order decay with a half-life of 480 s [36]. An exceptionally stable diradical was isolated by reaction of 1,1-dilithio-2,3,4,5-tetraphenylsilole with 1,1-dichloro-2,3-diphenylcyclopropene, for which the structure **13** was suggested on the basis of EPR data and theoretical calculations [46]. The remarkable unreactivity of this diradical has been explained by steric hindrance, as well as delocalization of the unpaired electrons over the silole ring.



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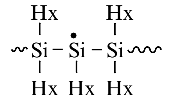
On the other hand, bulky trialkylsilyl substituents have a profound effect on the structure of silyl radicals. Indeed, by increasing the steric effect with more crowded trialkylsilyl substituents the persistency of silyl radicals increases substantially. Table 1.2 reports the EPR data for a variety of tris(trialkylsilyl)silyl radicals in comparison with the prototype $(Me_3Si)_3Si•$. Inspection of the data shows the α-^{29}Si hfs constants tend to decrease and the β-^{29}Si hfs slightly increase when the methyl group is progressively replaced by a bulkier group, the effect being cumulative, e.g., along the series $(Me_3Si)_3Si•$, $(Et_3Si)_3Si•$, $(i-Pr_3Si)_3Si•$ and $(Me_3Si)_3Si•$, $(Et_2MeSi)_3Si•$, $(t\text{-}Bu_2MeSi)_3Si•$. These trends have been associated with an increase of the polysilane skeleton flattening through the series [12,13,48–50]. Indeed, the half-lives of the radicals increase within the series and the $(t\text{-}Bu_2MeSi)_3Si•$ radical is found to be stable and isolable in a crystal form. Therefore, the radicals $(Et_3Si)_3Si•$, $(i\text{-}Pr_3Si)_3Si•$, $(t\text{-}BuMe_2Si)_3Si•$ and $(t\text{-}Bu_2MeSi)_3Si•$ have a practically planar structure due to the steric repulsions among the bulky silyl substituents. The small differences of their α-^{29}Si hfs constants are presumably due to different degrees of spin delocalization onto the Si—C β-bond, as a consequence of conformational effects in order to minimize the steric hindrance. Persistent silyl radicals have also been formed upon

Table 1.2 EPR data for a variety of tris(trialkylsilyl)silyl radicals

Silyl radical	*a*(α-^{29}Si)(G)	*a*(β-^{29}Si)(G)	*a*(others) (G)	*g* factor	Reference
$(Me_3Si)_3Si•$	63.8	7.1	0.43 (27 H)	2.0053	[47]
$(EtMe_2Si)_3Si•$	62.8	7.1	0.37 (18 H) 0.14 (6 H)	2.0060	[48]
$(Et_2MeSi)_3Si•$	60.3	7.3	0.27 (12 H) 0.15 (9 H) 3.2 (3 ^{13}C)	2.0060	[48]
$(Et_3Si)_3Si•$	57.2	7.9	0.12 (18 H) 3.0 (3 ^{13}C)	2.0063	[48]
$(i\text{-}Pr_3Si)_3Si•$	55.6	8.1	2.2 (3 ^{13}C)	2.0061	[49]
$(t\text{-}BuMe_2Si)_3Si•$	57.1	8.1	0.33 (27 H) 0.11 (18 H)	2.0055	[12]
$(Me_3SiMe_2Si)_3Si•$	59.9	7.4		2.0065	[50]
$(t\text{-}Bu_2MeSi)_3Si•$	58.0	7.9		2.0056	[13]

photolysis of poly(di-*n*-alkylsilanes) in solution via a complex reaction mechanism [8]. Radical **14** (Hx = *n*-hexyl) with $g = 2.0047$, $a(\alpha\text{-}^{29}\text{Si}) = 75\,\text{G}$ and $a(\beta\text{-}^{29}\text{Si}) = 5.8\,\text{G}$, showed line-broadening effects as the temperature was lowered. This observation has been correlated to the restricted rotational motion about the C—Si• bond and, in particular, to a rocking interchange of the two α-hydrogens. Isolation of 'allylic-type' silyl radical **15** has also been achieved [51]. The EPR spectrum consists of a broad singlet ($g = 2.0058$) with three doublet satellite signals due to coupling with ^{29}Si of 40.7, 37.4 and 15.5 G. The two doublets with 40.7 and 37.4 G broaden upon raising the temperature and coalesce at 97 °C due to the rotation of the t-BuMe$_2$Si group. The magnitude of ^{29}Si hfs constants is consistent with the delocalization of the unpaired electron over the three silicon atoms in the ring, but it is noteworthy that the coupling constants of the outer Si atoms are not equal. This is explained below.



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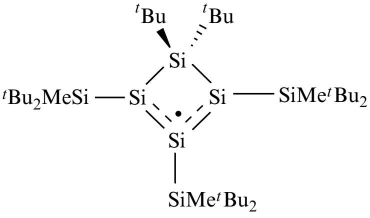

15

1.2.3 CRYSTAL STRUCTURES

The crystal structures of two isolable silyl radicals have recently been reported. The bulky substituted (t-Bu$_2$MeSi)$_3$Si• radical was isolated as air-sensitive yellow needles [13], whereas the conjugated and bulky substituted cyclotetrasilenyl radical **15** was obtained as red–purple crystals [51].

Figure 1.2 shows a completely planar geometry around the Si1 atom of (t-Bu$_2$MeSi)$_3$Si• radical. Indeed, the bond angles Si2—Si1—Si3, Si2—Si1—Si4 and Si3—Si1—Si4 are 119.49°, 120.08° and 120.43°, respectively, their sum being exactly 360°. The Si—Si bonds are larger (2.42 ± 0.01 Å) than normal. Interestingly, all the methyl substituents at the α-Si atoms (i.e., C1, C4 and C7) are located in the plane of the polysilane skeleton in order to minimize steric hindrance. As reported in the previous section, the planarity of this radical is retained in solution.

Figure 1.3 shows the ORTEP drawing of the conjugated radical **15**. The four-membered ring is nearly planar with the dihedral angle between the radical part Si1—Si2—Si3 and Si1—Si4—Si3 being 4.7°. The Si1 and Si2 atoms have planar geometry (the sums of the bond angles around them are 360.0° and 359.1°, respectively) whereas the Si3 atom is slightly bent (356.2°). This small asymmetry of the moiety where the radical is delocalized is also observed in the