

Index

a

- acetophenone 203, 212, 213, 221, 339
 acetylene 175, 214, 243
 activated alkene 31, 53, 54, 95–97, 99, 102, 114, 117, 181, 182, 184, 194, 195, 334
 activation barrier 123, 170, 175, 240
 1,2-additions 44, 101, 109, 215, 294, 318
 1,4-addition 101, 106, 215, 291, 292, 315–318, 326, 328–331, 337–338, 340–341
 Ae amide catalyst 186
 Ae catalyzed hydrogenation 187
 AeN₂ catalysts 196
 aggregation 10, 11, 13, 14, 189, 283–284
 agostic interaction 12
 alcoholysis 243
 aldehydes 93, 95, 96, 116, 201–203, 207, 208, 215, 220, 221, 314, 318, 339
 aldol reaction 339
 alkalide salt 16
 alkaline earth metals
 general 1–17
 alkenes 32, 53, 201, 203, 205, 207, 212, 334, 336
 activated alkene
 styrene 95, 97
 butadiene 31–54
 hydroamination 268, 271, 273, 274
 alkene hydrophosphination
 nitrogen-based ligands 97–110
 oxygen-based ligands 110–112
 alkene polymerization
 of modified styrene 40–43
 styrene polymerization 33–40
 alkenylamines 124, 125
 alkenylboron 315
 alkenylboronic acid 315
 alkenyl oximes 73
 alkenylphosphanes 135
 alkoxide 97, 110, 328, 331
 ligands 213
 alkoxylation 319, 321
 alkylboranes 203
 alkyl enol ethers 318
 alkyllithium reagents 3
 alkynes 60, 62, 63, 201, 203, 205, 207, 213
 alkyne metalation 213
 alkynyl alcohols 353
 hydroalkoxylation of 353–354
 α -amino- β -hydroxy esters 318
 α -aminoesters 326
 α -amino phosphine oxides 319
 α -chlorodiketones 319
 α -halo- α -amino ester 319
 α -hydroxy carbonyl compound 323
 α isosparteine 252
 α -isothiocyanate esters 338
 α -isothiocyanato 318
 α -ketoesters 315, 319, 334
 α -Me-styrene 108, 109, 112, 252
 α -methyl styrene 186
 α , β -dimamino acid 319
 α , β -unsaturated carbonyl
 compounds 291–292, 294, 315, 326, 328, 338

- α , β -unsaturated esters 115, 265, 267, 316, 318
 - α , β -unsaturated ketones 115, 267, 316
 - aluminate-catalyzed hydroboration 209–214
 - amide 229, 231, 241
 - reduction 221
 - amidinatocalcium complex 365
 - amidoborane 228, 229, 231–234, 236
 - amination 83, 300, 323, 333, 334
 - amines 321, 328, 329, 338
 - amine borane 228–230, 238, 245
 - 1:2 amine/silane reactions 239, 240
 - amino alcohols 318
 - aminoalkenes 60, 61, 65, 68, 71, 74, 76, 78, 254, 265, 324
 - aminoborane 227, 228, 231, 232, 236, 245, 365
 - aminolysis 228, 229, 237–239, 241
 - aminoalkenes 60, 61, 65
 - aminooxylation 323
 - aminotroponimate 78
 - ammonia borane 227, 228
 - anagostic interacton 13
 - ANDEN 266
 - anionic polymerization 34
 - anion metathesis 300
 - α -nitroacrylate esters 291
 - α -nitrogen 232
 - anti*-Markovnikoff 153, 156, 157, 159, 160
 - anti-Markovnikov products 104, 157, 201, 208
 - anti*-selectivities 338
 - α -olefins 153
 - Arrhenius analysis 105
 - arylcalcium 2, 4, 5
 - arylglycine 323
 - aryloxide 331
 - arylsilanes 239
 - asymmetric synthesis 311
 - atom economical 312
 - aza*-Darzens 319
 - azametallacyclopropane complexes 238
 - aza*-Michael addition cyclization 291
 - aza*-Morita–Baylis–Hillman-type products 340
 - aza*-Piancatelli reaction 302, 303
 - aziridine 314, 319, 321, 322, 333, 337
 - azlactones 331
 - azodicarboxylates 323, 333
- b**
- Bakelite 31
 - balanced reactivity 289
 - Baldwin rules 272
 - β -amino esters 319
 - barium phenoxide 339
 - base-catalyzed hydrogenation of ketones 194
 - Bayer–Villinger Oxidation 294
 - β -diketimate ligand 7, 16, 48, 49, 51, 52, 157, 178
 - benzophenone 191, 193, 210–213, 295
 - benzyl complexes 179, 355
 - Bergman cyclization 131
 - Bernoullian statistics 37
 - β -diketimate calcium hydride catalyst 163
 - β -hydride elimination 229, 231–234
 - β -hydride elimination/addition reaction 21
 - β -hydride transfer 228, 241
 - bimetallic 52, 85, 263, 352
 - BINAM 257–259, 273, 274
 - binaphtholate (BINOL) 115, 272, 316
 - BINOL 265, 273, 315, 316, 319, 321, 326, 331
 - biocompatibility 17, 53, 251
 - biodegradable plastic 45
 - bis(sulfonamide) 323, 337
 - bis(oxazolinyphenyl)amide (BOPA) 84, 271
 - bis(trimethylsilyl)amide 65, 74, 75, 79, 87, 136, 137, 252, 324, 340, 353, 365
 - bis(imidazolin-2-ylidene-1-yl)borate and triazenide complexes 79
 - 1,4-bis(diphenylphosphanyl)buta-1,3-dienes 136, 137

- bis(diphenylphosphanyl)butadienes
135, 136
- bis(1-imidazolyl)methane (BIM) based
calcium complexes 270
- 2,5-bis *N*-(2,6-diisopropylphenyl)
iminomethyl pyrrolyl complexes
78, 79
- bisoxazoline (BOX) 252, 269, 270,
313–315, 326, 328, 336
- β -ketoesters 323, 326, 334
- β -ketothioesters 331
- β -naphthols 316, 322
- ^{11}B NMR spectroscopy 202, 208
- bond activation 351
- bond dissociation energies (BDEs)
225, 226
- 9-borabicyclo[3.3.1]nonane 201, 235
- boranes 201, 202, 204, 205, 212, 215,
228
- borates 202, 218, 283
- borazine 228, 229, 235
- borohydride 201, 202, 207, 221, 236,
237
- boronate esters 201, 208, 212
- β -phenyl-substituted β -lactam 319
- Brassard's dienes 314
- bromination 333, 334
- Brønsted acid 62, 143, 144, 185, 265,
287
- Brønsted base 255, 267, 311–313, 324,
339, 341
- butadiynes 126, 128, 130–134, 145
- C**
- Ca(HMDS)₂ 324, 334, 336
- Ca(O^{*i*}Pr)₂ 324
- Ca Grignard reagents 5
- (Me₄TACD)₂Ca₂H₃⁺ 182
- calcium alkoxide 326, 331
- calcium amidoborane complex 233
- calcium anilides 236
- calcium-based catalysts
dianionic chiral ligands 273–275
monoanionic chiral ligands
269–173
- calcium complex, enantioselective
reactions
1,4-addition reactions 326–331
carbonyl compounds 324–326
with carbonyl compounds 333–334
cycloaddition reactions 334
epoxidation reactions 336
hydroamination reaction 334–336
with imines 331–333
ring-opening reactions of aziridines
337
- calcium dibenzyl 238
- calcium hexafluoroisopropoxide 293
- calcium hydrides 359
- calcium propargyl amidinates 356
- carbodiimides 112, 113, 117, 128, 137,
144, 145, 201, 215
- carbonyl-ene reactions 326
- carbonyls 201, 202, 205, 207, 208, 214,
219, 221
- cascade 315, 316, 318, 319
- (DMAT)₂Ca-(THF)₂ 179, 186, 188,
195
- cationic Me₃TACD-stabilized calcium
hydride complex 181
- C–H bond functionalization 243
- C(sp³)–H bond functionalization 324
- chiral 64, 69, 70, 83, 84, 251, 252, 263,
269
- chiral barium complex, enantioselective
reactions
1, 4-addition reactions 340–341
carbonyl compounds and imines
339–340
Diels–Alder reaction 341
- chiral calcium chloride–polymer-
supported Pybox (PS-Pybox)
complex 329
- C=N double bonds 187–192
- C–O bond cleavage 201, 217, 218, 299,
303
- C=O double bonds 191–194
- Cold Spray Ionization Mass
Spectrometry (CSI-MS) 326
- Complex-Induced-Proximity-Effect
(CIPE) 3
- computational analysis 240–242,
303–306, 349
- concerted cycloaddition 314

- conjugated diene 95–97, 101, 106, 117
 contact ion pair (CIP) 162, 213, 284
 continuous-flow 329, 330, 342
 (*R*)-convolutamydine 318
 coordination number 12, 95, 241, 281
 copolymerization 31, 40, 50, 51, 53
 counter anions 280, 282, 283, 285, 287,
 290, 307
 cross-coupling 93, 225, 242, 250
 cross-dehydrocoupling 226
 cross-dehydropolymerization 226, 243
 cyanosilylation 365
 cyclic diaminoboranes 231
 cyclic dimer 231, 232, 235
 [4+2] cycloaddition 334, 335
 [3+2] cycloaddition reactions 314,
 326, 328
 cycloheptatetraenes 131–133
 cyclohexadiene 156, 181, 186, 194,
 314
 cycloisomerization 303, 304, 307
 cyclopentadienyl 64, 87
 cyclopentenone 324
 cyclopropane 295, 303, 314, 322
 cyclopropyl carbinols 303
- d**
- Danishefsky's diene 314
 Darzens reaction 319
 daunomycin 323
 DBFox 319
 dearomatization 23, 81, 167, 316, 322
 dehydrocoupling 225, 226, 250, 349,
 362, 363
 dehydrogenation 185, 186, 225, 228,
 229, 235
 dehydrogenative aminolysis 228, 231,
 237, 241
 dehydrogenative coupling 19
 dehydropolymerization 225, 226, 243
 dehydroxylation 299–302, 305
 density functional theory (DFT) 15,
 21, 73, 100, 168, 170, 191, 195,
 233, 237
 methods 208
 study 359
- deoxygenation of C–O 358–361
 deprotonation 3, 4, 8, 19, 20, 22, 62,
 63, 68, 69, 71, 73, 83
 deprotonation/reprotonation equilibria
 106
 desilacoupling 245, 364
 desymmetrization 322
 Δ -hydrides 232
 Δ -hydride elimination 232–234
 dialkylphosphite 115, 116
 diamine boranes 231
 diaminoboranes 229, 231, 232
 1,2-dianilinoethane 127
 dianionic chiral ligands 257–259,
 266–269
 diarylcarbodiimides 137
 diastereoselective 23, 69, 177, 260,
 300–302, 328, 333
 diastereoselectivity 71, 73, 301, 303,
 338, 357
 1,4-Diazabicyclo[2.2.2]octane (DABCO)
 256
 1,3,2-diazaborinanes 231
 1,3,2-diazaborolidines 231
 1,3-diazadisilacyclobutane 210
 1,3,2,4-diazadisiletidine (Ph₂SiNBn)₂
 242
 dibenzylcalcium 5, 159
 diborane 201, 246, 366
 Diels-Alder reaction 295–296, 313,
 314, 341
 1,3-dienes 70, 71, 136, 303
 1,3-diester 319
 diffusion ordered NMR spectroscopy
 (DOSY) 14, 189, 213, 215
 4-dihydropyridide dimer 231
 1,4-dihydropyridine 167
 diisopropylamine 69, 70, 253
 2,6-diisopropylaniline (Dipp-NH₂)
 130
 1,3-di-isopropylcarbodiimide
 356
 dimethylamine borane (DMAB) 227,
 228, 231–234
 2-dimethylamino- α -trimethylsilyl-
 benzyl (DMAT) 33, 155, 179

- 2,2-dimethylpent-4-en-1-amine 81, 252
- dinuclear calcium
 amido-fluoroalkoxides 111
- dinuclear hydrido borohydride complex 237
- 1,3-diorganocarbodiimides 356
- 1,4-dioxane 263
- diphenylacetylene 125, 134–136, 139, 211
- diphenylbutadiyne 126–129, 131
- 1,1,-diphenylethylene (DPE) 36, 112, 156, 181, 182, 186
- 1,2-diphenylethylenediamine 337
- diphenylmagnesium 266
- diphenylphosphane oxides 138–140, 142, 145
- diphenylphosphine 96, 101, 266, 321
- 1,3-dipolar cycloaddition reaction 313–314
- [(DIPPnacnac)CaH-(THF)]₂ 178, 179
- [(DippNacNac)CaH-(THF)]₂ 178, 179
- DippNacNac ligand 76
- direct aldol reactions 339
- 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) 287
- diynols 304
- domino Mannich/cyclization reaction 319
- donor-acceptor cyclopropanes 294–295
- d-orbitals 1, 13, 21, 175, 178
- double bond polarization 287
- double metal cyanide 51
- double Michael addition 293
- dynamic kinetic resolution 314
- e**
- electron-deficient 9, 12
- electronegativity 9, 13, 296, 348
- electron paramagnetic resonance (EPR) 361
- electron-poor silanes 170, 239
- electrospray ionization (ESI) 265, 362
- electron-withdrawing 16, 72, 105, 109, 118, 236, 239, 240, 242
- electrophilicity 163, 183, 207, 290
- electrostatic bonding model 10
- element–hydrogen bonds 205–207
- enamides 333
- enamines 59, 124, 292–293
- enaminones 124
- enantioselective catalysis 23, 24, 84, 96, 251, 263
- enecarbamates 333
- ene-reactions 318
- enolate 115, 213, 256, 326, 331
- enolization 163, 164, 287, 290, 294
- enthalpy 203, 205, 206, 237
- entropy 60, 61, 68, 205, 237, 240
- epoxidation 324, 325, 336
- epoxide 50–53, 243, 255, 297, 321, 336
- equilibrium 16, 51, 52, 61, 66, 142, 144, 164, 178, 230, 237
- (-)-erythroccamide B 318
- esters 154, 162, 201, 203, 207, 208, 214, 217–220
- ethyl diazoacetate 318, 319
- ethynylamidine 356
- Eyring analysis 240
- E/Z*-isomerization 128, 131, 141, 145
- f**
- fluorinated 3-phenyl hydrotris (indazolyl)borate ligand 81
- Frankland 2
- Friedel–Crafts alkylation 298, 300, 322
- Friedel–Crafts reactions 290, 315, 326, 327
- Friedel–Crafts sulfonylation 298
- frustrated Lewis pairs (FLPs) 177, 228, 283
- functional group tolerance 21, 23, 24, 154, 194, 238, 286, 287
- g**
- γ , δ -alkenyl *N*-benzyl-hydrazones 73
- γ -deprotonation 316
- γ -functionalizations 316
- Grignard reagents 4, 5, 15, 64, 178, 269, 362, 363

h

- Haber–Bosch ammonia synthesis 31
 Hammett analysis 240
 Hammett's law 41
 hard-soft-acid-base (HSAB) 3, 281
 hemiacetals 318
 heteroaromatic 208, 236, 243, 244, 361
 heterobimetallic 53, 126, 195, 196
 hetero-Diels–Alder reactions 296, 314, 334
 heterodienes 334
 heterogeneous catalysis 24
 heterogeneous catalyst 51, 175, 330, 342
 heteroleptic 232, 238–241, 263, 264, 266, 267, 269, 270, 274
 heterometallic 68, 85, 86
 heteronuclear 225
 heteroscorpionate 49, 263, 272
 hexadimethylsilazane (HMDS) 298
 hexafluoropropanol (HFIP) 85, 303–306
 hexamethylphosphoramide (HMPA) 180, 256
 Hidden Brønsted Acid 287, 307
 homo-dehydrocoupling 226
 homo-dehydropolymerization 226
 homodinuclear 225
 homoleptic 65, 74, 75, 78, 84, 180, 238, 239, 245, 263, 269, 271
 HOMO/LUMO 175, 176
 HRMS 322
 2-hydrazinoketone 333
 hydrazone 73
 hydride 164, 181, 225, 228, 229, 230, 237, 244
 hydride shift 300, 324
 [1, 5]-hydride shift 324
 hydridoborate 209–214, 219
 hydroalkoxylation 306, 353–354
 hydroamination (HAs) 19–22, 124, 125, 127, 130, 131, 252–254, 257–260, 263–274, 324, 325, 334, 336
 aminoalkenes and-alkynes 61
 butadiynes 130–134
 early transition metals 63
 EMGM catalysis 65, 66, 68
 group 2 asymmetric
 cyclohydroamination 83–84
 group 1-based catalysis
 concerted reaction 68–71
 N-arylhydrazones and ketoximes 72–74
 radical-mediated intramolecular hydroamination 71–72
 group 2-based catalysis 74–83
 late transition metals 62, 63
 Lewis acidic metal cation catalysis 84–85
 mechanism 100
 nucleophilic attack 60
 with primary amines 128–130
 rare earth metals 63
 regioisomers 61
 with secondary amines 125–128
 Thorpe–Ingold effect 61
 hydroboration 19–21, 201, 202, 209–214, 358, 359, 361, 365
 base-catalyzed hydroborations 208–209
 β-diketimate magnesium-catalyzed hydroborations 215–217
 magnesium triphenylborate-catalyzed hydroboration 221
 mechanism 201
 supported catalysts 221
 tris(4,4-dimethyl-2-oxazolinyl)phenylborate 217–221
 unsaturated fatty esters 202
 hydroelementations 93, 96, 123, 124, 143–145, 205, 215
 hydrofunctionalization 123, 124, 131, 143–145, 306
 hydrogenation 19, 201, 203
 C=C double bonds 178–185
 C=N double bonds 187–192
 C=O double bonds 191–194
 hydrogen peroxide 336
 hydrogen storage 229
 hydrolysis 74, 162, 191, 201, 203, 265, 284, 294, 299, 357
 hydrolysis constant pK_h 284, 299

- 1,4-hydrophospanylation 267
hydrophospanylation 93, 124, 134, 136, 138, 142, 143
 alkenes and alkynes 135
 anti-Markovnikov products 135
 moderate reaction conditions 135
 1-phenylpropyne 135
 vinylphosphanes 134
1,2-hydrophospanylation 267
hydrophosphination 19, 20, 79, 94, 101, 124, 134
hydrophosphinylation 93, 95, 114, 116, 117, 318
1,4-hydrophosphinylation 115, 318
hydrophosphonylation 93, 95, 96, 116, 124, 138, 318, 319
 aldehydes and ketones 116–117
hydrophosphorylation 93, 124, 138, 143, 144
hydrosilylation 19, 203, 334, 358, 360
 C=C bond 155–161
 C=N bond 167–170
 C=O bond 161–167
 enantioselective 170
 history 151–153
 with non-precious metals 153–155
 with s-block metals 155–161
hydroxy diazoacetates 319
hydroxylation 323
- i**
- imidazoline-phosphonate 337
imines 151, 155, 167, 169, 170, 201, 203, 205, 207, 208, 216, 221, 292, 319, 320, 331, 333, 338, 339
imine hydrosilylation 151, 155, 167, 169, 170
imino-anilido precatalysts 101, 106
immobilization 329, 330
indoles 314, 315, 322, 331, 340, 341
inhibition 72, 237, 354
initiators 31–33, 35–41, 44, 47–49, 53
intramolecular cyclization 61, 242
intramolecular hydroamination of
 alkenes 59–87
ionic 9, 10, 12, 14, 35, 50, 64, 65, 76, 225, 244, 280, 281, 285, 324
ionic potential 281, 285, 286
ionic radius 14, 76, 95, 280, 281, 285, 313, 324, 337, 339
isatins 314
isocyanates 128, 145, 215, 352–353, 359
isocyanate trimerisation 352–353
isomerization 44, 68, 69, 73, 77, 137, 153, 167, 304, 340, 354
isoprene 31, 33, 43–45, 98, 106
isothiocyanates 128
- k**
- Karstedt catalyst 152–154
ketimines 188, 215, 216
ketoamides 323
ketoesters 315, 319, 323, 326, 334
ketoimines 338
ketone 95, 96, 115, 116, 151, 154, 158, 161–165, 170, 201–204, 207–209, 213, 215, 221
ketone hydrosilylation 155, 158, 163, 164
kinetic isotope effect 160, 193, 234
kinetics 3, 4, 105, 109, 216, 218, 240, 241
Knoevenagel condensation 290
- l**
- lactones 217, 314
lanthanide 63, 64, 66, 67, 76, 78, 311
lanthanide catalyzed alkene
 hydrogenation 177
lanthanum 219, 220
Lewis acid 17–19, 106, 151, 166, 178, 201, 251, 279–288, 293–297
Lewis acid B(C₆F₅)₃ 166, 178
Lewis acid/Brønsted base cooperative
 311–313, 324, 339, 341
Lewis acid catalysis
 alkaline and alkaline earth metals
 285–287
 bond dissociation energy 281
 chiral magnesium complex,
 enantioselective reactions 313
 counter anions 282–283

- Lewis acid catalysis (*contd.*)
- counter cations 279
 - Lewis base–metal interaction 281–282
 - polarized carbon–heteroatom double bonds
 - aldehydes, ketones, and formates 289–290
 - anhydrides and carbonates 288–289
 - α,β -unsaturated carbonyl compounds 291
 - Diels–Alder reaction and cycloaddition 295, 296
 - donor–acceptor cyclopropanes 294–295
 - imines and enamines 292–293
 - Mannich reactions 294
 - oxidation and reduction 294
 - polarized single bonds 296–297
 - s-block metals 280–281
 - solubility and aggregation 283–284
 - solvation 283
 - unpolarized double bonds 305–307
 - water tolerance 284–285
- Lewis acidity 231, 235, 279–285, 287, 294, 299, 302, 303, 307, 311, 312, 324, 331, 337, 339, 341
- ligand redistribution 65, 74–77, 79, 81, 83, 84, 96, 263, 269
- Li-halogen exchange 3
- Lipscomb 9
- Li-Sn exchange 3
- lithium-based catalysts
 - dianionic chiral ligands 257–259
 - monoanionic chiral ligands 255–257
 - neutral chiral ligands 252–254
- lithiumdiisopropylamide (LDA) 255
- lithium triphenylborohydride 221
- L-lactide polymerization 49
- Lochmann base 3, 4
- low-valent chemistry 1
- Luche reduction 294, 295
- m**
- Madelung constant 11
- magnesium amidoborane 233, 234, 236
- magnesium-based catalysts
 - dianionic chiral ligands 266–269
 - on monoanionic chiral ligands 263–266
- magnesium complex, enantioselective reactions
 - 1,4-addition reactions 315–318
 - carbonyl compounds 318–319, 323
 - with C(sp³)-H bond functionalization 324
- Diels–Alder and 1,3-dipolar cycloaddition reactions 313–314
- epoxide and aziridine reaction 321–322
 - with [1,5]-hydride shift 324
 - with imines 319–321
- magnesium fluoride 315
- magnesium Grignard 4
- magnesium iodide 314, 322
- magnesium isopropylamidoborane dimer 229
- magnesium-pyridinebisoxazoline (Pybox) 314
- magnesium triphenylborohydride 221
- magnesium tris(oxazolinyl)borate 238, 239, 241
- malonate 319, 326, 328, 330, 331, 337
- Mannich reactions 294, 319
- Mannich-type reaction 314, 319, 331–333, 338
- Markovnikoff and anti-Markovnikoff 61, 98, 101, 103, 106, 108, 110, 111, 117, 153, 156, 157, 159, 170
- mass spectroscopy 265, 271
- materials 225, 226, 228, 238, 244
- mechanism
 - ion-pair 164
 - metal hydride 165
 - silanide 159
- Meisenheimer anion (C₆H₇⁻) 195
- mesitylamine 129

- meso*-aziridines 322
meso-epoxides 321
 Me_4 TACD-stabilized cationic calcium hydride complex 182
 metal-exchange 3, 7, 13, 35
 metal-free imine hydrogenation 177
 metal hydride complexes 19
 metal-organic-chemical-vapor-deposition (MOCVD) 4
 metal–oxygen bonds 205–207
 metathesis 5, 6, 36, 63, 66, 76, 78, 98, 160, 219, 300, 348, 349, 364
 metathetical exchange 207
 methylalumoxane (MAO) 34
 1-methylimidazol 256
 methyl vinyl ketone 331
 Meyer–Schuster rearrangement 304
 Mg(I) complex 16, 197, 365
 Mg–Mg bond 16, 367
 Michael adduct 322
 monoanionic chiral ligands 255–257, 260–266, 269–273
 monomer 12, 13, 31, 38, 41, 47, 53, 237, 242
 monosilazane formation 239
 Morita–Baylis–Hillman reaction 324, 326
 Mukaiyama aldol 314
 Mulliken analysis 9
 multiple bond heterofunctionalization 349, 350
- n**
- N*-acyloxazolidinones 323
N-aryl-2,5-diphenylpyrroles 128, 132
 natural population analysis (NPA) 9, 17
 Nazarov cyclization 292, 303
N-benzylideneaniline 216
N-borylated methylamines 361
N-bromosuccinimide (NBS) 333
n-butyllithium (*n*-BuLi) 64, 68–71
N-Chlorosuccinimide (NCS) 333
 neutral chiral ligands 252–254, 269
 neutral tetradentate ligand Me_4 TACD 182
N-heterocyclic carbene 238
 nitriles 145, 201, 203, 207, 215, 217, 297, 300
 nitroalkenes 328–330
 nitrogen-based ligand 97–110, 117
 nitrone 73, 296
 nitrosocarbonyl compounds 323
N-methylephedrin 261
 NMR spectroscopy 14, 134, 142, 143, 189, 208, 213, 229, 231, 232
N,N'-dioxide 314, 316, 318, 322, 323
N,O-acetal 321
 nondirectional ionic bonding interactions 64
 non-innocent ligands 24, 197
 nonstabilized allenyl cations 303
 Noyori's Ru-catalyzed asymmetric hydrogenation of ketones 193
 nuclear magnetic resonance (NMR) 5, 37, 113, 134, 157, 202, 229, 256, 300
 nucleophilicity 1, 17, 71, 126, 146, 183, 210, 217, 241, 252, 258, 280, 288
 nucleophilic substitution 19, 297
- O**
- O*-arylhydroxylamine 339
 olefins 69, 94, 176, 252, 305, 306
 oligomeric products 180
 order in reactants 217, 236, 245
 organic isocyanates 128, 352–353, 357, 359, 361
 organocatalytic metal-free hydrogenation 177
 organometallics
 bonding and structure 8–13
 dynamics of 13–16
 future of 23–24
 group 1 synthesis 2–4
 group 2 synthesis 4–8
 history of 1–2
 Lewis acid catalysis 17–19
 s-block metal catalysis 19–21
 substrate activation, by s-block metals 21–23
 1,3-oxazinanes 321
 1,3-oxazolidine 321

- oxazoline 314
 - oxazoline-sulfoxide ligand 314
 - oxidant 294, 336, 363
 - oxidation state 16, 19, 62, 64, 159, 177, 280, 312, 358
 - oxygen-based ligand 110–112
 - oxyindole 333
- p**
- pentannulation product 322
 - phenolate 49, 79, 97, 110
 - phenol-oxazoline 316, 322
 - phenols 302, 315
 - phenoxide 311, 319, 326, 339
 - phenoxyamine 83, 324
 - phenylbut-1-yne-3-ene 126
 - phenylphosphinate 114
 - phenylphosphine 96
 - 3-phenylpropanal 324
 - 1-phenylpropyne 135
 - phosphane oxides 124, 138, 143, 144
 - phosphate 319, 321, 322, 331, 333–335, 339
 - phosphide 104, 105, 112
 - phosphination 93, 319, 321, 333
 - phosphine 93, 96, 98, 99, 105, 108, 109, 118, 245, 324, 326
 - phosphoric acid 315, 326, 331
 - phosphorous ylide 318
 - picolate 314
 - Pictet–Spengler reaction 293
 - pinacolborane 202, 235, 358–360
 - platinum black 153, 175
 - p*-methoxy styrene 186
 - polarity 9, 33, 65, 157, 205, 207, 225, 283, 287
 - polar silanes (R_3SiH) 196
 - polyaminoborane 228, 245
 - polybutadiene 43, 44
 - polycarbonates 50
 - polyfunctionalized furans 302
 - polylactide 45, 46, 48, 50
 - polymer 31, 32, 34, 37, 40, 41, 44–46, 49, 51, 53, 225, 226, 242
 - polymerization 101
 - alkene polymerization 43
 - anionic 31, 34, 40–42
 - atactic 34, 42
 - butadiene 43–45
 - coordination-insertion 34, 35, 39, 40
 - epoxide and CO_2 50–53
 - ethylene 32, 33
 - immortal 49
 - isoprene 43–45
 - isotactic 34
 - lactide 45, 48, 50
 - living 31–33, 35, 40
 - para-*t*Bu-styrene 41, 42
 - retarded anionic 32
 - ROCOP 50, 52, 53
 - stereoselective 40
 - styrene 33–40
 - syndiotactic 34, 47
 - vinylpyridine 42
 - polyoxygenates 32, 53
 - polysilazanes 238, 242–243, 245
 - polystyrene 33–38, 40–42, 156
 - potassium-based catalysts, monoanionic
 - chiral ligands 260
 - potassium thiocyanate (KSCN) 326
 - pre-equilibrium 231, 245
 - primary amine 74, 86, 128–130, 132, 134, 228
 - 2 propargylamidinate 358
 - protecting groups 243, 288
 - protodeborylation 201
 - protonation 19, 62, 63, 68, 125–127, 137, 253, 269, 272, 323, 330, 331
 - protonolysis 63, 66, 76, 77, 97, 98, 101, 264, 353, 356
 - proton transfer 83, 260, 268, 311, 312, 342
 - pseudo-intramolecular Lewis
 - acid/Brønsted base 312, 313, 324, 339, 341
 - pyranocoumarins 291
 - pyridine 21, 41, 42, 153, 167–169, 211, 214–216, 231, 232, 270
 - pyridine hydrosilylation 168, 169
 - pyridines 168, 201, 203, 211, 214–216
 - pyridylsulfonyl 337
 - pyrrolidines 230, 231, 238, 240, 257, 259, 272, 324
 - pyrroloindoline 314

q

quantitative deprotonation 69
 quaternary carbon stereocenters 338
 quinine–magnesium complex (type II)
 314

r

radical 71, 315
 pathway 244
 rate-determining step 51, 63, 76, 80,
 105, 145, 160, 218, 219, 234
 rate law 105, 110, 207, 216–219, 221,
 236, 240–243, 245
 rate-limiting 78, 100, 105, 113, 220,
 237, 241, 357
 reaction constant 240
 reaction mechanism 62, 65, 67, 72, 76,
 77, 80, 83, 226, 228
 reaction pathway 61, 129, 131, 202,
 205–208, 240, 260, 280, 360
 redox-transmetallation-protolysis
 (RTP) 8
 reduction 2, 5, 60, 137, 155, 161, 162,
 167, 178, 181, 186, 188, 190, 191,
 193, 196, 202, 221, 333
 regioisomers 61, 136
 regioselectivity 94, 101, 103, 106, 109,
 153, 156, 157, 159, 167, 202
 relative Lewis acidity 281
 reversible 227, 237, 239, 241
 rhodium complex 176
 ring-opening 294, 314, 321, 322, 337
 Rolipram 330

s

Salen 316, 338
 Salen–magnesium complex 316, 318
 salt metathesis synthesis 5, 6
 samarium–oxygen bond 206
 scandium 311
 Schiff base 49, 326
 Schlenk equilibrium 5, 15, 35, 36, 65,
 95, 96, 178, 263, 269, 274
 Schlenk, Wilhelm 2, 5, 15, 16, 24, 35,
 36, 48, 65, 74, 77, 79, 81, 83, 84,
 178, 263, 269, 272, 274
 Schlosser 4

Schwesinger base 21, 84, 272
 scorpionate ligand 49, 79, 263
 secondary amines 235, 238, 245
 Shvo/Noyori catalysts 189
 σ -bond 63, 66, 76
 σ -bond metathesis 98, 230, 237, 244,
 246
 σ -bond metathesis mechanism 179
 silanes 151, 153, 155, 156, 159, 161,
 162, 164, 167, 170, 225, 238, 243,
 245
 silanide 152, 157–160
 silazane 238, 241
 silicate 157, 158, 160–162, 164, 165,
 170, 241–244
 siloxide 111, 112
 siloxydiene 334, 341
 silver hexafluoroantimonate 314
 silylated nucleophile 322
 silylation 20, 153, 170, 244, 361, 362
 silylborane 244, 245
 single electron transfer (SET) 72, 347,
 361–363
 solubility 2, 5, 13, 145, 300
 solution dynamics 1
 solvation 44, 143, 193, 283
 solvent-free conditions 203, 212, 236,
 241
 solvent-separated ion pair (SSIP) 284
 solvent spheres 282
 sparteine 70, 252
 Speier catalyst 152
 spiroindole 316
 spiro lactones 314
 stereochemistry 43, 202, 333
 steric 6, 38, 63, 73, 76, 98, 113, 117,
 163, 235, 238, 239, 253, 283, 296
 stoichiometric reaction 21, 134, 160,
 163, 164, 166, 167, 236, 246, 256
 Strecker synthesis 292, 293
 strontium-catalyzed reaction 245
 strontium complex, enantioselective
 reactions
 1,4-addition reaction 337
 chiral 4-substituted cyclohexyldiene
 oximes 339
 with imines 338

- strontium hexamethyldisilazide 337
 strontium isopropoxide 337
 styrene derivative 94, 103
 styrene polymerization
 benzylcalcium initiator 40
 dilute cyclohexane solution 39
 DMAT ligand 36
 heteroleptic Ca initiators 37
 heteroleptic neutral LAeR complex 35
 homoleptic complex 35
 Lewis acidic species 34
 nBuLi initiator 34
 polystyrene tacticity 38
 Schlenk equilibrium 35
 steric control 38
 syndioselectivity of 37
 4-substituted cyclohexanones 257, 339
 4-substituted ketones 256
 substrate activation 21–23
 substrate scope 76, 156, 188, 191, 193, 197, 235, 236, 286, 303, 306
 sulfonylimidate 338
 superbases 2, 4
 symmetrical 230, 231
syn-diamino acid 319
 synthesis 2, 7
- t**
- Tamiflu[®] 341
 terminal olefins 69, 306
tert-butylamine 235
tert-butyl hydroperoxide 323, 324
 tertiary amine 311, 338
 tetradentate monoanionic ligand 181
 tetrahedral magnesium complex 314
 tetrahydrochromenones 291
 tetrahydropyran (THP) 5
 4,4,5,5-tetramethyl-1,3,2-dioxaborolane 202
 tetramethylethylenediamine (TMEDA) 32, 323
- tetrasubstituted chiral carbon stereocenters 318
 thermal decomposition 229
 thermal stability 233, 234
 thermochemistry 205–207
 thermodynamics 203–207, 234
 Thorpe–Ingold 61, 76, 84
 tight interaction 312
 Tishchenko coupling of aldehydes 352
 Tishchenko dimerization 351
 titanium alkoxide 221
 toluenesulfonamide 323
 toxic 63, 64, 311, 329
trans-amino ether 322
 transition metal 62, 63, 88, 93, 206, 311, 336, 341
 transition state 63, 66, 68, 69, 77, 80, 237
 tributyl phosphine 324, 326
 [6-6-5] tricyclic core 322
 triethylamine 202, 329
 trimethylsilyl enolates 256
 1,4,7-trimethyl-1,4,7,10-tetraazacyclododecane 181
 triphenylphosphine oxide 318
 tris(oxazoliny)borate 238, 239, 241
 turnover frequency (TOF) 76, 88, 207, 210
- u**
- unsaturated organic moiety 201
 unsymmetrical 230, 231, 246
- v**
- VAPOL phosphate 319, 322
 vicinal dihalides 261, 262
 vinylarene 96, 100, 101, 103–106, 108, 109
 vinyl ethers 334
 2-vinylpyridine 99–101
 2-vinyl-pyridine polymerization 41, 43

W

- Wanklyn 2
- water ligand exchange rate 14
- water tolerance 284–285
- weakly coordinating counteranion 30, 283, 284, 298, 305
- Wilkinson's catalyst 202
- Wittig-*oxa* Michael 318
- Wurtz coupling 2, 3

X

- X-ray diffraction methods 137

Y

- ytterbium 101, 136, 238
- yttrium 311

Z

- Ziegler, Karl 2
- Z-isomeric alkenyl-diphenylphosphanes 136
- zwitterionic 241

