

Contents

Foreword *xiii*

Preface *xv*

1	Catalytic Generation of Silicon Nucleophiles	1
	<i>Koji Kubota and Hajime Ito</i>	
1.1	Introduction	1
1.2	Silicon Nucleophiles with Copper Catalysts	2
1.2.1	Copper-Catalyzed Nucleophilic Silylation with Disilanes	2
1.2.1.1	Silylation of α,β -Unsaturated Carbonyl Compounds	2
1.2.1.2	Silylation of Alkylidene Malonates	3
1.2.1.3	Silylation of Allylic Carbamates	3
1.2.2	Copper-Catalyzed Nucleophilic Silylation with Silylboronate	4
1.2.2.1	Silicon–Boron Bond Activation with Copper Alkoxide	4
1.2.2.2	Silylation of α,β -Unsaturated Carbonyl Compounds	4
1.2.2.3	Catalytic Allylic Silylation	7
1.2.2.4	Catalytic Silylation of Imines	9
1.2.2.5	Catalytic Silylation of Aldehydes	9
1.2.2.6	Catalytic Synthesis of Acylsilanes	11
1.2.2.7	Silylative Carboxylation with CO ₂	11
1.2.2.8	CO ₂ Reduction via Silylation	13
1.2.2.9	Silyl Substitution of Alkyl Electrophiles	13
1.2.2.10	Decarboxylative Silylation	14
1.2.2.11	Silylative Cyclization	15
1.2.2.12	Silylative Allylation of Ketones	15
1.2.2.13	Silylation of Alkynes	16
1.2.2.14	Propargylic Substitution	19
1.2.3	Copper-Catalyzed Nucleophilic Silylation with Silylzincs	20
1.3	Silicon Nucleophiles with Rhodium Catalysts	21
1.3.1	Rhodium-Catalyzed Nucleophilic Silylation with Disilanes	21
1.3.2	Rhodium-Catalyzed Nucleophilic Silylation with Silylboronates	21
1.3.2.1	Conjugate Silylation	21
1.3.2.2	Coupling between Propargylic Carbonates to Form Allenylsilanes	22
1.4	Silicon Nucleophiles with Nickel Catalysts	22

1.4.1	Nickel-Catalyzed Nucleophilic Silylation with Alkyl Electrophiles	22
1.5	Silicon Nucleophiles with Lewis Base Catalysts	23
1.5.1	N-Heterocyclic Carbene-Catalyzed Nucleophilic 1,4-Silylation	23
1.5.2	Alkoxide Base-Catalyzed 1,2-Silaboration	24
1.5.3	Phosphine-Catalyzed 1,2-Silaboration	24
1.6	Closing Remarks	25
	Abbreviations	25
	References	26
2	Si—H Bond Activation by Main-Group Lewis Acids	33
	<i>Dieter Weber and Michel R. Gagné</i>	
2.1	Introduction to Silanes and the Si—H bond	33
2.1.1	Overview of the Discovery and the History of Silanes	33
2.1.2	A Comparison of Hydrocarbons and Hydrosilicons	34
2.1.3	Stability of the Silicon—Hydrogen Bond	35
2.1.4	The Silylium Ion	35
2.2	The Activation of Si—H Bonds by Boron Lewis Acids	36
2.2.1	Tris(pentafluorophenyl)borane (BCF)	36
2.2.2	The Catalytic Activation of Si—H Bonds by BCF and Other Boranes	36
2.2.2.1	The Mechanism of Borane-Catalyzed Si—H Bond Activation	36
2.2.2.2	Additional Mechanistic Aspects	38
2.2.3	Categorizing Reduction Types of π and σ Bonds Involving the η^1 -[B]-H-[Si] Adduct	40
2.2.3.1	Type I: The Reduction of Polar π Bonds (El=Nu/El \equiv Nu)	40
2.2.3.2	Type II: The Reduction of Polar σ Bonds (El—Nu)	45
2.2.3.3	Type III: The Reduction of Nonpolar π Bonds (A=A/A \equiv A)	55
2.2.3.4	Type IV: The Reduction of Nonpolar σ Bonds (A—A)	58
2.2.3.5	Combination of Reduction Types	61
2.2.3.6	Mechanistic Variation of Reduction Types	66
2.3	The Activation of Si—H Bonds by Aluminum Lewis Acids	72
2.4	The Activation of Si—H Bonds by Group 14 Lewis Acids	73
2.4.1	Introduction	73
2.4.2	Carbocations as Lewis Acids	73
2.4.3	Cationic Tri-coordinate Silylium Ions and Neutral Si(IV) Lewis Acids	74
2.5	The Activation of Si—H Bonds by Phosphorous-Based Lewis Acids	75
2.5.1	P(III) Lewis Acids	75
2.5.2	P(V) Lewis Acids	76
2.6	Summary and Conclusions	76
	Acknowledgments	77
	References	77

3	Si—H Bond Activation by Transition-Metal Lewis Acids	87
	<i>Georgii I. Nikonov</i>	
	References	111
4	Metal–Ligand Cooperative Si—H Bond Activation	115
	<i>Francis Forster and Martin Oestreich</i>	
4.1	Introduction	115
4.2	Cooperative Si—H Bond Activation with Carbene Complexes Across M—C Double Bonds	116
4.3	Cooperative Si—H Bond Activation at M—N Bonds	116
4.4	Cooperative Si—H Bond Activation at M—O Bonds	117
4.5	Cooperative Si—H Bond Activation at M—S Bonds	118
4.5.1	Introduction	118
4.5.2	Seminal Results in Cooperative Si—H Bond Activation Across M—S Bonds	119
4.5.3	Dehydrogenative C—H Silylation	123
4.5.4	Competing Dehydrogenative Coupling and Hydrosilylation	125
4.5.5	C—H Silylation by Hydrosilylation/Dehydrogenative Silylation/Retro-Hydrosilylation	126
4.6	Summary	127
	References	128
5	Cationic Silicon-Based Lewis Acids in Catalysis	131
	<i>Polina Shaykhtudinova, Sebastian Keess, and Martin Oestreich</i>	
5.1	Introduction	131
5.2	Deoxygenation and Hydrosilylation of C=X Multiple Bonds	131
5.2.1	Deoxygenation of C=O Bonds	131
5.2.2	Hydrosilylation of C=O, C=N, C=C, and C≡C Bonds	133
5.3	C—F Bond Activation	137
5.3.1	Hydrodefluorination	137
5.3.2	Defluorination Coupled with Electrophilic Aromatic Substitution (S _E Ar)	144
5.4	Friedel–Crafts C—H Silylation	149
5.5	Diels–Alder Reactions	153
5.6	Mukaiyama Aldol and Related Reactions	163
	References	167
6	Transition-Metal-Catalyzed C—H Bond Silylation	171
	<i>Yoshiya Fukumoto and Naoto Chatani</i>	
6.1	C(sp)—H Bond Silylation	171
6.2	C(sp ²)—H Bond Silylation	174
6.3	C(sp ³)—H Bond Silylation	198
	References	207
7	Transition-Metal-Free Catalytic C—H Bond Silylation	213
	<i>David P. Schuman, Wen-Bo Liu, Nasri Nesnas, and Brian M. Stoltz</i>	
7.1	Introduction	213

7.2	Lewis Acid	213
7.2.1	BCl ₃ Catalyst	213
7.2.2	B(C ₆ F ₅) ₃ , a “Frustrated” Lewis Acid Catalyst	214
7.2.3	Lewis Acid Conclusions	222
7.3	Brønsted Acid	222
7.4	Brønsted Base	224
7.4.1	Early Example of Catalytic C–H Silylation by Brønsted Base	224
7.4.2	Fluoride/Base Catalysis	224
7.4.3	Brønsted Base–Catalyzed C–H Silylation of Alkynes	226
7.5	Radical Dehydrosilylation	229
7.5.1	“Electron” as a C–H Silylation Catalyst	229
7.5.2	Discovery of Unusual KOt-Bu-Catalyzed C–H Silylation	231
7.5.2.1	KOt-Bu-Catalyzed C–H Silylation Methodology	232
7.5.2.2	Mechanistic Investigations of KOt-Bu-Catalyzed C–H Silylation and Related Chemistry	234
7.6	C(sp ³)–H Silylation	238
7.7	Conclusion	238
	References	239
8	Silyl-Heck, Silyl-Negishi, and Related Reactions	241
	<i>Sarah B. Krause and Donald A. Watson</i>	
8.1	Introduction	241
8.1.1	Activation of Silicon–Halogen Bonds	241
8.1.1.1	Oxidative Addition to Platinum Complexes	242
8.1.1.2	Oxidative Addition to Palladium Complexes	242
8.1.1.3	Oxidative Addition to Iridium and Rhodium Complexes	243
8.2	Silyl-Heck Reactions	244
8.2.1	Early Silyl-Heck Studies	245
8.2.2	Multicomponent Coupling	246
8.2.3	Improved Silyl-Heck Reaction Conditions	247
8.2.4	Mechanistic Considerations	252
8.2.5	Pre-catalyst Investigations	254
8.2.6	The Formation of Silyl Ethers and Disiloxanes via the Silyl-Heck Reaction	258
8.2.7	The Nickel-Catalyzed Silyl-Heck Reaction	260
8.3	Silyl-Negishi Reactions	263
8.4	Silyl-Kumada–Corriu Reactions	267
8.5	Summary and Conclusions	268
	References	269
9	Transition-Metal-Catalyzed Cross-coupling of Organosilicon Compounds	271
	<i>Tamejiro Hiyama, Yasunori Minami, and Atsunori Mori</i>	
9.1	Introduction	271
9.1.1	Historical Background of the Cross-coupling with Organosilicon Reagents	271

9.2	Improvements in the Cross-coupling Reaction of Organosilicon Compounds	275
9.2.1	Ligand Design for the Palladium Catalyst	275
9.2.2	Variation of Palladium Catalysts and Additive Systems	276
9.2.3	Alternative Electrophiles and Metal Catalysts	278
9.2.4	Cross-coupling Reaction of Functionalized Organosilicon Reagents	284
9.2.5	Cross-coupling Reaction of Organosilanes Through Directed C—H Bond Activation	285
9.2.6	Tandem Reaction Involving Silicon-Based Cross-coupling	288
9.3	Cross-coupling of Silanols, Silanlates, Oligosiloxanes, and Polysiloxanes	289
9.3.1	Silanols and Silanlates	289
9.3.2	Disiloxanes, Oligosiloxanes, and Polysiloxanes	294
9.4	Cross-coupling of Allylsilane, Arylsilanes, and Trialkylsilanes	296
9.4.1	Silacyclobutyl, Allylsilanes, and Benzylsilanes	296
9.4.2	Arylsilanes	300
9.4.3	Trialkylsilanes	304
9.4.4	2-Hydroxymethylphenyl(dialkyl)silanes	313
9.5	Summary	323
	References	323
10	Lewis Base Activation of Silicon Lewis Acids	333
	<i>Sergio Rossi and Scott E. Denmark</i>	
10.1	Introduction	333
10.2	Direct Transfer of a Silicon Ligand to a Substrate Not Coordinated to the Silicon Atom	338
10.2.1	Transfer of Hydride: Reduction of C=O and C=N Double Bonds Promoted by Trichlorosilane	338
10.2.2	Reduction of Nitroaromatic Compounds by Trichlorosilane	351
10.3	Direct Transfer of a Silicon Substituent to the Silicon-Coordinated Substrate	353
10.3.1	Opening of Epoxides	353
10.3.1.1	Lewis Base-Catalyzed Epoxide Opening with Chlorotrimethylsilane	353
10.3.1.2	Lewis Base-Catalyzed Epoxide Opening with Silicon Tetrachloride	355
10.3.2	Allylation of Substrates Using Allylic Trichlorosilanes	359
10.3.2.1	Allylation of C=N Bonds	359
10.3.2.2	Allylation of C=O Bonds	361
10.3.3	Aldol Reactions Involving Preformed Enoxysilane Derivatives	371
10.4	Interaction of the Silicon-Activated Substrate with an External Non-Coordinated Nucleophile	375
10.4.1	Allylation of Aldehydes Mediated by Silicon Tetrachloride	376
10.4.2	Aldol Reactions Involving Trialkylsilyl Enol Derivatives	378

10.4.2.1	Aldol Reactions Involving Trialkylsilyl Enol Ether Derivatives	378
10.4.2.2	Aldol Reactions Involving Trialkylsilyl Ketene Acetals	379
10.4.2.3	Vinylogous Aldol Addition	382
10.4.3	Synthesis of Nitrile Derivatives from Silyl Ketene Imines	385
10.4.4	Passerini Reaction	387
10.4.5	Phosphonylation of Aldehydes with Triethyl Phosphite	388
10.5	Interaction of the Activated Substrate with an Externally Coordinated Nucleophile	390
10.5.1	Direct Aldol Reactions and Double Aldol Reaction	390
10.5.1.1	Direct Aldol Addition of Activated Thioesters	395
10.5.2	Enantioselective Morita–Baylis–Hillman Reaction	396
10.5.3	Outlook and Perspective	397
	Acknowledgment	398
	References	398
11	Hydrosilylation Catalyzed by Base Metals	417
	<i>Yusuke Sunada and Hideo Nagashima</i>	
11.1	Introduction	417
11.2	Base-Metal Catalysts for Hydrosilylation of Alkenes with Alkoxyhydrosilanes and Hydrosiloxanes	418
11.2.1	Iron and Cobalt Catalysts	419
11.2.1.1	Catalysts Bearing Tridentate Nitrogen Redox-Active Ligands and Related Catalysts	419
11.2.1.2	Catalysts Containing CO, CNR, and NHC Ligands	421
11.2.1.3	Miscellaneous	425
11.2.2	Nickel Catalysts	426
11.3	Hydrosilylation of Alkenes with Primary and Secondary Hydrosilanes by Base-Metal Catalysts	427
11.4	Conclusion and Future Outlook	434
	References	434
12	Silylenes as Ligands in Catalysis	439
	<i>Yu-Peng Zhou and Matthias Driess</i>	
12.1	Introduction	439
12.2	Applications of Silylene Ligands in Catalysis	439
12.2.1	Carbon–Carbon Bond-Forming Reactions	439
12.2.2	Carbon–Heteroatom Bond-Forming Reactions	445
12.2.3	Reduction Reactions	451
12.3	Summary and Outlook	456
	Acknowledgment	457
	References	457
13	Enantioselective Synthesis of Silyl Ethers Through Catalytic Si–O Bond Formation	459
	<i>Amir H. Hoveyda and Marc L. Snapper</i>	
13.1	Introduction	459

13.2	Lewis Base–Catalyzed Enantioselective Silylations of Alcohols	460
13.2.1	Early Lewis Base–Mediated Enantioselective Silylations of Alcohols	460
13.2.2	Lewis– and Brønsted Base–Catalyzed Enantioselective Silylations of Polyols	461
13.2.3	Directed Lewis Base–Catalyzed Enantioselective Silylations of Polyols	469
13.2.4	Lewis Base–Catalyzed Enantioselective Silylations of Mono-Alcohols	473
13.2.5	Lewis Base–Mediated Enantioselective Desilylations of Mono-Alcohols	478
13.3	Brønsted Acid–Catalyzed Enantioselective Silylations of Alcohols	479
13.4	Hydroxyl Group Silylations with Organometallic Complexes	481
13.4.1	Directed, Catalytic Enantioselective Hydroxyl Group Silylations with Chiral Silanes	482
13.4.2	Metal-Catalyzed Enantioselective Hydroxy Group Silylations with Chiral Silanes	486
13.4.3	Directed, Enantioselective Catalytic Hydroxy Group Silylations with Achiral Silanes	487
13.4.4	Enantioselective Catalytic Hydroxyl Group Silylations with Achiral Silanes	488
13.5	Conclusions	490
	References	491
14	Chiral Silicon Molecules	495
	<i>Kazunobu Igawa and Katsuhiko Tomooka</i>	
14.1	Introduction	495
14.1.1	General Background of Chiral Silicon Molecules	495
14.1.2	History of Chiral Silicon Molecules	496
14.2	Preparation of Enantioenriched Chiral Silicon Molecules	497
14.2.1	Classification of Preparation Methods for Enantioenriched Chiral Silicon Molecules	497
14.2.2	Separation of Stereoisomers of Chiral Silicon Molecules	498
14.2.2.1	Classification of Separation Methods for Stereoisomers of Chiral Silicon Molecules	498
14.2.2.2	Separation of Silicon Epimers of Chiral Silicon Molecules	499
14.2.2.3	Kinetic Resolution of Enantiomers of Chiral Silicon Molecules	500
14.2.3	Asymmetric Synthesis of Chiral Silicon Molecules	503
14.2.3.1	Classification of Asymmetric Synthetic Methods for Chiral Silicon Molecules	503
14.2.3.2	Desymmetrization of Prochiral Silicon Atoms by Substitution of a Heteroatom Substituent	503
14.2.3.3	Desymmetrization of Dihydrosilane	506

14.2.3.4	Desymmetrization of Prochiral Silicon Atoms by Enantioselective Substitution of a Carbon Substituent	507
14.2.3.5	Desymmetrization of Prochiral Silicon Atoms by Transformations of Carbon Substituent(s) without Si—C Bond Cleavage	513
14.3	Stereoselective Transformation of Enantioenriched Chiral Silicon Molecules	515
14.3.1	Classification of Stereoselective Transformation of Chiral Silicon Molecules	515
14.3.2	Nucleophilic Substitution at a Chiral Silicon Center	515
14.3.3	Electrophilic Substitution at Chiral Silicon Center	518
14.3.4	Oxidation at Chiral Silicon Center	519
14.3.4.1	Oxidation of Hydrosilane	519
14.3.4.2	Oxidation of Alkenylsilane	521
14.3.5	Multistep Functionalization of Chiral Silicon Molecules	521
14.4	Application of Enantioenriched Chiral Silicon Molecules	523
14.4.1	Classification of Applications of Chiral Silicon Molecules	523
14.4.2	Application as Chiral Reagents	523
14.4.3	Application as Chiral Materials	525
14.4.3.1	Chiral Silicon Polymer	525
14.4.3.2	Circular Polarized Luminescence of Chiral Silicon Molecules	527
14.4.4	Applications as Bioactive Molecules	527
14.5	Summary and Conclusions	528
	References	528

Index 533