

# Contents

<b>I.</b>	<b>Introduction</b>	1
1.	Characteristic Differences between the Elements Silicon and Carbon . . . . .	1
2.	Functional Groups in the Chemistry of Silicon . . . . .	3
<b>II.</b>	<b>The Formation of Carbosilanes</b>	5
1.	The Formation of Carbosilanes by Thermal Decomposition of Methylsilanes . . . . .	5
1.1	The Homolytic Cleavage of Silanes . . . . .	5
1.2	Continous Flow Pyrolysis . . . . .	8
1.3	The Thermal Decomposition of SiMe <sub>4</sub> . . . . .	10
1.3.1	The Separation of Pyrolysis Products . . . . .	10
1.3.2	Compounds of Low Boiling Point Containing up to Four Si Atoms . . . . .	10
1.3.3	Compounds with Polycyclic Molecular Structures . . . . .	12
1.3.4	Influence of Distillation Temperature on the Composition of the Pyrolysis Products . . . . .	16
1.4	Formation of Si-Chlorinated Carbosilanes by Pyrolysis of Methylchlorosilanes . . . . .	19
1.5	Pyrolysis of the Methylsilanes Me <sub>3</sub> SiH, Me <sub>2</sub> SiH <sub>2</sub> and MeSiH <sub>3</sub> . . . . .	26
1.6	Reactions of Methylsilanes by Gas Discharge . . . . .	31
1.6.1	Reactions of SiMe <sub>4</sub> , Me <sub>2</sub> SiH <sub>2</sub> and MeSiH <sub>3</sub> . . . . .	31
1.6.2	Comparison of the Products Obtained from Reactions in Cold Plasma with those from Pyrolysis . . . . .	32
1.7	Mechanism of the Formation of Carbosilanes by Pyrolysis in the Gas Phase . . . . .	34
1.7.1	The Mechanism of Formation via Radical Reactions . . . . .	34
1.7.2	Insertion of CH <sub>2</sub> Groups into Si—Si Bonds . . . . .	35
1.7.3	Participation of Volatile Cyclic Compounds in the Pyrolysis Reaction . . . . .	36
1.7.4	Comments on the Formation of SiCl-Containing Carbosilanes from Methylchlorosilanes . . . . .	38
1.7.5	Pyrolysis Products Obtained from EtSiCl <sub>3</sub> in Comparison to those from Me <sub>2</sub> SiCl <sub>2</sub> . . . . .	40
1.8	Comparative Summary of the Carbosilanes Synthesized . . . . .	40
1.9	A Possible Chemical Pathway to the Synthesis of Polycyclic Molecular Skeletons . . . . .	41
2.	Formation of Carbosilanes by Direct Reaction of Halogenomethanes with Silicon . . . . .	46

2.1	Reactions of Silicon with Chloromethanes . . . . .	46
2.1.1	The Reaction with $\text{CH}_2\text{Cl}_2$ . . . . .	46
2.1.2	The Reaction with $\text{CHCl}_3$ . . . . .	47
2.1.3	The Reaction with $\text{CCl}_4$ . . . . .	51
2.2	Advantages Associated with Forming Carbosilanes in a Fluid Bed . . . . .	51
2.3	Comments on Mechanism of Formation . . . . .	52
2.4	The Reaction with $(\text{Cl}_3\text{Si})_2\text{CCl}_2$ . . . . .	52
3.	Formation of Polycyclic Molecular Skeletons through Rearrangement of Carbosilanes with $\text{AlBr}_3$ or $\text{AlCl}_3$ . . . . .	53
3.1	Introduction . . . . .	53
3.2	The Reactions of Structurally Different Carbosilanes . . . . .	54
3.2.1	The Effect of the Length of Skeletal C-Bonded Side Chains on Ring Formation . . . . .	55
3.2.2	Reactions of Carbosilanes Containing Side Chains Bonded to Si-Atoms in the Molecular Skeleton . . . . .	55
3.2.3	Ring Closure by Elimination of Methane . . . . .	57
3.2.4	Rearrangements Leading to the Formation of Larger Scaphanes or Carborundanes . . . . .	57
3.2.5	Rearrangement of Larger Rings . . . . .	62
3.3	Investigation into Ring Closure Reactions During Rearrangement Reactions of Carbosilanes . . . . .	62
3.4	Investigations into the Stability of Carbosilane Skeletons Towards $\text{AlBr}_3$ and $\text{AlCl}_3$ . . . . .	68
3.4.1	The Formation of $\text{CH}_2$ -Linked 1,3,5,7-Tetrasilaadamantanes . . . . .	69
3.4.2	Reactions of 1,3,5,7-Tetrasilaadamantanes with $\text{AlCl}_3$ . . . . .	71
3.4.3	The Behavior of Heptasiladiadamantanes Towards $\text{AlBr}_3$ . . . . .	73
3.4.4	The Behavior of Tetrasilatriscaphanes Towards $\text{AlBr}_3$ . . . . .	73
3.4.5	The Effect of the Lewis Acids $\text{BCl}_3$ , $\text{PCl}_3$ and $\text{SbCl}_3$ on Unstrained Carbosilanes . . . . .	76
3.4.6	The Behavior of Si-Halogenated Carbosilanes Towards $\text{AlBr}_3$ . . . . .	76
3.4.7	Summary . . . . .	77
4.	Organometallic Syntheses of Carbosilanes . . . . .	78
4.1	SiPh Groups as Important Protecting Groups in the Organometallic Synthesis of Carbosilanes . . . . .	78
4.1.1	Synthesis of Pentasiladecalin . . . . .	78
4.1.2	Synthesis of Hexasilaperhydrophenalene . . . . .	79
4.1.3	Synthesis of Heptasila[4.4.4]propellane . . . . .	79
4.2	Investigations into the Synthesis of Tetrasilaadamantanes . . . . .	80
4.2.1	Investigations of 1,3,5-Trisilacyclohexanes . . . . .	80
4.2.1.1	Synthesis of ( <i>t</i> -BuHSi— $\text{CH}_2$ ) <sub>3</sub> . . . . .	80
4.2.1.2	Synthesis of (PhHSi— $\text{CH}_2$ ) <sub>3</sub> . . . . .	81
4.2.1.3	Formation of (RBrSi— $\text{CH}_2$ ) <sub>3</sub> through Bromination . . . . .	81
4.2.1.4	Synthesis of (PhHSi— $\text{CH}_2$ ) <sub>3</sub> via (Ph <sub>2</sub> Si— $\text{CH}_2$ ) <sub>3</sub> . . . . .	81
4.2.1.5	The Cleavage of Si—Ph Bonds in (Ph <sub>2</sub> Si— $\text{CH}_2$ ) <sub>3</sub> . . . . .	81
4.2.2	Attempts to Synthesize Tetrasilaadamantanes . . . . .	82
4.3	Synthesis of Si-Substituted 1,3,5,7-Tetrasilaadamantane Me <sub>3</sub> (Me <sub>2</sub> Si— $\text{CH}_2$ —SiMe <sub>2</sub> — $\text{CH}_2$ —SiMe <sub>2</sub> — $\text{CH}_2$ )Ad . . . . .	83

4.4	Synthesis of C-Bridged Cyclic Carbosilanes . . . . .	83
4.4.1	Syntheses via Metallation of $\text{CBr}_2$ Groups. . . . .	84
4.4.1.1	C-Metallation and Reactions of 2,2-Dibromo-1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane . . . . .	84
4.4.1.2	Synthesis of C-Bridged Spiro Carbosilanes. . . . .	85
4.4.2	Syntheses via Metallation of $\text{CH}_2$ or CH Groups. . . . .	87
4.4.2.1	Synthesis of $\text{Me}_4\text{Ad}(-\text{SiMe}_2-\text{CH}_2-\text{SiMe}_2\text{Ph})$ and of $\text{Me}_4\text{Ad}(-\text{SiMe}_2-\text{CH}_2-\text{SiMe}_2-\text{CH}_2-\text{SiMe}_3)$ . . . . .	87
4.4.2.2	Synthesis of $(\text{Me}_3\text{Si})_2\text{CH}-\text{SiMe}_2-\text{CH}_2-\text{SiMe}_2-\text{CH}_2-\text{SiMe}_3$ . . . . .	88
4.4.2.3	Synthesis of $(\text{Me}_3\text{Si})_2\text{CH}-\text{SiMe}(\text{CH}_2-\text{SiMe}_2-\text{CH}_2-\text{SiMe}_3)_2$ . . . . .	89
4.4.2.4	Synthesis of $(\text{Me}_3\text{Si})_3\text{C}-\text{SiMe}_2-\text{CH}_2-\text{SiMe}_2-\text{CH}_2-\text{SiMe}_3$ . . . . .	89
4.4.3	Synthesis of C-Substituted Carbosilanes through Metallation of $\text{CH}_2$ or CH Groups . . . . .	90
4.4.3.1	2-Trimethylsilyl-2-dimethyl(phenyl)silyl-1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane and 2,2-Bis(trimethylsilyl)-1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane . . . . .	90
4.4.3.2	Synthesis of C-Silylated 6-Trimethylsilyl-1,3,5,7,9-pentasiladecaline . . . . .	91
4.4.3.3	Synthesis of C-Bridgehead Silylated Tetrasilatricaphanes. . . . .	94
4.5	Synthesis of 1,3-Disilapropanes . . . . .	94
4.5.1	Synthesis of 2,2-Dichloro-1,3-disilapropanes . . . . .	94
4.5.2	Synthesis of 2-Methyl-2-chloro-1,3-disilapropanes. . . . .	96
<b>III.</b>	<b>Reactions of Carbosilanes . . . . .</b>	<b>99</b>
1.	Introduction . . . . .	99
2.	The Introduction of New Functional Groups on the Carbosilane Molecular Skeleton . . . . .	99
2.1	C-Halogenation of Carbosilanes . . . . .	99
2.1.1	C-Chlorinated Carbosilanes . . . . .	99
2.1.2	C-Brominated Carbosilanes . . . . .	101
2.1.3	Photobromination of Si-Methylated Carbosilanes . . . . .	103
2.2	Formation and Reactions of Si-Hydrogenated Carbosilanes. . . . .	105
2.2.1	Hydrogenation of $\text{SiCl}$ - and CH-Containing Carbosilanes. . . . .	105
2.2.2	SiH-Bromination of Carbosilanes . . . . .	106
2.2.2.1	$(\text{H}_3\text{Si})_2\text{CH}_2$ . . . . .	106
2.2.2.2	$(\text{H}_3\text{Si}-\text{CH}_2)_2\text{SiH}_2$ . . . . .	107
2.2.2.3	$(\text{H}_2\text{Si}-\text{CH}_2)_3$ . . . . .	107
2.2.3	C-Chlorinated, SiH-Containing Carbosilanes . . . . .	108
2.2.4	Reaction of $(\text{Cl}_3\text{Si})_2\text{CBr}_2$ with $\text{LiAlH}_4$ . . . . .	113
2.2.5	Partly C-Chlorinated, SiH-Containing Carbosilanes. . . . .	113
2.2.6	Reactions of Perchlorinated Carbosilanes with Perhydrogenated Carbosilanes . . . . .	113
2.3	Si-Fluorinated Carbosilanes . . . . .	116
2.3.1	Fluorination of SiCl-Containing Carbosilanes. . . . .	116
2.3.2	Cyclic Carbosilanes Containing $\text{SiF}$ and $\text{CCl}$ Groups. . . . .	117
2.3.3	Partly C-Halogenated, Si-Fluorinated Carbosilanes . . . . .	122

3.	Reactions with MeMgCl and MeLi . . . . .	122
3.1	SiH-Containing Carbosilanes. . . . .	122
3.1.1	Reactions of $(\text{H}_3\text{Si}-\text{CH}_2)_2\text{SiH}_2$ and $(\text{H}_2\text{Si}-\text{CH}_2)_3$ . . . . .	122
3.1.2	Linear $\text{CCl}_1$ -, SiH-Containing Carbosilanes. . . . .	126
3.1.3	$(\text{H}_3\text{Si})_2\text{CHCl}$ , $\text{H}_3\text{Si}-\text{CClH}_2$ , $\text{H}_3\text{Si}-\text{CCl}_2\text{H}$ and $\text{H}_3\text{Si}-\text{CCl}_3$ . . . . .	129
3.1.4	$\text{H}_3\text{Si}-\text{CCl}_2-\text{SiH}_2-\text{CH}_2-\text{SiH}_3$ . . . . .	129
3.1.5	$(\text{H}_3\text{Si}-\text{CCl}_2)_2\text{SiH}_2$ . . . . .	132
3.2	Si- and C-Chlorinated Carbosilanes . . . . .	138
3.2.1	Reaction of $(\text{Cl}_3\text{Si})_2\text{CCl}_2$ . . . . .	138
3.2.2	Mechanism of Formation of Methylidene Groups. . . . .	139
3.2.2.1	$(\text{Me}_3\text{Si})_2\text{CMeCl}$ . . . . .	139
3.2.2.2	Varying Si-Chlorinated 2-Methyl-2-chloro-1,3-disilapropanes. . . . .	141
3.2.2.3	Reactions of 2,2-Dichloro-1,3-disilapropanes . . . . .	142
3.2.3	Reaction Pathways Taken by $(\text{Cl}_3\text{Si})_2\text{CCl}_2$ . . . . .	145
3.2.4	Reactions of 1,3,5-Trisilapentanes. . . . .	146
3.2.4.1	$(\text{Cl}_3\text{Si}-\text{CCl}_2)_2\text{SiCl}_2$ and MeMgCl . . . . .	146
3.2.4.2	$(\text{Cl}_3\text{Si}-\text{CCl}_2)_2\text{SiCl}_2$ and MeLi . . . . .	148
3.3	Reactions of 1,3,5-Trisilacyclohexanes . . . . .	151
3.3.1	Reactions of $(\text{Cl}_2\text{Si}-\text{CCl}_2)_3$ with MeMgCl . . . . .	151
3.3.2	Reactions of Partly Chlorinated 1,3,5-Trisilacyclohexanes with MeMgCl	156
3.3.3	Si-Hydrogenated 1,3,5-Trisilacyclohexanes . . . . .	157
3.3.4	Reactions of Si-Methylated, Partly C-Brominated 1,3,5-Trisilacyclohexanes wit BuLi and EtMgBr . . . . .	158
3.3.5	Consideration of Chemical Behavior and NMR Chemical Shift of 1,3,5-Trisilacyclohexanes . . . . .	159
3.4	$\text{SiF}_1$ , $\text{CCl}_1$ -Containing Carbosilanes . . . . .	162
3.4.1	$(\text{F}_3\text{Si})_2\text{CCl}_2$ . . . . .	162
3.4.2	$\text{F}_3\text{Si}-\text{CCl}_2-\text{SiF}_2-\text{CH}_2-\text{SiF}_3$ and $\text{F}_3\text{Si}-\text{CCl}_2-\text{SiF}_2-\text{CHCl}-\text{SiF}_3$ . . . . .	163
3.4.3	$(\text{F}_3\text{Si}-\text{CCl}_2)_2\text{SiF}_2$ . . . . .	164
3.4.4	Reactions of Si-Fluorinated 1,3,5-Trisilacyclohexanes. . . . .	165
3.4.4.1	Reactions with MeMgCl and MeLi . . . . .	165
3.4.4.2	Reactions with Phenyllithium and PhMgBr. . . . .	166
3.4.5	Summary of the Behavior of SiH- and SiF-Containing C-Chlorinated Carbosilanes . . . . .	167
3.4.6	$\text{CF}_2$ -Containing 1,3-Disilapropanes . . . . .	168
3.4.6.1	Formation of Si— $\text{CF}_2$ —Si Groups by Insertion of a $\text{CF}_2$ Carbene into the Si—Si Bond . . . . .	168
3.4.6.2	Reactions of $\text{CF}_2$ -Containing Carbosilanes . . . . .	168
4.	Metallation of Carbosilanes . . . . .	169
4.1	Metallation of Skeletal C-Atoms in Si-Methylated Carbosilanes. . . . .	169
4.1.1	$(\text{Me}_2\text{Si}-\dot{\text{C}}\text{H}_2)_3$ . . . . .	169
4.1.2	$\text{Me}_4\text{Ad}$ . . . . .	173
4.1.3	Summary . . . . .	174
4.2	Metallation of Bridging C Atoms in $\text{CCl}_1$ - and $\text{SiCl}_1$ -Containing 1,3-Disilapropanes . . . . .	175
4.2.1	Evidence of $\text{CCl}_2$ -Lithiation in the Presence of $\text{SiCl}_1$ Groups. . . . .	175

4.2.2	Metallation of $\text{Me}_3\text{Si}-\text{CCl}_2-\text{SiMe}_2\text{Cl}$	175
4.2.3	Formation of 2,2,4,4-Tetramethyl-1,3-bis(trimethylsilyl)-2,4-disilabicyclo[1.1.0]butane	176
4.2.4	The Reactive Behavior of 2,2,4,4-Tetramethyl-1,3-bis(trimethylsilyl)-2,4-disilabicyclo[1.1.0]butane	179
4.2.5	Lithiation of $\text{Me}_3\text{Si}-\text{CCl}_2-\text{SiMeCl}_2$	180
4.3	The Si-Metallation of 1,3,5-Trisilacyclohexanes with Transition Metal Complexes	182
4.3.1	Si-Metallation via Salt Elimination	182
4.3.1.1	Singly Metallated Trisilacyclohexanes	182
4.3.1.2	Doubly Metallated Trisilacyclohexanes	183
4.3.1.3	Triply Metallated Trisilacyclohexanes	185
4.3.1.4	Reaction of $(\text{Cl}_2\text{Si}-\text{CH}_2)_3$ with $\text{KFe}(\text{CO})_2\text{cp}$	185
4.3.2	Cobalt-Substituted 1,3,5-Trisilacyclohexane Complexes	187
4.3.2.1	Multiply Cobalt-Carbonylate-Substituted Trisilacyclohexanes	187
4.3.2.2	Reactions of $(\text{H}_2\text{Si}-\text{CH}_2)_3$ with $\text{Co}_2(\text{CO})_8$	188
4.3.3	Influence of $\text{cp}(\text{CO})_2\text{Fe}$ Groups on the Reactive Behavior of Trisilacyclohexanes	190
5.	Reactions of C-Chlorinated Carbosilanes with Silylphosphphanes	192
5.1	Formation and Reactions of the Ylide $(\text{Cl}_3\text{Si})_2\text{CPMe}_2\text{Cl}$ and the Effect of Substituents on Ylide Formation	192
5.2	The Triylide $(\text{Cl}_2\text{Si}-\text{CPMe}_2\text{Cl})_3$	194
5.3	Influence of Si-Substitution on the Formation, Structure and Rearrangement of Ylides	194
6.	The Reactive Behavior of Further Cyclic Carbosilanes	197
6.1	1,3-Disilacyclobutanes	197
6.2	1,3-Disilacyclobutane Rings in Hexasilaasteranes	200
6.3	1,3-Disilacyclopentenes	201
6.3.1	Tetramethyl-1,3-disilacyclopentenes	201
6.3.2	4-Trimethylsilyl-tetramethyl-1,3-disilacyclopentene	202
6.4	Tetrachloro-1,3-disilacyclopentane	204
6.4.1	Stepwise Photochlorination	204
6.4.2	Reaction of 1,3-Disilacyclopentanes with $\text{MeMgCl}$	204
6.5	Tetrasilabicyclo[3.3.0]oct-1(5)ene	207
7.	Investigations into the Cleavage of Si—Me Bonds in Carbosilanes	208
7.1	Si-Chlorination of $(\text{Me}_2\text{Si}-\text{CH}_2)_3$ with $\text{HSiCl}_3/\text{H}_2\text{PtCl}_6$	209
7.2	Cleavage with ICl	209
7.2.1	Hexamethyl-1,3,5-trisilacyclohexane	209
7.2.2	Linear Carbosilanes	209
7.2.3	1,3,5-Trisilacyclohexanes with Side Chains	210
7.2.4	Adamantanes	210
7.2.5	Adamantanes with Side Chains	211
8.	Substituent Effects in Carbosilanes	211
9.	Hydrosilylation in Carbosilane Chemistry	214
9.1	Formation of Cyclic Carbosilanes Through Hydrosilylation	214
9.2	Linking of Linear SiH-Containing Carbosilane Units Over $\text{HC}\equiv\text{CH}$	217

<b>IV. Results of Structural Investigations of Carbosilanes . . . . .</b>	<b>218</b>
1. X-Ray Investigations of Crystal Structures . . . . .	218
1.1 1,3,5-Trisilacyclohexanes with Different Substituents. . . . .	218
1.1.1 $(\text{Cl}_2\text{Si}-\text{CH}_2)_3$ and $(\text{Cl}_2\text{Si}-\text{CH}_2)_3$ . . . . .	218
1.1.2 $(\text{Ph}_2\text{Si}-\text{CH}_2)_3$ . . . . .	218
1.1.3 1-Cyclopentadienyl dicarbonyl-iron-1,3,3,5,5-pentachloro- 1,3,5-trisilacyclohexane and 1,3-Bis(cyclopentadienyldicarbonyl-iron)- 1,3,5,5-tetrachloro-1,3,5-trisilacyclohexane . . . . .	220
1.1.4 The Ylides $(\text{Cl}_3\text{Si})_2\text{CPMe}_2\text{Cl}$ , $(\text{Cl}_3\text{Si})_2\text{CPMe}_3$ and $(\text{Cl}_2\text{Si}-\text{CPMe}_2\text{Cl})_3$ , as well as $\text{Cl}_2\text{Si}(\text{CH}_2-\text{SiCl}_2)_2\text{CPMe}_2\text{Cl}$ and $\text{Me}_2\text{Si}(\text{CH}_2-\text{SiMe}_2)_2\text{PMe}_2\text{Br}$ . . . . .	225
1.2 Structures of Si-Adamantanes . . . . .	229
1.2.1 1,3,5,7-Tetrasilaadamantane, $\text{Si}_4\text{C}_{10}\text{H}_{24}$ . . . . .	229
1.2.2 Hexamethyl-heptasila-hexacyclo-heptadecane, $\text{Si}_7\text{C}_{16}\text{H}_{36}$ . . . . .	231
1.2.3 Octamethyl-octasila-heptacyclo-octadecane, $\text{Si}_8\text{C}_{18}\text{H}_{40}$ . . . . .	233
1.3 Structures of Si-Scaphanes . . . . .	234
1.3.1 Heptamethyl-tetrasila[2.2.2]barrelane, $\text{Si}_4\text{C}_{11}\text{H}_{28}$ . . . . .	234
1.3.2 Octamethyl-hexasila-hexascaphane, $\text{Si}_6\text{C}_{15}\text{H}_{36}$ . . . . .	236
1.3.3 Tetramethyl-octasila-dodecasphane, $\text{Si}_8\text{C}_{17}\text{H}_{36}$ . . . . .	237
1.4 Dodecamethyl-heptasila[4.4.4]propellane, $\text{Si}_7\text{C}_{19}\text{H}_{48}$ . . . . .	239
1.5 trans-trans-1,3,3,5,7,7,9,11,11-Nonamethyl-1,3,5,7,9,11- hexasilatricyclo[7.3.1.0 <sup>5,13</sup> ]tridecane, $\text{Si}_6\text{C}_{16}\text{H}_{36}$ . . . . .	241
1.6 Structures of Carbosilanes with Small Rings . . . . .	242
1.6.1 Hexadecamethyl-octasila-dispiro[5.1.5.1]tetradecane, $\text{Si}_8\text{C}_{22}\text{H}_{56}$ . . . . .	242
1.6.2 cis-2,4-Dichloro-2,4-bis(trimethylsilyl)-1,1,3,3-tetramethyl- 1,3-disilacyclobutane, $\text{Si}_4\text{C}_{12}\text{H}_{30}\text{Cl}_2$ . . . . .	243
1.6.3 2,2,4,4-Tetramethyl-1,3-bis(trimethylsilyl)-2,4-disilabicyclo[1.1.0]butane, $\text{Si}_4\text{C}_{12}\text{H}_{30}$ . . . . .	244
1.6.4 Octachloro-hexasila-asterane, $\text{Si}_6\text{C}_6\text{H}_8\text{Cl}_8$ . . . . .	247
1.6.5 Tetrasilabicyclo[3.3.0]oct-1(5)ene, $\text{Si}_4\text{C}_{12}\text{H}_{28}$ . . . . .	247
1.7 Octamethyl-tetrasila-cyclooctane, $\text{Si}_5\text{C}_{12}\text{H}_{32}$ . . . . .	250
2. Electron Diffraction Studies . . . . .	251
<b>V. References . . . . .</b>	<b>253</b>