## Contents

Foreword xiiiPreface xv

1	Catalytic Generation of Silicon Nucleophiles 1	
•	Koji Kubota and Hajime Ito	
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	
1.2.1.1	Silylation of Alkylidene Malonates 3	
1.2.1.3	Silylation of Allylic Carbamates 3	
1.2.1.3	Copper-Catalyzed Nucleophilic Silylation with Silylboronate	
1.2.2.1	Silicon–Boron Bond Activation with Copper Alkoxide 4	
1.2.2.1	Silylation of α,β-Unsaturated Carbonyl Compounds 4	
1.2.2.3		
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 <sub>2</sub> 11	
1.2.2.8	CO <sub>2</sub> 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	

vi	Contents	
	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 Dieter Weber and Michel R. Gagné	
	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 $\pi$ and $\sigma$ Bonds Involving the $\eta^1$ -[B]–H–[Si] Adduct 40
	2.2.3.1	Type I: The Reduction of Polar π Bonds (El=Nu/El≡Nu) 40
	2.2.3.2	Type II: The Reduction of Polar $\sigma$ Bonds (El–Nu) 45
	2.2.3.3	Type III: The Reduction of Nonpolar $\pi$ 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 Georgii I. Nikonov	
	References 111	
4	Metal-Ligand Cooperative Si—H Bond Activation 115 Francis Forster and Martin Oestreich	
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 Polina Shaykhutdinova, Sebastian Keess, and Martin Oestreich	
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 $\equiv$ C Bonds 133	
5.3	C—F Bond Activation 137	
5.3.1	Hydrodefluorination 137	
5.3.2	Defluorination Coupled with Electrophilic Aromatic Substitution $(S_EAr)$ 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 Yoshiya Fukumoto and Naoto Chatani	
6.1	C(sp)—H Bond Silylation 171	
6.2	C(sp <sup>2</sup> )—H Bond Silylation 174	
6.3	C(sp <sup>3</sup> )—H Bond Silylation 198	
	References 207	
7	Transition-Metal-Free Catalytic C—H Bond Silylation 213 David P. Schuman, Wen-Bo Liu, Nasri Nesnas, and Brian M. Stoltz	
7.1	Introduction 213	

viii	Contents	
	7.2	Lewis Acid 213
	7.2.1	BCl <sub>3</sub> Catalyst 213
	7.2.2	$B(C_6F_5)_3$ , 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 KO <i>t</i> -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
		Sarah B. Krause and Donald A. Watson
	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
		Tamejiro Hiyama, Yasunori Minami, and Atsunori Mori
	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		
, · <b>_</b> · ·	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, Silanolates, Oligosiloxanes, and Polysiloxanes 289		
9.3.1	Silanols and Silanolates 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	<b>Lewis Base Activation of Silicon Lewis Acids</b> 333 Sergio Rossi and Scott E. Denmark		
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		
10.2.1	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		

x	Contents	
	10.4.2.1 10.4.2.2	Aldol Reactions Involving Trialkylsilyl Enol Ether Derivatives 378 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
		Yusuke Sunada and Hideo Nagashima
	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
		Yu-Peng Zhou and Matthias Driess
	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
		Amir H. Hoveyda and Marc L. Snapper

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	
	Kazunobu Igawa and Katsuhiko Tomooka	
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	

xii	Contents	
	14.2.3.4	Des

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*