

Index

a

Abramov-type phosphorylation of aldehydes 389
acetonitrile 102, 105, 157, 369, 443
achiral cyclic ketones 371
achiral methyl ketones 371
acid-catalyzed indole silylation 223
activated substrate interaction, externally coordinated-nucleophile
direct aldol addition, of activated thioesters 395–396
enantioselective Morita–Baylis–Hillman reaction 396–397
acyclic nucleophiles 371
acylhydrazone esters, allylation of 361
acylsilanes 11
adamant-1-yl methyl ketone 451
agostic bis(silyl) hydridorhodium(III) complex 444
aldehyde-derived trichlorosilyl enol ethers 375
aldehydes, allylation of 3, 336, 362–364, 366, 368, 369, 375–378
aldol addition 371–373, 375, 378–386, 391, 393–396
aldolization process 371, 373
aldol reactions
 preformed enoxysilane derivatives 371–375
 trialkylsilyl enol ether derivatives 378–379

trialkylsilyl ketene acetals 379–382
aliphatic aldehydes 10, 11, 61, 67, 366, 368, 369, 373, 376, 379, 385–388, 391, 395
alkene hydrosilylation 57, 89–90, 421, 429, 431, 432, 450
primary and secondary hydrosilanes
 alkoxyhydrosilanes 427
 hydrosilanes 427
 monohydrosilylation 427
 platinum-catalyzed hydrosilylation, chlorohydrosilanes 427
 TOF 428
alkene isomerization 250, 433
alkenylsilanes 18, 288, 294, 296, 298, 299, 303, 519, 521
alkenylsilanols 292
alkenyl[tris(trimethylsilyl)] silanes 275
alkoxide base-catalyzed silaboration, of aromatic alkenes 24
alkoxyhydrosilanes 418–427
1-alkyl-1'-arylethylenes 430
alkyl chloro silyl ether 366, 376
alkylsilanes 241, 263, 265–267
alkynyltrimethylsilanes 308
allylacetone 454
allylating reagent 366, 376
allylation of aldehydes 3, 336, 362–364, 366, 367, 375–376
allylation, of benzaldehyde 3, 336, 362–364, 366, 368–370, 376–378

- allylation of substrates
 allylic trichlorosilanes
 allylation, of C=N bonds 359–361
 allylation, of C=O bonds 361–371
 allylation of trichlorosilanes 361
 allylation reaction 361, 365, 366, 369, 370, 377, 382
 allylic alcohol 304, 361
 allylic amines, formation of 361
 allylic nitriles 387
 allyl silanes 241, 245, 250, 252
 formation 421
 allyltributylstannane 376
 allyltributyltin 336, 375
 allyltrichlorosilanes 336, 359–364, 366, 369–371, 376
 to aldehydes 363
 with *N*-oxides 369
 allyltrifluorosilanes 361, 362
 allyltrimethoxysilane 360, 361
 α,β -unsaturated aldehydes 4, 5, 371, 387, 394 β
 α,β -unsaturated ketones 68, 385, 387, 394
 (E) - α,β -unsaturated nitriles 387
 α -chloroimines 342
 α -hydroxy amides 387
 α -hydroxysilanes 9–11
 α -hydroxy oxime ethers 488, 491
 α -substituted phosphonyl compounds 389
 α -substituted trimethylsilyl enol ethers 379
(aminomethyl)pyridine cobalt(II) dihalide 426
ammonia-borane (NH_3BH_3) 454
anilide moiety 340
anionic radical α -diimine ligands 427
anti-homoallyl alcohol 361
anti-Markovnikov addition 422, 428, 429, 434
anti-Markovnikov hydrosilylation of alkenes 91, 426, 431
antimuscarinic agents 521, 527, 528
Arbuzov-type dealkylation 390
arene–arene interactions 340
arene borylation 446
aromatic aldehydes 4, 336, 363, 369, 375, 376, 379, 381, 385, 387, 388, 390, 395, 396
aromatic C–H silylation 218
aromatic ketimines 342
aromatic *N*-alkyl ketimines 345
aromatic *N*-aryl ketimines 345
aryl-HOMSi reagents 313, 315, 317, 319
arylmethyamines 346
arylpropylsilole derivatives 196
aryl(trimethyl)silanes, desilylative
 acetoxylation of 313
asymmetric catalyst efficiency (ACE) 344
asymmetric Diels–Alder reaction, with silylnitrilium ion 156, 157
asymmetric Hosomi–Sakurai reaction 166–167
asymmetric hydrosilylation 428, 430
asymmetric hydrosilylative reduction of ketones 44
asymmetric imine reduction 346
asymmetric Mukaiyama–Michael reaction 164
asymmetric silylation protocol 461, 479
asymmetric synthesis, of chiral silicon molecules 503
desymmetrization
 dihydrosilanes 506–515
 of prochiral silicon atoms 503–506, 513–515
atoms in molecules (AIM) 335, 336
 α -trichlorosilyloxy phosphonate 390
auxiliary based kinetic resolution strategy 482
axial chirality 369, 497
- b**
- Bartlett-Condon-Schneider reaction 73, 75
base-catalyzed C–H silylation
 method 224, 230, 232–234
base-metal catalysts, for alkenes hydrosilylation

- iron and cobalt catalysts
containing CO, CNR, and NHC
ligands 421–425
tridentate nitrogen redox-active
ligands 419–421
nickel catalysts 426–427
 $B(C_6F_5)_3$ -catalyzed C–H
silylation 215–216, 220
BCF-catalyzed hydrosilylative
reduction, of carbonyl
compounds 38
BCF-catalyzed hydrosilylative reduction
of thioketones 42
BCF-catalyzed silylative reductions with
silanes 39
 BCl_3 -catalyzed C–H silylation
213–214
benzaldehyde 361
allylation 364, 366
benzil, stereocontrolled hydrosilylative
reduction of 43
benzodiazepinones 344
benzoxazinones 344
benzoyl hydrazones 359, 361
benzyldimethylsilyl-based various
nucleophiles 299
 β -amido enones 346, 347
 β -aryl substituted β -amino esters 350
 β -diketiminato silylene ligand 454
 β -enamino esters 344, 350
 β -hydroxy activated thioesters 396
 β -hydroxy dimethyl acetal 379
 β -hydroxy esters 379, 381
 β -hydroxy trifluoroethyl
thioesters 395
 β -ketiminato cobalt(I) complexes 425
 β -phenethyl 422
 β -silicon stabilizing effect 34
 BF_3 -catalyzed hydrosilylation of
carbonyl compounds 37
biaryl synthesis 274
bicyclic guanidines 460
bidentate bis(NHSi)-ferrocene
ligand 454
bidentate catalysts 339, 365
bimetallic activation, of R_2SiH_2 432
 β -imino esters 346–347
binaphthyl-based sulfur-stabilized
silicon cations 158, 162
biomass conversion 48, 50
biphenyl-silyl scaffold 216
biscarboiline *N,N*-dioxides 368
1,1'-bis(diphenylphosphino)ferrocene
(dpfpf) 284, 430
bisphosphine oxide derivatives 346
bisphosphinoxides 347
bisphosphoramides 359, 364–366,
371, 376–378, 381, 385
bisphosphoramido- $SiCl_4$
complexation 378
bis(imino)pyridine (PDI) 419–421,
428–430, 434
cobalt complexes 429
cobalt(I) complexes 420
iron(0) complexes 420
bis-silylene ligand 441, 443, 454
bis-silylene with $Ni(COD)_2$ 441
bissulfonimide 346
bis[(trimethylsilyl)methyl]iron(II)
complexes 420
borane catalyzed Si–H bond
activation 36–38
borylation
of fluoro- and trifluoroarenes 448
of furan 448
borylation, of pyridine derivatives 447
bromoacetophenone 441
1-bromo-2-(3-bromopropyl)
benzene 483
Brønsted acid-catalyzed
enantioselective, silylations of
alcohols 479–481
Brønsted base-catalyzed C–H silylation,
of alkynes 226–229
Brookhart–Wei mechanism 97
Buchwald–Hartwig amination 449
bulkiest catalyst 369
butyl-HOMSi reagent 318
- C**
- carbocations 51, 56, 71, 73–75, 106,
138, 515
carbon–carbon bond formation, of
Grignard reagents 442

- carbon–carbon bond-forming reactions 397, 439, 441, 443–444
- carbon–carbon double bond 15, 381
- carbon–heteroatom bond-forming reactions 445–451
- carbon–nitrogen double bonds 338
- carbon–oxygen double bonds 338
- carbon–phosphorus bonds 389
- carbonyl compounds 371
- BCF-catalyzed hydrosilylative reduction 38
 - BF_3 -catalyzed hydrosilylation of 37
 - Piers' seminal hydrosilylative reductions 37
 - reduction of 61
- carbonyl hydrosilylation 92, 101, 118, 451
- carboxy amide groups 342
- catalytic asymmetric synthesis 430
- catalytic C–H silylation
- Brønsted acids 222–224
 - Brønsted bases 224–229
 - Lewis acid 213–222
- catalytic cyclotrimerization 444
- catalytic dehydrogenative borylation, of arenes 447
- catalytic H/D exchange reaction 447
- catalytic hydrosilylation, of C=O bonds 91, 99, 102, 103, 119, 120, 207, 314, 418, 434
- catalyzed HSiCl_3 imine reduction 351
- catalyzed silylation, of alcohols 459
- cationic iridium complex 94, 96
- cationic silicon Lewis acids 142, 155, 159
- C=F bond activation 137
 - cationic silylene complexes 91
 - cationic trichlorosilyl species 376
- C₂/C₃-selective C–H silylation of heteroarenes 190
- chair-like arrangement 366, 373
- chalcone 157, 158, 160–163, 454
- C–H bond functionalizations 200, 445
- C(sp)–H bond silylation 171–174
- chelation-assisted benzylic C(sp³)–H silylations 201
- chelation-assisted C(sp³)–H silylation, of 2-substituted pyridines 202
- chelation-assisted regioselective silylation, of aryl C–H bonds 176
- chiral aldehydes 375
- chiral allenic bisphosphine oxide 357
- chiral bidentate phosphoramides 363
- chiral Brønsted acid 479, 480
- chiral Brønsted base 467, 469
- chiral–carbon-free enantioenriched chiral silicon molecules 499
- chiral diamine 9, 361
- chiral enolates 375
- chirality 20, 22, 157, 166, 369, 495, 497, 498, 504
- chiral NHC-catalyzed enantioselective conjugate silylation 23
- chiral *N,N'*-dioxides 375
- chiral *N*-oxides 368
- chiral phosphoramide 359, 363, 366, 507
- chiral pyridine N-oxides 370
- chiral silane 482–488
- chiral silicon molecules 495
- vs. chiral carbon molecules 495
 - history 496–497
- chiral siloxane 496
- chiral silylguanidinium salt 461
- chiral sulfinimides 346
- chiral sulfoxides 369
- chiral transition metal catalyst
- promoted reactions 513–515
- chlorosilanes 336, 483, 499, 500, 519, 522
- C(sp³)–H silylation 198–207, 238
- cinchona-based picolinamide 347
- classical Ojima mechanism 91
- Cleroindicin D, C, and F 467
- $\text{Co}(2\text{-ethylhexanoate})_2$ 421
- (IPr)cobalt amide complexes 424
- cobalt catalysts 418–426
- $\text{Co}(\text{I})[\text{bis(imino)pyridine}]^{2-}$ 421
- CO_2 hydrosilylation 108
- cationic complexes 110
 - iridium complex 110
- (^DI_PP CCC)CoN₂ 424, 425

- condensative vinyl-THP 52
conjugated *N*-heterocycles
 hydrosilylation 104
continuous flow reductions 349
cooperative catalysis, at Ru–S
 bonds 127
cooperative Si–H bond activation
 by iron oxide complex 118
 at metal–carbene complexes 117
 at metal–sulfur bonds 118
 at M–N bonds 116–117
 at M–O bonds 117
 at Rh–S and Ir–S bonds 120
copper-catalyzed dehydrogenative
 coupling of hydrosilanes 488
copper-catalyzed nucleophilic silylation
 of aldehydes 10
 of aldimines 10
 of alkylidene malonates 3
 of alkynes 16–19
 of allylic carbamates 3
 of allylic silylation 7
 of anhydrides 11
 of α,β -unsaturated carbonyl
 compounds 2, 4
CO₂ reduction with silylboronate 13
decarboxylative radical silylation of
 aliphatic carboxylic acid
 derivatives 14
of imines 9
silicon–boron bond activation with
 copper alkoxide 4
silylative alkylation of ketones and
 allenes 15, 16
silylative carboxylation with
 CO₂ 11–13
silylative cyclization of
 allenes 15–16
with silylboronate 4
silyl substitution of alkyl
 electrophiles 13–14
with (PhMe₂Si)₂Zn reagent 20
copper-catalyzed regiodivergent
 silacarboxylation, of allenes 12
Cp^{*}₂ScMe-catalyzed C–H silylation, of
 methane 200
cross-coupling reactions, of
 organosilicon compounds
 alkenylsilanes 299
 alkenylsilanols 292
 alkyl(bis-catecholato)silicates 282
 allylsilane compounds 296–300
 arenediazonium salts 278
 aryldimethylsilanol 290
 arylsilanes 300–304
 aryl(oligofluoro)silanes with allylic
 carbonates 272
 aryl(triethoxy)silanes with
 idoarenes 280
 aryl(trimethoxy)silane with aryl
 halides 274
 bromoalkanes 282
 bromofluoroiodobenzene 283
 disiloxanes 294–296
 2-(hydroxymethyl)phenyl(dialkyl)
 silanes 313–323
 neutral tetracoordinate
 organosilane 272
 oligomeric siloxanes 295
 organic silanolates 293
 organobenzylsilanes 298
 organo(hydro)silanes with organic
 halides 280
 organosilanols 290
 organosilicon reagents
 functionalized 284–285
 history of 271–275
 palladium catalyst
 with additive systems, variation
 of 276–277
 ligand design for 275
 palladium-catalyzed allylic
 substitution 274
 pentafluoroaryl(vinyl)silanes with
 idoarenes 302
 with phenyl iodide 272
 PhSi(OMe)₃ and 2-nitrobenzoic
 acid 281
 polysiloxanes 295
 secondary alkyl bromides with
 aryltrifluorosilanes 279
 secondary ammonium salt with
 haloarenes 283

- cross-coupling reactions, of organosilicon compounds (*contd*)
- silacyclobutanes 296
 - silanediols 291–292
 - silanols 291
 - tosylates and mesylates 278
 - trialkylsilanes 304–313
 - vinyl(thienyl)dimethylsilanes with iodoarenes 300
 - vinylsilanes with iodoarenes 303
 - vinyltrimethylsilane with vinyl iodide 273
 - crotyltrifluorosilanes 361
 - C3-silylated indoles 60
 - C*₂ symmetric biquinoline *N,N*-dioxide 366
 - C*₂-symmetric diene 358
 - cyclic and acyclic meso-1,2-diols 461, 464, 470
 - cyclic imines, reduction of 346
 - cyclic trichorosilyl enol ether derivatives 371
 - cyclization of *ortho*-biaryl silanes 194
 - cyclohexanecarboxaldehyde 376
 - cyclohexanone-derived silyl enol 375
 - cyclohexanone-derived trichlorosilyl enol ether 371, 375
 - cyclohexenone 466
 - cyclopentene 422
 - cyclotrimerization 443, 444
 - [2 + 2 + 2] cyclotrimerization reaction, of phenylacetylene 443
- d**
- debromination, of alkylbromides 55
 - defluorination
 - coupled with electrophilic aromatic substitution 144–149
 - of organofluorines 54
 - dehydrocarbonative silylation 47, 54, 61, 62
 - dehydrochlorination reaction 441
 - dehydrogenative C–H silylation 123, 226, 232
 - dehydrogenative enamine silylation 126
 - dehydrogenative silylation 421
 - of alcohols 46
 - of alkyl-substituted alkynes 172
 - of amines 46
 - of anilines 59
 - of anisole derivatives 182
 - catalysts 429
 - of hydrogen chloride 46
 - of *o*-alkylphenylsilanes 204
 - of thiols 46
 - deoxygenation
 - of amides 65
 - of C=O bonds 131–133
 - of imides 65
 - desorption electrospray ionization-mass spectrometry (DESI-MS) 236
 - desymmetrization of
 - dihydrosilanes 506
 - enantioselective Si–C bond formation 507
 - stereoselective Si–O or Si–N bond formation 506–507
 - desymmetrization of *meso*-diols 467, 468, 471
 - desymmetrization of prochiral silicon atoms
 - chiral transition metal catalyst
 - promoted reactions 513–515
 - enantioselective substitution of carbon substituent 507
 - Si–alkynyl bond cleavage 512
 - Si–Ar bond cleavage 512
 - Si–Me bond cleavage 512
 - enantioselective substitution of carbon substituent Si–C bond cleavage of silacyclobutanes 511
 - lipase-catalyzed asymmetric esterification 513
 - by substitution of heteroatom substituent 503–506
 - transformation of carbon substituents 513
 - deuterium labeling 51, 56, 72, 119, 186, 188, 426
 - DFT calculations 90, 93, 94, 97, 98, 106, 185, 273, 351, 376, 395

- 1,1'-dialkylethylene 430
 diaryl-*tert*-butyl phosphine
 ligands 250
 diastereoselectivity 42, 43, 163, 167,
 375, 382, 387, 395, 397, 505, 510
 dibenzoazepine reduction 454
 dichloromethane 105, 288, 358, 369
 Diels–Alder reactions 153
 of cyclohexa-1,3-diene and
 3-acryloyloxazolidin-2-one 155
 of cyclohexa-1,3-diene and
 chalcone 157, 158, 161–163
 of cyclohexa-1,3-diene and methyl
 acrylate 153
 of cyclopentadiene and
 cinnamates 163–164
 of cyclopentadiene and
 cyclohexa-1,3-diene 159
 $[\text{Et}_3\text{Si}(\text{toluene})]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$
 catalyzed 155
 ferrocene-stabilized silicon
 cation 156
 with silylnitrium ion 157
 diethylzinc (Et_2Zn) 247
 dihalo- or dicarboxynato-(PDI)
 CoX_2 429
 diisopropylethylamine 368, 375, 390, 471
 2,6-diisopropylphenyl group 419, 428
 dilithium catecholates 361
 dimethylalkylsilanes 431
 dimethylphenylsilylalkenes 313
 dinitrogen complexes, of iron 419
 1,2-diols, stereoselective reduction
 of 50
 1,3-dioxane scaffold 343
 diphenyldiallylsilane 297
 direct aldol addition 396
 of activated thioesters 395–396
 directed Lewis base-catalyzed
 enantioselective, silylations of
 polyols 469–473
 direct enantioconvergent
 transformation, in copper-
 catalyzed allylic silylation 8
 direct transfer 336
 of silicon ligand
 hydride, transfer 338–351
 nitroaromatic compounds
 reduction,
 trichlorosilane 351–353
 of silicon substituent, silicon-
 coordinated substrate epoxides
 opening 353–359
 di(2-furyl)(methyl)(phenyl)silane 300
 disilylarenes 307
 1,1-disubstituted hydrazines, synthesis
 of 349
 donor-stabilized silicon cations, Lewis
 acidity of 116
 double reductive amination
 approach 42
 double-silylation selective
 disproportionation C–H
 silylation 221
- e**
- E*- and the *Z*-oxime isomers 488
 (*E*)- and (*Z*)-crotyltrichlorosilanes 361
 (*E*)-crotylsilane 361
 electron, as C–H silylation
 catalyst 230
 electron-donating substituents 371,
 379
 electron-withdrawing
 substituents 371, 387, 477
 electrophilic aromatic
 substitution 123, 126, 144–149
 electrophilic substitution, of chiral
 silicon molecules 518–519
 enantioenriched β -hydroxy
 nitriles 386
 enantioenriched chiral silicon molecules
 bioactive molecules 527–528
 chiral reagents 523–525
 chiral silicon polymers 525–527
 circular polarized
 luminescence 527
 preparation methods
 asymmetric synthesis 503–515
 classification 497–498
 separation of
 stereoisomers 498–502
 stereoselective
 transformation 515–523

- enantioenriched 4*H*-1,3-oxazines 347
 enantioenriched silicon-stereogenic hydrosilane 122
 (*S*)-enantiomer 366
 enantiopurity, of monophosphoramido 364
 enantioselective allylic silylation, chiral NHC/copper-catalyzed 7
 enantioselective catalysts 343
 enantioselective catalytic intramolecular C(sp²)-H sylations 196
 enantioselective catalytic intramolecular C(sp³)-H sylations 207
 enantioselective Morita–Baylis–Hillman reaction 396–397
 enantioselective reduction, of imines 341, 342, 344, 346, 348, 349
 enantioselectivity 4, 7, 9, 11, 21, 43, 157, 159–161, 167, 339, 342–348, 359, 364, 368, 369, 373, 375, 386, 387, 397
 enantiotopic hydroxyl groups 463, 469
 enolizable ketones and imines, dehydrogenative coupling of 125
 enoxysilane derivatives 371–375, 385
 enoxytrichlorosilane derivatives 371
 enzymatic kinetic resolution of chiral silicon molecules 500
 epoxides, opening lewis-base catalyzed epoxide opening, chlorotrimethylsilane 353–355
 η^3 -allyl ligands 433
 η^6 -arene iron(0) complex 454
 η^6 -arene ligands 433
 η^1 -[B]-H-[Si] adduct 38 reduction of non-polar π bonds 55–58 of non-polar σ bonds 58–61 of polar π bonds 40–45 of polar σ bonds 45–55
 η^3 -silane complex 90
 η^1 -silane complexes 91, 94
 η^2 -silene hydride complex formation 199
 5-ethylthiotetrazole 467
 $[\text{Et}_3\text{Si}(\text{toluene})]^+$ -promoted Mukaiyama aldol reaction 164
- f**
- Fe(CO)₃(divinylsiloxane) catalyst 421
 ferrocene bridged bis-silylene ligand 443
 fluoride-catalyzed C–H sylation 224–226
 fluorous silica 347
 Friedel–Crafts C–H sylation 149–153
 Friedel–Crafts reactions, with arene solvents 144–145
 frustrated Lewis pairs (FLP) 40, 214
 functionalized organosilicon reagents, cross-coupling reactions of 284–288
- g**
- Gade–Hoffmann mechanism 92, 93
 γ -chloro silyl enol ether 396
 γ -selective propargylic substitution 19–20
 gas-phase direct silylation 224
 Gibbs free energy 354
 γ -imino esters 344
 glycolate aldol reaction, aldehydes 382
 glycolate-derived silyl ketene acetals 379, 383
 Grignard reagents 267, 271, 441, 442, 483, 505
 Gutmann's semiempirical analysis 333
- h**
- half-sandwich-Sc-catalyzed acceptorless C(sp²)-H *ortho*-silylation 183
 Heck coupling 441 of bromoacetophenone 441
 1,1,1,3,5,5-heptamethyltrisiloxane (MD'M) 420
 heteroaromatic aldehydes 379
 heteroarylethylene 430
 heterobimetallic Ni/Cu intermediate 442
 hexacoordinate cationic silicate 373

- hexacoordinate cationic species 336
 hexacoordinate silicate species 373
 hexacoordinate silicon atom 361, 362
 hexacoordinate silicon species 334,
 338, 350, 358, 369
 hexamethyldisilazide (HMDS) 479
 $^1\text{H}/^2\text{H}$ scrambling experiments 122
 hindered silyl activators 467
 homoallylic alcohol 167, 363, 368, 369,
 376
 homoallylic benzoyl hydrazines 359
 Hoveyda/Snapper imidazole 462
 Hoveyda/Snapper's initial transition
 state model 462
 Hoveyda/Snapper's kinetic resolution,
 of racemic diols 463
 H-source yielded (*E*)-alkenes 454
 hybrid orbital (Ψ^2) 334
 hydrodefluorination
 of CF_3 -substituted
 anilines 108–109
 silicon cation-promoted
 of $\text{C}(\text{sp}^3)\text{-F}$ bonds 143
 chalcogen-stabilized silicon
 cations 141
 counteranion stability effect 142
 initiated by stibonium ion 144
 intramolecularly stabilized silyl
 hydronium/fluoronium
 ions 141
 mechanism of 138
 reactivity of silicon
 electrophile 138, 139
 hydrodesulfurization, of thioethers 54
 hydroformylation
 reactions 443
 of styrene 443, 444
 hydrogenation
 of alkenes 455
 of carbonyl compounds 456
 hydrosilanes 177, 222
 $\text{HSiMe}_2(\text{OSiMe}_3)$ 181
 intermolecular C–H silylation of
 methane 199
 Ir-NHC-catalyzed $\text{C}(\text{sp}^2)\text{-H}$ *ortho*-
 silylation of
 2-phenylpyridines 180
 $\text{Ru}_3(\text{CO})_{12}$ -catalyzed $\text{C}(\text{sp}^2)\text{-H}$
 ortho-silylation of 2-
 phenyloxazolines 178
 hydrosiloxanes 418–427, 434
 hydrosilylation 417, 428
 of α,β -unsaturated carbonyl
 compounds 69
 of alkenes 418, 422, 427, 450, 451
 of alkenes and alkynes 55–58
 of alkoxyhydrosilanes 421
 of allyl ethers 420
 of aromatic alkynes 56
 of benzaldehyde 119
 of C=O , C=N , C=C , and C=C
 bonds 133–137
 of dienes 434
 of hex-1-ene 426
 of hydrosiloxanes 421
 of internal alkenes 433
 of ketones 452, 453
 of ketones mediated by silicon
 cations 133
 of oct-1-ene 420, 426
 of oct-2-ene 422
 of silyl enol ethers 56
 of ynamides 57
 hydrosilylative reduction, BCF^-
 catalyzed of thioketones 42
 hydrosilylative reduction of imines 41
 hyperbonding 335
 hypercoordinate allylsiliconates 361
 hypercoordinate cationic silicon
 species 375
 hypercoordinate silicon
 compounds 333
 hypercoordinate silicon species 336–
 337, 353, 390, 396
 hypervalency 335
 hypervalent bonding 334
 molecular orbitals 335
 hypervinylogous aldol additions 385,
 386

i
 I_2 -catalyzed $\text{C}_{(\text{sp})}\text{-H}$ silylation, of
 phenylacetylene 172
 imidazolinones 350

(bis)iminopyridine ligand 421
 immobilized catalyst 348
 1-indanols 477, 478
 indenylnickelphosphine complexes 431
 intermolecular electrophilic C–H silylation, of N-protected indoles 123–124
 intramolecular C–H silylation 231
 of biarylsilanes 229
 biphenyl-silyl scaffold 216
 mechanism for 231
 optimization of 230
 intramolecular electrophilic C–H silylation, of arenes 124
 intramolecular proximity 469
 intramolecular silole synthesis 217
 intramolecular silylation mechanism 217
 intramolecular silyloxy migration 71
 Intrinsic Reaction Coordinate (IRC) 353
 intrinsic silylicity descriptor 110
 (*E*)-1-iodooct-1-ene 442
 Ir(acac)(cod)-catalyzed C(sp²)–H *ortho*-silylation, of 2-phenylpyridines 181
 Ir₄(CO)₁₂-catalyzed C(sp³)–H silylation, of 4-alkylpyridines 200–201
 Ir-NHC-catalyzed C(sp²)–H *ortho*-silylation, of 2-phenylpyridines 180
 iron and cobalt catalysts containing CO, CNR, and NHC ligands 421–425
 tridentate nitrogen redox-active ligands 419–421
 iron catalysts 422
 iron complex [Cp(CO)(Ph₃P)Fe(η^2 -HSiEt₃)]⁺ 88
 [Ir(OMe)(diolefin)]₂/PAr₃-catalyzed reaction 173
 Ir₄(CO)₁₂/PPh₃-catalyzed C(sp)–H silylation 172
 [Ir(OMe)(cod)]₂/tmphen-catalyzed C–H silylation, of arenes 188
 Ir(V) trihydride complex 98

isocyanide ligands 421–423
 isothiourea catalyst 476, 478
 isothiourea (–)-tetramisole 474
 Itsuno–Corey reductions 43

k

ketone hydrosilylation 89–90, 93
 Brookhart’s complex 98
 cationic oxazoline–carbene complex 92
 oxorhenium(V) oxazoline complex 95
 kinetic resolution, of 1-cyclohexenylsilanol 502
 KOT-Bu-catalyzed C–H silylation 233, 234, 236
 Kumada–Corriu coupling reactions 443
 Kumada–Corriu-type cross-coupling reactions 443

l

Lewis acid-catalyzed C–H silylation 214
 B(C₆F₅)₃ catalyst 214–222
 BCl₃ catalyst 213–214
 Lewis-acidic metal complexes 104, 111
 Lewis acidic silicon species 157, 333, 338
 Lewis acidity 4, 36, 39, 73, 75, 76, 115, 137, 142, 153, 157, 296, 303, 304, 334, 353, 362, 484
 Lewis acid-Lewis base complexation 334
 Lewis-acid metal induced mode, of silane activation 87
 Lewis acids 73, group 14
 aluminium 72
 boron 36
 neutral Si(IV) 75
 P(III) 75–76
 P(V) 76
 tris(pentafluorophenyl)borane 36
 Lewis and Brønsted base-catalyzed enantioselective, silylations of polyols 461–469

- Lewis base–catalyzed allylations 336, 364
 Lewis base–catalyzed enantioselective, silylations of mono-alcohols 473–478
 Lewis base–mediated enantioselective, desilylations of mono-alcohols 478–479
 Lewis base–mediated enantioselective, silylations of alcohols 460–461
 Lewis bases (LB) 336, 338
 Lewis basic activator 343
 Lewis basicity 48, 49, 140, 142, 366, 478
 Lewis basic solvent 361
 Lewis–Langmuir octet rule 333
 ligand close packing (LCP) model 335
 ligand free copper-catalyzed protosilylation, of alkynes 17
 linear (or near-linear) bond geometry 335
 lipase-catalyzed asymmetric esterification of bis(hydoroxyethylaryl) silane 513
 (R) -lisofylline synthesis 50
- m**
 Markovnikov switching 430
 $\text{Me}_3\text{N-Si(O)Cl}_2$ 353
 $(-)$ -menthoxy silane 496, 499
 $(\text{EtO})_2\text{MeSiH}$ 423, 424, 431
 $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_{m-}$ ($\text{MeHSiO})_n\text{SiMe}_3$ 420
meso-1,2-and 3-diols 461
meso-bis-silylated glycerols 471
meso-1,3-cyclic diols 461
meso-diol desymmetrization 462, 470
meso-1,3-diols 471
meso-diol substrates 469
meso-epoxides 355–357
meso-hydrobenzoins 471, 481
 metal–ligand cooperative Si–H bond activation. *See* cooperative Si–H bond activation
 metallocenes 71
 metal-mediated hydroxyl group silylations
- achiral silanes
 directed, enantioselective catalytic hydroxyl group silylations 487–488
 enantioselective catalytic hydroxyl group silylations 488, 490
 chiral silanes
 directed, metal-catalyzed asymmetric hydroxyl group silylations 482–486
 metal–catalyzed asymmetric hydroxyl group silylations 486–487
 METHOX 369, 370
 methoxyoxazolidine 469
 2-methyl-2-butene 360
 methyl-capped oligoethylene glycol 420
 methyldialkylsilanes 431
 modified Chalk–Harrod cycle 418
 molecular orbital theory (MO) 334
 mono-and bis-phosphoramides 376
 monodentate NHSi ligand 454
 monodentate N -oxide 375
 monodentate silylene ligands 443
 monodentate silylene-Pd(0) complex 439, 440
 monohydrosilylation 427
 monomeric nickel hydride 427
 monophosphine/copper complex-catalyzed regioselective protosilylation, of alkynes 17
 monophosphoramide 355, 364, 376
 mono-silylated glycerols 471
 Mukaiyama aldol 163–167, 375, 378, 381, 473
 Mukaiyama–Michael addition reaction 387
- n**
 Nakata’s guanidine catalyst 478
 N -alkyl substituted ketimines 344
 naphthalene-1,8-diyl-derived intramolecularly stabilized silicon cations 140
 N -aryl substituted ketimines 344
 natural bond orbital (NBO) 334

- natural resonance theory (NRT) 334
- N*-benzoylhydrazones, allylation of 360
- neutral hexacoordinate species 336, 369, 390
- neutral Lewis bases 336
- neutral ruthenium borate complexes 91
- neutral Si(IV) Lewis acids 74–75
- neutral tetracoordinate organosilane 272
- N*-formyl amino acids 340, 342
- N*-formyl cyclic amines 339, 340
- N*-formyl derivatives 341
- N*-formyl prolinamide catalyst 350
- NHC/copper complex-catalyzed regioselective protosilylation of alkynes 17
- NHC ligands structure of 424
- N*-heterocyclic carbene-catalyzed nucleophilic 4-silylation 1, 23–24
- N*-heterocyclic carbenes (NHC) 4, 92, 242, 275, 418, 434, 449, 484
- N*-heterocyclic silylcarbene 443
- N*-heterocyclic silylene (NHSi) ligands 439, 440
- N*-heterocyclic silylene (NHSi)-silane scaffold 444
- Ni(η^2 -H₂C=CHSiMe₃)₂(ⁱPr₂Im)-catalyzed C–H silylation, of polyfluoroarenes 193
- Ni(PEt₃)₄-catalyzed reaction, of cyclic disilane 186
- nickel catalysts 260, 418, 426–427, 431, 433, 512
- nickel-catalyzed carbon–carbon bond formation 441
- nickel-catalyzed nucleophilic silylation, of alkyl electrophiles 22–23
- nickel-catalyzed silyl-Heck reactions 260–263
- nitrile hydrosilylation 102
- nitriles, chemoselective reduction of 42
- nitrile synthesis, from silyl ketene imines 385–387
- nitrogen-containing heterocyclic additives 468
- nitrosomethane 353
- N*-methyl formamide moiety 340
- N*-methyl indoles reactivity 59
- N*-methyl-(*S*)-valine 341
- N*-methyl-(*S*)-valine-derived Lewis basic catalysts 340
- (*R*)-*N,N'*-(dimethylamino)binaphthalene scaffold 344
- N,N*-dimethylbenzamide hydrosilylation 99
- N⁺N⁺N-pincer ligand 431
- N⁺N⁺N-tridentate ligands 429
- nonaromatic ketimines 342
- non-chelation-assisted C–H silylations 187
- non-chelation-assisted intermolecular silylations 186
- non-enantioselective allylic silylation, copper-catalyzed 7
- non-metal hydride 338
- non-nucleophilic hydroxyl group 468
- “non-pyridine-type” *N*-oxide 369
- N*-oxide-based catalysts 367
- N*-oxides 63, 64, 369
- N*-picolinoyl derivatives 343, 344
- N*-picolinoylpyrrolidines 343
- N*-picolinoyl-(2*S*)-(diphenylhydroxymethyl)pyrrolidine 343
- N*-silylated dihydropyridine 108
- N*-silyl vinylketene imine 387
- N*-*tert*-butylsulfinyl-L-proline-derived amide 350
- nucleophilic attack 24, 39, 53, 56, 58, 61, 87, 93, 104, 144, 146, 167, 216, 272, 336, 353, 359, 375, 376, 462
- nucleophilicity, of enoxysilane derivatives 371
- nucleophilic reactivity 334
- nucleophilic silicon ligand 338
- nucleophilic substitution, of chiral silicon molecules 515–518

- N*-unsubstituted β -enamino esters 350
- o**
- oct-1-ene 420, 422, 423, 426, 428, 429, 431, 432, 450
- Oestreich's copper-catalyzed kinetic resolution of pyridine 486
- one-electron chemistry 418
- one-pot hydrosilylation/dehydrosilylation procedure 216, 218
- organobenzylsilanes 298
- organo-HOMSi reagents 315–319
- organometallic complexes 417, 418
- organosilanes 35, 241, 245, 247, 268, 275, 278, 279, 285–288, 313
- organosilanol 290
- organosilicon cross-coupling reagents disiloxanes 294–296 silanediols 291–292 silanetriols 291
- 1-organosilyloctane 422
- O-silyl enolate 395
- outer-sphere ionic hydrosilylation of alkynes 105
- oxasilacyclic compounds 207
- oxazaborolidines 43
- oxazoline-derived organocatalysts 345, 346
- oxazoline scaffold 345
- oxidation of alkenylsilane 521 of hydrosilane 519–521
- oxime nitrogen 488
- oxorhenium(V) oxazoline complex 93, 95
- p**
- π -accepting CO ligands 422
- π -acceptor 421, 439
- packed bed reactors 348
- para*-Quinone methides 6
- Passerini reaction 387–390
- Pd(OAc)₂-catalyzed 8-aminoquinoline-directed regioselective C–H silylation 202
- Pd(OAc)₂-catalyzed *ortho* C–H silylation, of benzamide derivatives 176–177
- Pd(OPiv)₂-catalyzed para-selective direct C–H bond silylation 185
- penta*-coordinate cationic silicate 373
- pentacoordinate* silylcatecholate 272
- penta*-coordinate species 369
- penta*-coordinate structure 362
- pentafluoroaryl(vinyl)silanes 302
- penta*-or *hexa*-coordinate silicon species 334
- peripheral atoms 334
- phenathroline-supported complexes 104
- phenyltriallylsilane 297
- phenyltrimethylsilane 310
- phosphine-catalyzed 2-silaboration, of alkynyl esters 1, 24–25
- phosphine oxides 76, 339, 346, 357, 361, 364, 369, 375, 389–391, 393–397
- phosphonylation of aldehydes 389 of aldehydes, triethyl phosphite 388–390
- phosphoramides 345, 362–365, 369, 373, 376, 377
- photochemically driven iridium(III)/nickel(0)-catalyzed coupling 284
- Piers enone reduction and hydrosilylation 68
- Piers–Rubinsztajn reaction 47
- pinwheel conformation 382, 395
- platinum catalysts 417, 420
- P(III) Lewis acids 75–76
- P(V) Lewis acids 76
- P^N^AN ligands 429, 430
- poly(phenylmethylsiloxane) 295
- polydimethylsiloxane 422
- polymeric vinyl-and hydrosiloxanes 426
- polymer-supported cyclic silyl ether 320–321
- polymethacrylate 347

- poly(dimethyl)siloxane 422
 polystyrene-anchored chiral catalysts 348
 proline 339, 343, 345, 350, 369, 395
 (S) -prolinol scaffold 346
 pseudo-enantiotopic hydroxyl groups 463
 Pt₂(dba)₃/P(OCH₃)₃C^tEt-catalyzed C(sp²)-H silylation, of aromatic imines 175
 pyridine hydrosilylation 103, 106–107
 pyridines, 4-selective hydrosilylation of 1, 126–127
 2-pyridyl(allyl)dimethylsilane 297
- q**
- quasilsilatranes 336
 quinoline-type mono N-oxide 369
 QUINOX 369, 370
 quinoxalinones 344
- r**
- racemic 2-diols 1, 464, 469
 rapid-injection NMR spectroscopy 373
 redox-active ligands 418, 419, 421, 434
 redox activity, of bis(imino)pyridine ligands 419
 reduction of α,β -unsaturated nitriles 70
 of alkyl halides by Brookhart's complex 96
 of carbonyl compounds to alcohols and alkanes 61
 of carboxylic acids to aldehydes 62
 chemoselective reduction of conjugated C=C double bonds 68
 of CO₂ to methane 66
 to silylformates 65
 of ketones and aldehydes 62
 of nitrated hydrocarbons to amines 63
 of non-polar π bonds 55–58
 of non-polar σ bonds 58–61
 of oxalic acid 62
- of phosphonates and phosphinates to phosphines 64
 of polar π bonds 40–45
 of polar σ bonds 45–55
 selective reduction of substituted pyridines 69
 of sulfones and sulfoxides to sulfides 63
 of sulfoxides and N-oxides 63
 of tertiary amine N-oxides 64
 reductive aldol reaction, BINAPO 394
 reductive coupling reactions 65–67
 reductive etherification of carbonyl compounds 66, 67, 72
 regiodivergent copper-catalyzed protosilylation, of alkynes 19
 regioselective hydrosilylation 434
 regioselective monodeoxygenation, of vicinal diols 50
 retro-hydrosilylation 126–127
 [Rh(OH)(coe)]₂/bisphosphine-catalyzed C–H silylation, of arenes 187
 RhCl(cod)]₂/TMS-segphos-catalyzed intramolecular ring expansion, of silacyclobutanes 198
 rhodium-catalyzed conjugate silylation, with silylboronate 22
 rhodium-catalyzed hydroformylation of styrene 443
 rhodium-catalyzed nucleophilic silylation of aryl and alkenyl cyanides 21
 with disilanes 21
 with silylboronates 21–22
 rhodium-catalyzed stereospecific silylation, of propargylic carbonates 22
 rhodium/(R)-BINAP-catalyzed enantioselective intramolecular C–H silylation, of bis(biaryl) dihydrosilanes 194
 Rh(OH)(cod)]₂/(R)-TMS-segphos-catalyzed enantioselective reaction, of biarylhydrosila cyclobutanes 198

- R_3SiH -type silanes 39
 $Ru_3(CO)_{12}$ -catalyzed *ortho* C(sp²)–H silylation, of 2-heteroarenes 184
[$RuCl(p\text{-}cymene)]_2$ -catalyzed acceptorless C(sp²)–H *ortho*-silylation 182
 $RuH_2(CO)(PPh_3)_2$ -catalyzed C(sp₃)–H silylation, of diaminomethylboranes 202
 $RuHCl(CO)(PCy_3)_2$ -catalyzed silylation 173
Ruppert–Prakash reagent 224–225
ruthenium–thiolate complex catalyzed reactions 128
ruthenium thiolate complex-catalyzed regioselective silylation, of N-methylindoles 192
- S**
scaffolding catalyst 469–471
σ-donors 334, 439, 449
secondary interaction between silicon and hydrogen atoms (SISHA) 422
secondary silyl alcohols 479
selective cross-metathesis, of C–Si/Si–H bonds 59, 60
1,4-selective hydrosilylation, of pyridines 126–127
semi-hydrogenation, of alkynes 454, 457
separation of stereoisomers, of chiral silicon molecules classification 498–499
kinetic resolution of enantiomers 500–502
silicon epimers 499–500
shell higher olefin process (SHOP) 431
 $SiCl_4$ -mediated allylation 376
 $SiF_4\cdot 2NH_3$ complex 333
Sigamide 342, 343
(EtO_3)₂SiH 420–427
(MeO_3)₂SiH 431
Si–H bond activation 106
silacyclobutanes 198, 199, 296, 297, 511
silacyclopentane triols 523, 528
silafluorenes 59, 230
Sila–Friedel–Crafts type reactions 58–61
silaindenes 59, 217, 230
silane alcoholysis 87–88
silane carboxylic acid 13, 303
silanediols 291–292
silanes discovery and history of 33
vs. hydrocarbons 34–35
silane σ-complexes 87, 101, 107
silanolates 289–293
silanols 289–293, 297, 519, 522
silatranes 336
silicon-activated substrate, external non coordinated-nucleophile aldehydes, allylation of, by silicon tetrachloride 376–378
aldol reactions, trialkylsilyl enol ether derivatives 378–379
aldol reactions, trialkylsilyl ketene acetals 379, 381–382
silicon-based cross-coupling reaction 288, 323
Silicon-based Lewis acids 333
silicon cation-promoted arylation of aliphatic C–H bonds 152
of C(sp²)–H bonds 151
of C(sp³)–H bonds 151
silicon cation-promoted C(sp²)–F bond activation 146, 148–149
silicon cation-promoted C–H silylation, of electron-rich (hetero) arenes 154
silicon cation-promoted deoxygenation, of carbonyl compounds 132–133
silicon cation-promoted hydrosilylation of alkenes 135
benzosiloles preparation 136, 138
of C–X multiple bonds 136
reduction of imines 134
of silatetralins synthesis 136, 137
silicon-containing polymers 57

- silicone polymers 418
 silicon–halogen bonds 241
 oxidative addition
 to iridium and rhodium complexes 243–244
 to palladium complexes 242–243
 to platinum complexes 242
 silicon–hydrogen (Si–H) bonds
 aluminium Lewis acids 72–73
 boron Lewis acids 36–40
 group 14 Lewis acids 73–75
 phosphorous based Lewis acids 75–76
 stability of 35
 silicon nucleophile, catalytic
 generation of
 copper catalysts 2
 Lewis-base catalysts 23–25
 nickel catalysts 22–23
 representative pathways for 2
 rhodium catalysts 21–22
 silicon 3p orbitals 334
 siloxy-tethered diene, ring-closing
 metathesis of 289
 silylated nucleophiles 45, 460
 silylative dehalogenation, of
 organohalides 54–55
 silylative deoxygenation, of alcohols and ethers 47–54
 silylative desymmetrization
 of *meso*-diols 468, 482
 silylative kinetic resolution 473, 474, 477–481, 487
 silylative *meso*-diol
 desymmetrization 470
 silylative reduction
 of furans 53
 of monosaccharides 48
 1-silyl-butadienes synthesis 300
 silyl chlorohydrin formation 366
 silylene-based mechanism 91
 silylene–Co(I) complex 444
 silylene ligands 439, 443, 451, 456
 silylene–metal complexes 440, 446, 452
 silylene–Ni complex 442, 443
 silylene–Pd(II) complex 441
 silylene–Rh(I) and –Ir(I) complexes 454
 silylenes ligands, in catalysis
 carbon–carbon bond-forming
 reactions 439, 441, 443–444
 carbon–heteroatom bond-forming
 reactions 445, 447–450
 reduction reactions 451–456
 silyl enol ethers 56, 101, 125, 373, 379
 silyl–Heck reactions 245–246
 allylsilanes formation 250
 allyl/vinyl ratio 253
 chlorosilanes utilization 249
 electron-rich ligands 250
 improved conditions 247–252
 with [(JessePhos)PdI₂]₂ 257
 ligand identification 248
 ligand/metal ratio 254
 mechanistic
 considerations 252–254
 multi-component coupling 246–247
 nickel-catalyzed 260, 262–263
 non-styrenyl, alkene substrates
 in 250
 palladium precatalysts 254
 with (JessePhos)₂PdCl₂ 257
 (alkyl)(diaryl)phosphines 254
 with second-generation ligand 252
 silyl ethers and disiloxanes
 formation 258–260
 with styrene substrates 249
 of tert-butyl-substituted
 alkene 253
 vinylsilanes kinetic stability 252
 silylium ion-promoted Mukaiyama aldol reaction 165
 silylium ions 35–36, 73–76, 121, 123, 127
 silyl ketene acetals 163, 167, 379–382, 385
 silyl ketene imines 385–387
 silyl–Kumada–Corriu reactions 267–268
 silyl–Negishi reactions 263–267
 silyloxonium ion-promoted asymmetric reaction
 Hosomi–Sakurai reaction 166
 Mukaiyama–Michael reaction 164

- single electron transfer (SET) process 13 type mechanism 230 S_N2' displacement of silyloxonium ions 67–68 Sonogashira coupling, of phenylacetylene 442 Sonogashira cross-coupling reaction 442 sp^3d hybridization 334 *S*-phenyl thioesters 395 stereochemical efficiency 343, 347, 363, 375, 379 stereochemical integrity 352, 482 stereochemical model, benzaldehyde 381 stereoselective bisvinylogous aldol additions 386 stereoselective hydrosilylation, of alkynyl ketones 43 stereoselective transfer semi-hydrogenation 454, 457 stereoselective transformation, of chiral silicon molecules 515 electrophilic substitution 518–519 multistep functionalization 521–523 nucleophilic substitution 515–518 oxidation reactions 519 stereospecific copper-catalyzed silyl substitution, of alkyl triflates 14 stereospecificity 20, 361 Stoltz–Grubbs silylation system, electron and hydride transfer in 237 *s-trans* conformation 387 strong field ligands 418, 434 substrate (SB) 2, 3, 7, 19, 97, 111, 204, 218, 238, 336 sulfinamide phosphinate 346 sulfinamides 345, 346, 369 sulfonamides 361, 369, 371 sulfoxide moiety 369 sulfoxides 63, 361, 369 sulfur-stabilized silylum ions 121, 123, 127 Suzuki cross-coupling 439, 440 syn-adduct 361 syn aldol 371 syn diastereomer 371 *syn*-vicinal diol enantiomer 463
- t**
- Tamao–Fleming oxidation 55–57, 70, 258, 428 Tan's regiodivergent resolution, racemic 2-diols 1, 472 Tan's “scaffolding catalyst,” 469 470 Tan's silylative *meso*-diol desymmetrization 470 *t*-butyldimethyl silyl chloride 461 *t*-butyldimethylsilyl chlorides 459 *t*-butyldimethylsilyloxy group (TBDMS) 305, 459, 460 2,2';6,2”-terpyridine 420 *tert*-butyltrichlorosilane 483 tertiary amide hydrosilylation 100 tertiary hydrosilanes 419–422, 424, 427 tetrachlorosilane 336, 353, 355, 358, 379 tetradentate nitrogen ligand 432 tetraorganosilicon reagents 296 titanocene sulfido complex 119–120 tosylates, chemoselective defunctionalization of 53 *trans*-1,2-diols 471 *trans*-2,5-diphenyl-pyrrolidine *N*-oxide 369 transition metal-catalyzed cross-coupling reaction 271 transition metal-catalyzed direct silylation C(sp)–H bond silylation 171–174 C(sp²)–H bond silylation 174–198 C(sp³)–H bond silylation 198–207 transition-metal-free catalytic C–H silylation 213, 222 transition states, phosphoramides 365 trialkyl phosphites 389 trialkylsilanes 187, 304–313, 323, 419, 427, 488 trichlorosilane 338, 345, 347–349

- trichlorosilane mediated C=N reductions 346
- trichlorosilyl derivatives, of enolates 371
- trichlorosilyl enol ethers 372–373, 375, 390, 394, 395
- trichlorosilyl ether 371, 376
- tri-coordinate silylium ions 73–75
- triethyl(trifluoromethyl)silane 309
- trifluoroethyl thioesters 395
- trifluoromethylated cyclic silyl ether 320
- triisopropylsilyl ketene imines 386
- trimethylsilyl enol ethers 379
- trimethylsilyl-HOMSi reagent 318
- triphenylbenzene 443
- triphenylmethyl ion (trityl cation) 73
- tris(pentafluorophenyl)alane Al(C₆F₅)₃ (ACF) 72
- tris(pentafluorophenyl)borane (BCF) 36
- electrophilic C–C multiple bond activation 70–71
 - in polymerization 71
- tris(pentafluorophenyl)silanes 336
- tris(trimethylsilyl)silyl (TTMSS) group 275
- 1,2,4-trivinylcyclohexane 420
- tunable hydrosilylative reduction of nitriles 42
- turnover frequency (TOF) 87, 419, 428, 454
- turnover number (TON) 108, 140, 142–144, 174, 276, 420, 454, 481
- two-electron redox process 418, 434
- U**
- uncatalyzed reaction 373
- unsymmetric diarylmethanes 301
- V**
- valence shell electron pair repulsion (VSPER) model 335
- vicinal diol 50, 381, 463
- vinylogous aldol addition 382–385
- vinylsilanes 183, 241, 245, 303
- vinyl(β-methallyldimethyl)silanes 297
- W**
- ω-bonding 335
- Wiskur's Mukaiyama aldol/silylative kinetic resolution 473
- Z**
- (Z)-crotylsilane 361
- Z enolates 375
- Zhen–Chang mechanism 92, 93
- zinc fluoride 361
- zinc transmetalating agents 247
- Z-ketene acetals 381
- Z-trichlorosilyl enolates 375
- Z-vinylsilanes 185