

Index

a

- ABC system 94
 ABTS 266
p-acceptor complexes 194
p-acceptor ligand 194
 acetyl-uns-penp ligand 45
 acid-base equilibria 265
 acid-base titration 240
 acid-dependent rate constant 279
 acid-induced ring opening 137
 acrylglycolate 422
 – Diels-Alder reaction 422
 activation principles 23
 adduct dioxygen 46
 aerobic cobalt(II)-catalyzed oxidations 386
 – mass balancing 386
 aerobic monooxygenation 381
 aerobic oxidation(s) 385, 389, 390
 aerobic oxidative alkenol cyclization 385
 agostic alkenyl groups 172
 agostic complexes 96
 agostic interaction(s) 92, 93
 alcoholate coligands 422
 aliphatic olefins 321
 aliphatic thioether linkage 3
 allopyranoside ligands 150, 162
 allylic alcohols 105
 – reaction 105
 – mono-substituted 238
 amines methyl groups 157
 – ¹H NMR signals 157
 amino acid-bridged dicatechol ligands 420, 421
 – dinuclear titanium(IV) complexes 420
 aminoalkenes 153
 – intramolecular hydroamination 153
 ammonium salts 157
 ancillary ligand, *see* secondary protonation

 anhydrous iron(II) salts 100
 – iron(II) triflate 100
 anionic complexes 250
ansa-cycloheptatrienyl-cyclopentadienylss (Cht-Cp)complexes 135, 137
 – ring-opening polymerization 137
 – ring-opening reactions 135
 – Si–Pt-bridged 138
ansa-metallocene 210
 – allyl-substituted 210
ansa-zirconocene framework 210
ansa-zirconocene unit 214
 – planar-chiral 214
 antiallergic natural product 380
 – magnosalicin 380
anti-Bredt-bridgehead olefins 427
 aromatic *N*-heterocycles 183
 – role 183
 aromatic olefins 320, 321, 328, 330
 – epoxidation 320, 321
 – iron-catalyzed asymmetric epoxidation 330–331
 aromatic systems 185
 – large-surface 185
 artificial photolyase models 355
 aryl-pyrrole linkage 361
ate complex 366
 autoxidation products 388
 azamacrocyclic complexes 353
 – zinc(II) cyclen 353
 azide-alkynecycloaddition, *see* Huisgen reaction
 azido-nitrido complexes 280

b
 back-side approach 397
 – side chains 72
 bicyclic bridged complexes 192
 bidentate bridging ligand 150

- bifunctional *ansa*-zirconocene/trimethylene-9-BBN system 211
 - bifunctional Co/B complex 216
 - bifunctional Ir/B systems 224
 - bifunctional phosphorus/boron systems 223
 - bifunctional systems 210
 - bifunctional zirconium/boron systems 210
 - binding cavity(ies) 2, 12, 53
 - bowl-shaped 2, 53
 - directing effect 12
 - protecting effect 12
 - binding pocket(s) 5, 7, 9, 12, 13, 421
 - binucleating supporting ligands 2–5
 - coordination chemistry 4
 - metalated container molecules 2
 - structures 5
 - synthesis 3
 - bio-inspired approaches 315
 - biological systems 65, 315
 - co-enzymes 315
 - cytochrome oxygenases 315
 - hemoglobin 315
 - hydrogenase 315
 - iron-containing enzymes 315
 - myoglobin 315
 - non-heme oxygenases 315
 - biomimetic iron-catalyzed epoxidation 318
 - biomimetic ligand design 65
 - biomimetic non-heme Fe catalysts 325
 - biphasic system 67
 - 2,2'-bipyridines synthesis 432
 - bisazines 183, 185
 - molecular architectures 185
 - bis(2,2'-bipyridyl)-substituted 2,2'-dihydroxy-1,1'-binaphthyl (BINOL) 429
 - based ligand 439
 - MOM-protected 439
 - bis(chelating) ligands 430, 434
 - covalent assembly 430
 - dinuclear metal complexes 434
 - synthesis 434
 - 1,8-bis(hexamethylphosphazanyl)naphthalene (HMPN) 19, 20
 - bis-homoallylic alcohol(s) 392
 - cyclization 393
 - bispidine complexes 53
 - properties 53
 - tuning of structures 53
 - bispidine ligands 53, 54, 64
 - electronic properties 53
 - bis-pyrimidine cyclobutanes 352
 - bleaching process 302
 - p*-bonding ligands 90
 - bond dissociation energies (BDEs) 381
 - bond-formation process 257
 - bond valence sum (BVS) values 236
 - bridging ligands 183, 193
 - bridging motifs 90
 - bromine-magnesium exchange 367
 - Brønsted-basic groups 291
 - building block 430
 - buttressing effect 19
- C**
- CAB-process 379
 - calixarene-like structures 13
 - camphor-bound P450_{cam} 258, 260
 - active site coordination sphere 258
 - carbanion coordination 94
 - carbanionic iron(III) complex 96
 - carbanionic ligand 96
 - carbene ligands 112
 - carbohydrate ligand 148
 - carbohydrate-titanium compounds 151
 - β-carbon atom 281
 - carbon-fluorine bonds 166
 - carbonyl ligand 101
 - carbonyl ylides 301
 - carboxylate ligands 7
 - exchange of 7
 - carboxylato-bridged zinc complexes 6
 - catalyst system 77, 304
 - catalytic activation 360–366
 - catalytic ammonia synthesis 274
 - catalytic cycle 176, 245, 269, 275
 - steps 275
 - catalytic ethene polymerization 176–178
 - catalytic experiments 115
 - catalytic hydroaminomethylation 71
 - pentene 71
 - piperidine 71
 - styrene 71
 - catalytic hydrodefluorination 178
 - catalytic metal-mediated bond activation 359
 - catalytic oxidation cycle 266–271
 - catalytic oxidation processes 104, 262, 313, 397
 - catalytic reaction 352
 - mode 294
 - catalytic regioselective epoxide opening 398, 399
 - catalytic systems 329
 - catecholate complexes 43, 433
 - catechol dioxygenases 43
 - 1,2-dioxygenase activity 43, 44
 - C–C bonds 199, 203
 - coupled polynuclear complexes 199
 - formation reactions 199

- C–C coupling reactions 185, 192, 199, 202, 209
- C–H bond activation 297
- reactions 199, 202
 - molecular architectures 199
- C–H bond functionalizations 298
- directed 298
- C–F bond(s) 168, 171, 178
- activation 173, 177
 - catalytic hydrodefluorination 178
 - elementary steps 177
 - stoichiometric cleavage 171
- CD-data 341
- CD-pattern 344
- CD-signal 344
- CD-spectroscopy 340, 341, 343, 434
- CD-spectrum 344, 436
- chameleon character 434
- charge transfer process 261
- Chatt cycle 276, 280, 282, 285, 294
- DFT calculations 282–285
 - mechanistic investigation 276
 - N–N cleavage 278
 - protonation of N₂ 276
- Chatt system 282
- C–H bond(s) 92, 93, 228, 339, 374
- activation 173, 201, 203, 209, 298, 303, 361, 363, 375
 - functionalizations 297, 298
 - insertion reactions 301
 - oxidation(s) 298, 305
 - substitution pattern 361
- chelate ring 43
- chelating ligand units 433
- types 433
- chiral alcohols 405, 423
- REO for 405
 - synthesis 405
- chiral cavities 429, 430
- chiral cyclopentadienyl ligand 155
- chiral dirhodium complexes 298
- chiral ligands 432, 433, 435
- N-donor 432
 - structures 432
- chiral propargylamine 365
- conversion 365
- chiral ruthenium catalysts 316
- m*-chloroperoxybenzoic acid (*m*-CPBA) 264, 269
- chromophore's redox potential 350
- chromophoric bipyridine units 437
- cis-stilbene concentration 269
- C–P bond activation 91, 92
- cleft-type dinuclear complex 419, 423
- closed-shell host molecules 1
- cobalt complex 393
- concentrations 388
- cobalt method 379, 380
- cobalt(II)-catalyzed oxidations 379
- cobalt(II)-diketonate complexes 382
- coligands 7
- activation 7
 - coordination modes 7
 - variation 7
- combinatorial-activity approach 322
- combustion analysis 383
- complementary directing effects 371
- complex reaction mechanism 93, 245
- condensed heterocycles 362
- condensed polycyclic alkaloids
- preparation 360
 - C–H bond activation 360
- construction kit 66, 85
- coordination cap 89, 100
- square-pyramidal 89
- copper-analog rebound mechanism 30
- copper(I) helicates 440
- computer models 440
- copper(II) bispidine complexes 55, 58
- efficiency 58
 - thermodynamic properties 58
- coupling constant 225, 226, 289, 290
- crystallographic mirror plane 124
- C_s symmetry 237
- C₂-symmetrical ligands 341
- C_{2v} symmetry 92, 94, 97, 238
- Cu(I)/QUINAP complex 365
- cyanide nucleophile, *see* iminium salt trap
- cyclic azolium precursors 106
- cyclic polycarbene ligands 110
- cyclic tungstophosphate 241
- framework 235
 - precursor 235
- cycloheptatrienyl (Cht) ligands 123, 125
- metal interaction 126
- cycloheptatrienyl-cyclopentadienyl (Cht-Cp) complexes 123, 126, 140
- fragment 127
 - group preparation 124
 - metal moiety 143
 - rings 133, 141
- cycloheptatrienyl ring 131, 135
- cyclohexane 345
- oxidation 345
- cyclometalation 92
- cyclooctene 324
- derived oxidation products 59
 - epoxidation 324

- cyclopentadienyl ligand(s) 155, 186, 188
 – Cht rings 128
 – Cht-sandwich moieties 139, 140
 – preparation 140
 cyclopentadienyl ring systems 214, 215, 220
p-cymene ligand 233
 cytochrome C enzymes 18
 cytochrome P-450 245, 246, 254, 255, 258,
 260, 262–263, 271, 315
 – catalytic oxidation cycle 262
- d**
- d-block metal ions 231
 density functional theory calculations 381
 depe-dpepp complex 290
 deprotonation/alkylation sequences 112
 deprotonation reactions 368, 371
 – *ortho*-direction 371
 detoxification processes 339
 DFT-based analysis 60, 61, 132
 DFT calculations 25, 27, 55, 59, 160, 275, 276,
 288, 289, 318
 – GIAO calculations 288
 1,8-diaminonaphthalene (DMAN) 18, 19
 dianionic ligand 193, 194
 diaqua complex 247, 255
 diastereotopic interaction(s) 157, 158
 diazo ester 300
 – push-pull 300
 – photochemically activated 300
 – silylated 301
 diazo compounds 301
 dicatechol ligands 412
 dication structure 96, 97
 Diels-Alder adducts 12
 Diels-Alder products 12
 Diels-Alder reaction 10–12, 159, 412, 422, 423
 Diels-Alder reactivity 10
 differential scanning calorimetry (DSC) 135
 – studies 135
 different states of protonation 95
 diffusion-controlled reaction 349, 355
 dihedral angle 148
 β -diketone 382
 diketonate complexes 383
 diketonate ligand 383
 dimeric Cu/QUINAP complex 364
 dimethylformamide dimethylacetal
 (DMFDMA) 72
 dimethylphosphinite ligand 99
 dimethylsilanediyl-linked ligand system 210
 dinuclear complex 45, 49
 – chelate complexes 195
 – formation 45
 dinuclear helical metallocsupramolecular
 coordination compounds 427, 430
 – self-assembly 427, 430
 dinuclear helicates 429, 436
 – CD-spectra 436
 – diastereoselective self-assembly
 concept 429
 dinuclear iron peroxo complexes 40–42
 dinuclear sugar compound 154
 dinuclear titanium complexes 438
 dinuclear titanium(IV) complex(s) 418, 420,
 422
 dioxygen activation 39
 diphenyl *ansa*-zirconocene 214
 – allyl-substituted 214
 diphosphine ligands 104, 105, 285
 directed metalation group (DMG) 370, 371
 – chelation 370
 – polar 371
 dirhodium complexes 298
 di-*tert*-butylferrocenylphosphine ligand 142
 dissociative (D) mechanism 247, 250, 255
 divergent reactions of racemic mixtures, *see*
 parallel resolutions
 DNA 18, 340, 351, 429
 – lesions 351
 – oxidative cleavage 340
 – photolyase 351
 – repair systems 351
 – strands 351
 DNA photoprobes 203
 σ -donating *trans* ligands 287
 donor-acceptor distance 45
 σ -donor/ π -acceptor ligands 135
 driving force 117
- e**
- EDTA 350, 351
 eight-membered palladacycle 363
 electron-deficient polyfluorinated
 porphyrin 325
 electron donor-acceptor dyads 349
 electron-poor molecules 22
 electron-rich aromatic substrates 370
 electron transfer reactions 39
 electrophilic activation 297
 electrophilic substitution 179
 electro spray ionisation techniques 112
 enantiopure ligands 340, 420
 end-on copper dioxygen complex 25
 – molecular structure 25
 end-on superoxo iron complex 46
 epoxidation catalyst 314, 316
 – development by using H₂O₂ 314

epoxide opening 397
 – nucleophilic substitution 397
 epoxides manufacturing process 313
 – chlorohydrin process 314
 – direct oxidation process 314
 – hydrogen peroxide process 314
 – peroxidation process 314
 equilibrium-controlled processes 427
 Eschweiler–Clarke conditions 4
 ESI mass spectroscopy 27, 31, 149, 435
 – experiments 435
 – FT-ICR mass spectrometry 419
 ethylene polymerization 82, 152
 exchange reaction 157
 Eyring equation 43

f

F-bridged binuclear titanium complexes 171
 Fe(III) complexes 246, 260
 – NO activation 246–260
 – peroxide activation 260–271
 Federal Ministry of Education and Research 332
 Fe–O–Fe dimers 339
 Fe(III) porphyrin complexes 246–254, 260, 263–266
 Fe(III) systems 260
 ferrocene-containing compounds 123
 ferrocenophanes 139
 – metal-catalyzed polymerization 139
 ferrous κ -N-nitro complex 90
 five-membered metallacycles 170
 – reactions with B(C₆F₅)₃ 170
 – zirconacyclocumulenes 170
 flavin adenine dinucleotide (FAD) 349
 flavin chromophore 352
 flavin-containing peptides 352
 flavin isothiocyanate 354
 flavin mononucleotide (FMN) 349
 flavin photocatalysis 349, 351
 – substrate binding sites 349
 flavin photooxidations 353
 – templated 353
 – use 353
 flavin photoreductions 351
 – templated 351
 flavin redox cycle 350
 flexible triangular ligands 412
 fluoride effect 176
 force constants 281, 289
 force-field analysis 55, 61
 force field calculations 55, 57
 – electronically doped 55

free hydroxyl radical 319
 frontier orbitals 132

g

gas phase basicity (GB) 18
 gauche conformation 8
 gel permeation chromatography 82, 152, 153
 germanium–carbon bond 135
 German Science Foundation (DFG) 49, 62
 – priority program 17, 24, 26
 germylene-bridged *ansa*-complexes 131
 GIF systems 306
 glucopyranoside ligand(s) 148, 150, 162
 Grignard reagents 366
 guanidine copper complexes 24
 – chemistry 24–31
 guanidine functionality 17
 – properties 17
 guanidine ligand 34
 guanidine zinc complexes 31
 – chemistry 31

h

hafnium indenyl complexes 128
 halogen–magnesium exchange 366, 367
 – scope 366
 Heck coupling reaction 75–77
 – palladium-catalyzed 75, 76
 – products 77
 heteroaromatic carboxylic acids 368
 – functionalization 368
 heterocyclic building blocks 379
 heterocyclic ligands 193
 heterolysis 263, 267
 – acid-catalyzed 267
 hexaaza-dithiophenolate ligand 3
 hexaazatrinaphthylene (HATN) titanium complexes 200, 203
 – formation 200, 203
 – ligands 200
 highest occupied molecular orbitals (HOMO) 125, 133
 – LUMO gap 132
 high-pressure kinetic techniques 246
 high-spin complex 255, 260
 high-spin ferryl complex 59, 60
 – stabilization 59
 high-spin oxo-iron(IV) center 59
 high-spin pentacoordinate complex 61
 high-valent mononuclear oxo complexes 46
 homogeneous catalysis 65, 66, 123, 143, 349
 homogeneous catalyst 326
 homolysis 263
 host-guest chemistry 79, 411, 412, 417, 423

- host-guest interactions 2, 7
 - H₂pydic system 324
 - Huisgen reaction 353
 - hydrido borate system 223
 - hydroamination reactions 162
 - hydroboration reaction 218, 219
 - reagent 211
 - hydrodefluorination (HDF) 178
 - reaction 179
 - hydrogenation catalysts systems 228
 - hydrogen bond(s) 354, 427
 - donor 112
 - interaction 6, 48
 - network 31
 - hydrogen peroxide 314, 319, 320, 321, 325
 - oxidation 302
 - hydroperoxo complex 47
 - hydrophobic cavity 5
 - hydroxo-bridged complex 6
 - 2-hydroxyalkyl isocyanides, ligand 107, 108
 - hydroxy-ruthenium species 239
- i**
- imidazole derivatives 103
 - imidazole ligand 322
 - imido-azido systems 280
 - imido complexes 280
 - reactivity 280
 - iminium salts trap 159, 160
 - *in situ* synthesis 160
 - infrared spectroscopy(IR) 69, 346
 - spectrum 9, 217
 - in-situ* generated catalyst 321, 325
 - epoxidation 325
 - in-situ* generation method 321
 - intramolecular hydroamination reactions 154
 - intramolecular hydrogen bond (IHB) 18, 20, 34
 - interactions 23
 - ligand interactions 31
 - stabilized molecular complex 35
 - intrinsic proton affinity 21
 - iodine-magnesium exchange 367
 - functional group tolerance 367
 - iron catalysts 298, 313, 323
 - development 313
 - modification strategy 324
 - iron-catalyzed epoxidation systems 322, 329
 - iron-catalyzed oxidations 305, 306
 - iron-catalyzed oxidative transformations 307
 - iron complex(es) 39, 45, 49, 339
 - iron-containing enzymes 39, 339
 - dioxygen activation 39
 - heme proteins 339
 - iron-sulfur clusters 339
 - nonheme proteins 339
 - oxidases 39
 - oxygenases 39
 - iron dioxygen-activating enzymes 40
 - mechanisms 40
 - iron isothiocyanato complexes 286
 - iron-molybdenum cofactor 273
 - iron-oxo complex(es) 245, 262, 271
 - oxidation state 262
 - iron(III) complex(es) 41, 43
 - NO activation 245
 - peroxide activation 245
 - tetra-nuclear oxo-bridged 41
 - iron(IV) oxo compounds 48
 - D-isomannide-based ligand complexes 434
 - isocyanide ligand(s) 133
 - coordination 133
- j**
- Jacobsen's system 403
 - Jahn–Teller-distorted cobalt(III) complexes 61–62
 - Jahn–Teller isomerism 55
 - Jahn–Teller-type distortions 58, 62
- k**
- Keggin cluster anion 236
 - α-Keggin-type tungstosilicate 236
 - mono-ruthenium(III)-substituted 236
 - Keggin unit 236–238
 - kinetic isotope effect 302
 - kinetic resolutions 402
 - Krebs group 41
- l**
- lanthanide complex 235
 - latter system(s) 289, 290
 - Lewis acid(s) 71, 72, 79, 170, 180, 209
 - catalyst 209
 - induced tautomerization 211
 - interaction 80
 - Lewis acid–Lewis base pairs 21
 - Lewis-basic species 282
 - ligand-anion-solvent combinations 29
 - ligand development 77
 - ligand-enforced structures 57
 - ligand exchange reactions 6
 - ligand-field-derived energy term 57
 - ligand field effects 33
 - ligand framework 291
 - ligand generations 430
 - molecular building blocks 430

- ligand-ligand interactions 31
- ligand matrix 6
 - functions 6
- ligand self-organization 66
 - cooperative effects 66
- ligand system 76
- ligand-to-metal bonds 183
- ligand-to-metal charge transfer (LMCT) 132
- ligand-to-metal π -donation 125
- light-emitting diode 354
- lithium allylcyclopentadienide reagent 216
- lowest unoccupied molecular orbital (LUMO) 126, 128, 133
- low-valent titanium complexes 185, 195
 - corners 184
 - nitrogen complexes 183
 - reaction pathways 185
- m**
- macrocyclic porphyrins 316
- macrocyclic supramolecular metal coordination compounds 428
- magnesium/zinc bases 368
 - disadvantages 368
- Magnolia salicifolia* 391
- magnoalicin 390, 391
 - derivative 390
 - stereoselective synthesis 391
- Mannich reaction 291
- Marcus theory 349
- mass spectroscopy 343
- M-C bond cleavage 174
 - exchange reactions 174
 - stoichiometric formation 174
 - concentration 266
- Me₃-TACN 302
- menthyl-substituted titanocene compound 154
- meso-epoxides 401, 402
 - enantioselective opening 401
- meso-helicates 438
 - diastereoselective self-assembly 438
- metalated container molecules 1
 - chemistry 1
 - development 1
 - overview 2
- metal/boron systems 216
- metal-carbon bonds 125, 133
- metal catalysts 315
- metal-catalyzed oxidation reactions 106, 302
 - TACN derivatives 302
- metal-catalyzed polymerization 139
- metal-cogland bonding interactions 5
- metal complexes 5
 - molecular/electronic structures 5
 - *N*-alkylation effects 5
- metal coordination sites 2
- metal-donor bond distances 62
- metal isocyanide complexes 129
- metallacyclopropenes 166
 - reactions with (C₆F₅)₃ 166
- metal-ligand interaction(s) 132, 134
- metallocene (Cp₂M) 165
 - bis(trimethylsilyl)acetylene complexes 165
 - difluoride complexes 180
- metalloenzymes 420
 - mimicry 420
- metal-metal distances 417
- metal-oxygen clusters 231
- metal peroxy-mechanism 393
- metal-ring axis 128
- meta*-/*para*-functionalization 372
 - novel synthetic strategies 372
- meta-substituted systems 74
 - mono-functionalized 74
- methane monooxygenase (MMO) 39
 - mimic 320
 - self-assembling 320
- methoxide-induced cleavage 94
- 4-methoxybenzyl alcohol 353, 354
 - catalytic oxidation 354
- Mexican hat potential energy surface 55
- Mitsunobu reaction 366
- mixed *P/N* ligands 291
- M₄L₄ tetrahedron 412, 414
- MNN bending force constants 277
- Mo diphos systems 287
- Mo-dppe complex(es) 280, 289
- Mo(I)-ammine complex 284, 285
- Mo(I) fluoro complex 282
- Mo/W complexes 291
- molecular architectures 185
 - formation 185
- molecular containers 1
 - calixarenes 1
 - resorcinarenes 1
- molecular oxygen 379, 391
- molecular pocket 22
- molecular receptors, *see* DNA photoprobes
- molecular rectangle 190
 - synthetic routes 190
- molybdenum(III) complex 274
- monodentate ligand 100
- monohydroxo-ligated species 254
- mono-N₂ complex 293
- mononuclear chelate complex 147, 413
- mononuclear iron peroxo complexes 46–49

- mononuclear oxo species 29, 30
 - degradation pathways 29, 30
 - formation pathways 29, 30
 - iron oxo species 48–49
- mononucleating ligand systems 2
 - structures 2
- monosaccharide-derived ligands 147
- monosaccharide-metal complexes 147
- Mosher's acid 154, 155
- multidentate superbasic guanidine ligands 22
 - metal cations receptors 22
 - research program 22
- μ -oxo complex 90
- n**
- N-alkylated macrocycles 13
- N-arylpyrroles 360
 - C-H activation 360
- natural product magnosalicin 380
 - retrosynthetic strategy 380
- natural product synthesis 379
- nature's metalloproteins 420
- nature's systems 345
- N-donor ligands 203
- neutral dititanium compound 155
- N-heterocycles 171, 188, 200, 201, 360
 - carbene ligand(s) 106, 109, 111, 129
 - coupling 200
 - polycyclic 360
 - titanium-coordinated 188, 201
- N-heterocyclic carbenes (NHCs) 75, 103, 108
 - complexes synthesis 110
 - ligands 103, 106
 - metal complex 103, 113
 - properties 103
 - stability 103
- N-heterocyclic donor ligands 194, 212
 - benzimidazole derivatives 212
 - imidazole 212
 - oxazole 212
- N-heterocyclic system 200
- NH-functional guanidine ligand 23, 35
- NH,NR-stabilized carbene ligands 111, 115, 116
- NHNH₂ complex 284
- nitric oxide (NO) 251, 252, 254
 - activation parameters 251, 252
 - addition mechanism 254
 - binding 254
 - rate constants 251, 252, 260
- nitrido complexes 280
 - reactivity 280
- nitrogenase proteins 273
 - molybdenum-iron protein 273
- nitrogen donor ligands 65, 90
 - monodentate saturated 90
- nitrosyl complex 250
- nitrosyl-nitrite complex 259
- NMR 98, 341, 419, 421
 - analysis 343
 - ¹³C signals 212, 217
 - ¹³C spectrum 221,
 - ¹⁹F signal(s) 168, 169, 211, 212, 215, 220
 - ¹H experiments 156
 - ¹H ROESY spectra 437
 - ¹H sample 158
 - ¹H signal 93, 157, 195
 - ¹H spectroscopy 161
 - ¹H spectrum 80, 92, 154, 156, 219, 434, 437, 439
 - ¹H techniques 112
 - line 246
 - ³¹P *trans* coupling constants 289
 - ³¹P spectrum 69, 94, 98, 290
 - ³¹P resonance 71, 225
 - ³¹P spectroscopy 72, 287
 - scale reaction 154
 - signals 6, 7
 - spectra 198, 215, 418, 435
 - time scale 93, 133, 238
 - titration experiment 20, 129, 133, 418
- NMR spectroscopy 6, 69, 148, 177, 287, 414, 439
 - analyses 97
 - data 97, 441
 - investigation 288
 - pentaphosphine complexes 287–291
 - ³¹P time scale 70
 - study 132, 234, 417
- N–N bond 275, 276
 - cleavage process 278, 284
 - force constant 277
 - order 277
 - stretching frequencies 289
- N,N'-dimethylethylene diamine (DMEDA) 20
- nonaromatic pyrrole isomers 210
- noncovalent molecular capsules 1
- non-cyclic rigid ligands 53
 - phenanthroline 53
- novel ruthenium 313
 - development 313
- NP₄ donor set 99
- N-protected α -silyl- α -amino benzyl esters 301
 - rhodium-catalyzed reactions 301

nuclear non-heme iron enzymes, *see* catechol dioxygenases
 nucleophile-functionalized isocyanide ligands 107
 nucleophilic addition 159
 nucleophilic aromatic substitution reaction 79, 179, 223, 400
 nucleophilic products 355

o

Octahedral complexes 343
 O-donor ligands 433
 off reaction(s) 248, 250, 254, 257, 260
 olefin(s) 317, 319, 320, 323, 328
 – asymmetric epoxidation 319, 328
 – epoxidation reaction 302, 313
 – polymerization 178
 – Ru-catalyzed epoxidation 317
 – ruthenium catalysts 319
 oligomeric manganese complex 302
 oligotopic organic ligands 411
 oligo(trocenylsilanes) 139
 – synthesis 139
 on reaction(s) 248, 250, 254, 260
 one-electron oxidation process, *see* homolysis
 organic-inorganic hybrid polymers 345
 organic synthesis 368
 organometallic complex(es) 147, 165
 organometallic compounds 147
 organometallic metallo coligands 7
 organoruthenium groups 234
 organoruthenium units 233
 organoruthenium(II) 232
 – 49-tungsto-8-phosphate 232
 organotitanium carbohydrate compounds 147, 152
 – synthesis 147
 organozirconium carbohydrate compounds 155
 ORTEP plot 149–151, 161
ortho-directed metalation 116
ortho-F atom(s) 167–169
ortho methyl substituents 66
ortho-substituted systems 74
 – mono-functionalized 74
ortho-toluic acid 116
 oxazoline moieties 340, 341, 345
 oxidant 307
 oxidative cyclizations 388
 oxidative transformation 307
 – iron-catalyzed 307
 oxo-iron porphyrin radical cation 264, 268
 oxo-ligands 345
 oxygen activation 380

– schematic presentation 380
 oxygen-bridged ligands 346

p

palladium-catalyzed synthesis 304
 palladium complex 74, 75
 – meta-functionalized arylphosphines 75
 – solid state structure 75
 – synthesis 74, 75
 – T-shaped 142
 parallel resolution(s) 398, 403
 paramagnetic sandwich moieties 123
para-substituted ethyl iodobenzoate 372
 partial protonation 31
 – acetylenes 90
 – arenes 90
 – olefins 90
 P/B system 225
 P-cluster 273
 P,C-chelation 66
 Pd–Zr complex 142
 – molecular structures 142
 Pelargonium sidoides 370
 pentaammine-coordinated metal ion 90
 pentaammine donor set 89
 pentacoordinate complexes 81
 pentacoordinating bis(oxazoline) ligands 339, 340, 342, 345, 347
 – examples 340
 – modular strategy 342
 – secondary binding sites 339
 pentagonal bipyramidal complexes 344
 pentamethylcyclopentadienyl ligand 168
 pentamethylguanidine (PMG) 17, 18
 pepdidylglycine- α -hydroxylating monooxygenase 27
 – XRD structure 27
 permethylmetallocene alkyne complexes 167
 peroxide-based oxygenations 390, 392
 peroxide shunt pathway 262
 phase-transfer catalyst 67
 σ -phenyl ligand 214, 215
 phenylmethylsulfide 345, 346
 – iron-catalyzed oxidation 346
 – oxidation 345
 phosphine ligand(s) 66–77, 276
 – polypodal 92
 – tetrapodal pentadentate 100
 – zirconium/hafnium 143
 phosphines substituents 72
 phosphinite ligand 98
 phosphorus-carbon bond 101
 phosphorus donor ligands 65
 photochemical activation 349

- photochemical homogeneous reactions 349, 350
 - general structure 350
 - photolyase activity model 351, 352
 - equivalent 158
 - photoredox catalysis 349
 - picket-fence approach 26
 - π - π^* -transitions 437
 - Piers borane 216
 - pivaloyl chloride 158
 - planar zigzag chains 73
 - platinum (IV) catalyst 297
 - P,N*-ligands 75, 291
 - P450_{cam}/NO system 259
 - PNP-ligands 292
 - polycyclic structures 361
 - polyether bridged dipyrazolopyridine 81
 - ¹H NMR spectrum 81
 - polyether-bridged tridentate ligands 79
 - polyether linked systems 80
 - polyether linker units 67
 - synthesis 67
 - polyethylenes 82
 - material properties 82
 - polymerization reaction 153
 - polynuclear core structures 2
 - polyoxometalates (POMs) 231
 - organoruthenium 231
 - polyphosphine ligands 91
 - four coordinating arms 91
 - three coordinating arms 91
 - potential mechanism 201
 - potential photocatalyst lead structure 354
 - PPh₃ ligands 67
 - p_{π} - d_{π} interactions 199, 201
 - primary interaction 166
 - primary/secondary aminoalkenes 151
 - product ratio 302
 - propargylamines 363, 364
 - enantioselective three-component synthesis 364
 - one-pot three-component enantioselective synthesis 363
 - terminal alkynes activation 363
 - propargylamines synthesis 363, 364
 - advantages 363
 - mechanism 364
 - protic media 113
 - proton acceptors 18
 - proton affinity (PA) 18
 - protonated hydrazido complexes 293
 - protonation 95
 - proton β -pyrrole signal 248
 - proton-sponge catalyst complex 18–21
 - molecular structure 21
 - proton shift 1,4 221, 301
 - pyrazole-based chelating ligands 85
 - pyrazole-derived compounds 79
 - pyrazole substituents 72
 - pyrazolopyridine linker unit 68
 - synthesis 68
 - pyridine-2,6-bisoxazoline (pybox) 83, 318
 - complexes 84
 - ligand 321, 328
 - ruthenium complex molecular structure 83, 84
 - synthesis 84
 - pyridine-iron-carbonyl moiety 97
 - pyridine ring 292
 - pyridyl amines 305
 - pyrimidine substituents 72
 - pyrrole adduct 222
 - 2*H*- 222
 - molecular structure 222
 - pyrrole isomer 212
 - 2*H*- 212
 - tautomer 212
 - pyrrole ligand 221
 - 2*H*- 221
- q**
- quantum-chemical calculations 276
 - quantum chemistry-assisted normal coordinate analysis (QCA_NCA) 288
 - quasi-tetragonal symmetry 290
 - quinoid aci-form 8
- r**
- racemic ligands 439
 - racemic substrate(s) 398, 399
 - radical-induced C–C coupling reactions 195, 196
 - molecular architectures 195, 196
 - radical anion, *see* semiquinone radical
 - radical trap 401
 - Raman data 25, 278
 - Raman spectroscopy 276
 - rapid-scan detector 267
 - rapid-scan spectroscopy 245, 263
 - rate-enhancing effect 355
 - reaction channels 392
 - receptor molecules 1
 - redox-active acceptor ligands 203
 - redox co-factors 349
 - flavin adenine dinucleotide (FAD) 349
 - flavin mononucleotide (FMN) 349
 - redox potential(s) 249, 259
 - redox tautomers 117

- tautomeric equilibrium 118
 - redox-variable metals 113
 - reductive epoxide opening 400
 - concept 400
 - electron transfer 400
 - mechanism 401
 - titanocene(III) reagents 400
 - regiodivergent epoxide opening (REO) 397, 398, 402, 407
 - aspects of catalyst design 398
 - catalyst 402
 - mechanistic implications 398
 - subclasses 398
 - synthetic potential 398
 - regioselective substrate activation 103
 - regioselectivity 401, 403
 - Rehm–Weller equation 351
 - relative potential energy 136
 - resonance signals 157
 - rhodium complexes 69, 71
 - rigid ligand backbone 62
 - rigid ligand cavity 62
 - rigid triangular ligands 415–420
 - ring-opening polymerization 135, 136, 139, 397
 - metal-catalyzed 139
 - ROESY NMR experiments 436
 - 2D spectrum 436
 - ruthenium-catalyzed asymmetric epoxidation system 315–318
 - ruthenium-containing polyoxotungstates 231
 - redox activity 231
 - structure 231
 - ruthenium complex, activation 80, 84
- S**
- saddle-shaped conformation 4
 - Schiff base(s) 68, 69
 - functionalized phosphines synthesis 69
 - macrocycles 4
 - phosphine-substituted
 - Schrock cycle 282
 - secondary protonation 291
 - secondary interaction(s) 67, 72, 85, 166
 - C–F bonds 166
 - self-assembly processes 427, 435, 437, 439, 441
 - Semenov Institute of Chemical Physics 302
 - semiquinone radical 350
 - sharpless epoxides 405, 406, 407
 - TBS-protected 406
 - side-on superoxo complexes 26
 - silaferrrocenophanes 137
 - dimethylsilyl-bridged derivative 137
 - α -silyl- α -amino acids 300
 - rhodium-catalyzed preparation 300
 - synthesis 300
 - silylated diazo esters 300
 - silylene-bridged *ansa*-complexes 131
 - silylene-bridged derivatives 131
 - α -silyl- α -hydroxy acids 300
 - rhodium-catalyzed preparation 300
 - synthesis 300
 - single-atom bridges 5
 - single-crystal X-ray structure analysis 73, 186
 - site-directing heteroatoms 300
 - acetals 300
 - cyclic ethers 300
 - S_N2-mechanism reaction 397, 398
 - limitations 397
 - solvent effect 384
 - spectroscopic methods 5
 - EPR 5
 - ⁵⁷Fe-Mössbauer spectroscopy 5
 - IR 5
 - UV/Vis 5
 - spin-forbidden process 30
 - spirobifluorenes 431
 - 9,9'- 431
 - based ligand complexes 437
 - resolution 431
 - synthesis 431
 - square-pyramidal coordinated phosphine iron fragments 89
 - SQUID capillary 26
 - Stack's catalyst 321
 - stereochemical induction 162
 - stereoselective hydroxylation reactions 340
 - stereoselective reactions 391, 411
 - stereoselectivity survey 388–390
 - steric effects 361
 - steric interactions 402
 - stoichiometric activation pathway 360, 366–375
 - stoichiometric ligand oxidation 28
 - stoichiometric metal-mediated bond activation 359
 - stopped-flow system 267
 - stopped-flow techniques 24, 40, 47
 - subsequent S_{EAr} reaction 218
 - subsequent S_{NAr} reaction 223
 - substrate-catalyst-complex 104
 - substrate-controlled reaction 406
 - substrate-selective hydrogenation 118
 - superbasic guanidines chemistry 17
 - superbasic proton sponges, design 18

- supramolecular containers 411
 supramolecular interactions 106
 Suzuki cross-coupling reaction 298, 363
 synthetic nitrogen fixation 273, 285
 – mixed *P/N* ligands 285
 – phosphine 285
- t**
- TACN 301
 – *N*-arylated 303, 304
 tautomerization reaction 221
 terminal chloro ligands 155
tert-amylalcohol 83
tert-butyl hydroperoxide (TBHP) 306, 385, 393
tert-butyl isocyanide 129
 tetraethylammonium ion 160
 tetraketone 78
 – molecular structure 78
 tetrakis(tetrahydrofuran) (THF) 151, 165, 188, 191, 195, 197, 216, 368, 369, 383
 tetrameric pyrazine-bridged complex 187
 2,2,6,6-tetramethylpiperidine (TMPH) 369
 tetrazine-bridged complex 187
 – single crystals 187
 tetrazine derivatives, *see* bridging ligands
 thermochemical considerations 381–382
 Thorpe-Ingold effect 155
 three-component synthesis 365
 time-dependent (TD) DFT 276
 titanium complex(es) 184, 197
 – pyrazine-bridged 197
 titanium compounds 153
 titanium(IV) complexes 173, 414
 – formation 414
 titanocene (Cp_2Ti) 165
 – acetylene complexes 199
 – based catalysts 154, 401
 – C–F bonds reactions 165
 – complexes reactions 186, 189
 – fragment 192
 – precursor 185
 titanocene-catalyzed regiodivergent epoxide opening (REO) 402–404, 406
 – synthetic realization 402
 – mechanistic analysis 404
 titanocene(II) corner units 186
 titanocene(III) complex(es) 190, 400
 TMPS complex 247
 – Fe^{III} (TMPS) 264, 265
 Tolman's cone angle 66
 TP-TACN 302
trans-acetonitrile complex 288, 290
trans- β -methylstyrene 315, 326
trans-dioxo ruthenium porphyrin complex 315
trans-fluoro complex 289
trans-nitrile dinitrogen complex 288
trans-stilbene 325–329
 – epoxidation 325, 326
 – iron-catalyzed asymmetric epoxidation 329
 – oxide 323
 transition metal 79, 125
 – catalysis 1
 – centers 285
 – complexes 7, 53
 – coordination chemistry 7
 – coordination sphere 183
 – macromolecules 135
 – mediated process 116
 – phosphine complexes synthesis 141
 – state 260
 – tetraphos ligands 285–287
 TRENAM ligand 44, 413
 – mononuclear complex 413
 triangular ligands 412, 419
 – ethylene linkages 419
 triazacyclonones (TACNs) 301, 304, 305
 – 1,4,7- 301, 304, 305
 – di-arylated 304
 – ligands 304
 – metal complexes 302
 – *N*-arylated derivatives 303, 304
 trigonal bipyramidal complex 346
 trimethylsiloxyphenyl isocyanide, synthesis 107
 trimethylsilylalkynyl-borane moiety 169
 trinuclear chelate complex 197
 triphenyl phosphine ligands 69, 70
 – gold complexes 69
 – rhodium complexes 70
 triphenylphosphine oxide 109, 111
 tripodal tetradentate ligands 42–46, 92
 – *tmpa* derivatives 42–44
 – *uns-penp* derivatives 44
 tris(penta-fluorophenyl)borane (BCF) 21, 209
 Tröger's base 432, 439, 441
 – based ligand complexes 437
 – derivatives 431
 – resolution 431
 – synthesis 431
 tungsten-oxo framework 235
 tungstosilicate Keggin units 236
 – mono-ruthenium(IV)-substituted 236
 turnover numbers (TON) 316, 318, 354

- two-electron oxidation process, *see* heterolysis
 two-electron reduced species 194
- u**
- α,β -unsaturated carboxylate ligands 10
 uns-penp ligands 44, 49
 – synthesis 44
 UV/Vis absorptions 384
 UV/Vis measurements 132
 UV-Vis spectra 25, 47, 276, 383, 384, 432
 UV-Vis spectroscopy 239, 269
 UV/Vis titration 112
- v**
- van der Waals interactions 7, 8
 vibrational spectroscopic investigation 288
 vinylacetic acid 115
- w**
- Wells-Dawson derivatives 232
 Wells-Dawson fragments 236
 Werner's concept 89
 Werner-type coordination compounds 89
 Wilkinson's catalyst 116
 Wittig reaction 419
- x**
- X-ray crystal structure analyses 7, 75,
 94, 160, 189, 190, 197, 212, 217, 219,
 221, 222, 225, 227, 286, 341, 344,
 413, 414
 X-ray crystallography 4
 X-ray diffraction analyses 83, 124, 137, 161,
 200, 202, 210, 214, 217, 219, 225
- X-ray diffraction data 55, 78
 X-ray investigations 421
 XRD analyses 20, 25, 236
 – low-temperature 25
- z**
- Ziegler-Natta catalyst systems 209, 228
 Ziegler-Natta olefin polymerization catalysts
 209
 zig-zag trimethylene chain 217
 zinc precursor complex 33
 zinc(II)-complexes 342, 346, 347
 – synthesis 347
 zirconate complex 158, 159, 160
 – stabilization 160
 zirconium complex 156, 168, 176
 zirconium systems 228
 zirconocene (Cp_2Zr) 165
 – C–F bonds reactions 165
 – complexes 172
 – derivatives 129
 – dichloride moiety 214
 – fluoro complexes 176
 – reactions 175
 – 2-vinylpyridine complex 175
 zirconocene difluoride 174
 – alkyl-monofluoride complexes 174
 – preparation 174
 zirconocene halides 175, 178
 – catalytic formation 175
 – $\text{Cp}'_2\text{ZrCl}_2$ 178
 – MAO 178
 zwitterionic complex 166, 167, 171
 – characteristic feature 167

