

Subject Index

Entries are in letter-by-letter alphabetical order ignoring spaces and punctuation marks. Page numbers in *italic* refer to Figures and Tables not included in the relevant page ranges.

- A-1,3 strain
 - stereoselective cyclopropanation, 259, 262–263, 264
 - substrate-induced diastereoselection, 919
- Abietic acid, diastereoselective Reformatsky reaction, 817
- ab initio* calculations
 - dimethylzinc alkyl–Zn exchange, 197–198
 - electric field gradient, 156
 - electronic structure calculations, 157
- Absolute asymmetric synthesis,
 - enantioselective asymmetric autocatalysis, 583–584, 586
- Acetals
 - chiral auxiliaries, 268, 269
 - diastereoselective Reformatsky reaction, 818–819
- Acetonitrile, electrosynthesis of arylzinc compounds, 783–785, 789–790
- Acetophenone, Ni-catalyzed alkylation, 533, 539
- Acetoxycrenulide, stereoselective cyclopropanation, 260
- Acetylene, alkynylmetal allylzincation, 936
- Achiral alkenes, cyclopropanation using zinc carbenoids, 247–256
- Acid anhydrides, activated Zn allylation, 768
- Acidic cleaning, Zn metal, 801
- Activated olefins, arylation, 793–794
- Activated Schiff bases, diarylzinc addition, 327, 328
- Activation, Zn metal, 758–769, 800, 801–808, 868
- Activation barriers
 - allylzincation of alkenylmetals, 913
 - C–Zn exchange dynamics
 - intermolecular, 196, 199, 201, 203, 204
 - metallotropic, 206, 210, 215
 - C–Zn inversion dynamics, 220
- Activation energy
 - allylzincation of alkenylmetals, 913
 - C–Zn inversion dynamics, 218, 220, 222
- Activation entropy, C–Zn inversion dynamics, 220
- Activation parameters
 - C–Zn exchange dynamics, 199, 206–208, 212–214
 - C–Zn inversion dynamics, 218, 221–222
 - NMR spectroscopy, 230–232
 - relationships, 232–233
- Acylation
 - arylzinc compounds, 793
 - Cu-catalyzed, 346–349
 - fluorinated vinylzinc reagents, 729–730
 - Pd- or Ni catalyzed, 370, 371, 542–544
 - perfluoroalkylzinc reagents, 740–741
 - perfluoroalkynylzinc reagents, 738
 - thioesters, 370, 371
- Acyl chlorides, Pd-catalyzed alkynylation, 506
- Acyloxymethylzinc, structure, 242, 244
- Addition reactions
 - allenylzinc reagents, 422–427
 - aldehydes, 422–428, 446–447
 - imines, 446–447
 - ketones, 422–428
 - regiochemistry, 425
 - stereochemistry, 425–427
 - sulfoximines, 451
 - transition state calculations, 427–428
 - chloroallenylzinc reagents, 451–454
 - Cu-catalyzed, 349–352
 - elimination–addition mechanism, 328, 329
 - enantioselective, 555–593

- Addition reactions (*continued*)
alkynylzincs to aldehydes/ketones, 565–566
asymmetric amplification, 556, 570, 573–576, 578–580
asymmetric autocatalysis, 556, 576–584
consecutive reactions, 583
high enantioselectivity, 576–578
spontaneous absolute asymmetric synthesis, 583–584, 586
conjugate addition, 568–569, 576, 798
dialkylzincs to carbonyl compounds, 556–569
aldehydes, 97–99, 556–558, 563–564, 576–584
alkenylation, 563–564
aryl transfer, 566–567
asymmetric addition, 560–561, 566–567
enones, 568–569
functionalized, 560–561
ketones, 561–564
Lewis base catalysts, 556–560
diorganozincs to imine derivatives, 569–573
organozincs to carbonyl compounds, 560–569
intramolecular 1,4-addition, 331, 333, 666–667
oxidative, 289–296, 783, 801
sp³-geminated organozinc reagents, 665–667
uncatalyzed intermolecular carbozincations, 865–867
zincates, 690–694
zinc enolates
and alkenes
intermolecular, 964–971
intramolecular, 959–964, 965
and alkynes, 956–958
see also Conjugate addition reactions;
Michael addition
- Additives
cyclopropanation using zinc carbenoids, 246–247
Pd- or Ni-catalyzed cross-coupling, 467, 481
- Aggregation
organozinc compounds, 194, 198
Zn(II) porphyrins and phthalocyanines, 402
- β -Agostic interaction, β -dehydrometalation, 525
- AIDS, Efavirenz drug, 374, 376
- Alcohol dehydrogenase (ADH), zinc enzyme reactions, 8–9
- Aldehydes
allylzinc reagent addition, 422–427, 446–447
allylation with trifluoroprenyl bromide, 767–768
allyl zinc stereoselectivity, 317, 318–319
benzylic zinc reactivity, 768–769
chloroallylzinc reagent addition, 451–453
enantioselective reactions
alkenylation, 563–564
alkynylzinc addition, 565–566
diphenylzinc addition, 566
isoprenylation, 760
methylene homologation, 611–614
propargylation, 760
sp³-geminated organozinc methylenation, 651, 652
- Aldimines
cyclic, 570
Gilman–Speeter reactions, 819–820
- Aldol-type products, enantioselective addition of dialkylzincs, 372–373
- Alkaline phosphatase (ALP), zinc enzyme reactions, 18–19
- Alkaloids, cinchona, 565
- Alkanols, enantioselective asymmetric autocatalysis, 577, 578
- Alkenes
achiral, 247–256
acyclic, 261–266
alkylzincation, 471–472
chiral, 256–266
cyclic, 257–260
cyclopropanation using zinc carbenoids
achiral alkenes, 247–256
mechanism, 245–246
reaction solvent, additives and temperature, 246–247
stereoselective
acyclic alkenes, 261–266
chiral alkenes, 256–266
chiral auxiliaries, 266–273
chiral catalysts, 279–281
cyclic alkenes, 257–260
ring contraction, 266, 267
stoichiometric chiral reagents, 273–278
N-substituted alkenes, 250–251
synthetic scope, 246–281
unfunctionalized alkenes, 277
- ethylzincation, 471
hydrozincation, 316–317, 318, 470–471
intermolecular allylzincation
1,1-dimetalated alkenes, 623–624
uncatalyzed, 891–898
intermolecular carbozincations
allylzinc reagent reactivity, 945–948
hydrazone zinc enolates, 840
metallo-ene reactions, 890–891
transition metal-catalyzed, 881–885
uncatalyzed, 866–867
intramolecular carbozincations

- allenylzinc reagent reactivity, 948–950
 - uncatalyzed, 870–876
 - Zn–alkene interaction, 870, 871, 872
- methylene homologation, 610
- Pd–alkene π -complexes, 519
- trimethylsilyloxy-substituted, 249
- unfunctionalized, 276
- zinc enolate addition
 - intermolecular, 840, 964–971
 - intramolecular, 959–964, 965
- Zn π -interaction substrate-induced
 - diastereoselection, 925–927, 929
- Zr-catalyzed asymmetric carboalumination, 464
- Alkenylalanes
 - Pd catalysis
 - alkenyl–benzyl coupling, 524
 - Pd- and In-cocatalyzed cross-coupling, 481, 482
- Alkenyl–alkenyl coupling
 - Pd- or Ni-catalyzed, 461, 462, 492–499, 501, 503
 - natural product synthesis, 492–497
- Alkenyl–alkyl coupling, Pd- or Ni-catalyzed, 526
- Alkenylalkylzinc, enantioselective addition, 563–564
- Alkenyl–alkynyl coupling, Pd-catalyzed, 501
- Alkenyl–allenyl coupling, Pd-catalyzed, 522
- Alkenyl–allyl coupling, Pd- or Ni-catalyzed, 519, 523
- Alkenyl–aryl coupling
 - Pd- or Ni-catalyzed, 461, 462, 487–491
 - natural product synthesis, 490–491
- Alkenylation
 - enantioselective, 563–564
 - Pd-catalyzed, 463–467, 489
 - α -alkenylation, 513, 515
- Alkenyl–benzyl coupling, Pd- or Ni-catalyzed, 519, 524
- Alkenylboranes, allylzincation, 914
- Alkenyl chlorides
 - Pd- or Ni-catalyzed cross-coupling, 488–490, 527
 - alkylation, 528
- Alkenyl 1,1-dimetallic reagent
 - alkynylmetal allylzincation, 936–937, 940
 - functionalization, 940–945
 - allenylzinc cyclization, 950
 - silyl/germyl/boryl substituted, 659, 660
- Alkenyl electrophiles, Pd-catalyzed
 - alkynylation, 506–507, 516, 517
- Alkenyl Grignard reagents, alkenylmetal allylzincation, 908–909
- Alkenyl halides
 - electrosynthesis of arylzinc halides, 787
 - Pd-catalyzed cross-coupling, 462
 - alkynylation, 506–507
- Alkenyllithium reagents, alkenylmetal allylzincation, 908–909
- Alkenylmetals
 - allenylzincation, 945–946
 - allylmetalation, 614–623
 - allylzincation, 908–932
 - diastereoselective
 - mutual, 915–916, 917, 921
 - substrate-induced, 917–927
 - gem*-diorganometallic species, 908–913, 931, 965, 966
 - sp^3 -dimetalated carbon stereocenters, 675–676, 927–932
 - theoretical studies, 626–627, 913–915
 - (*E*)-Alkenylmethylzinc, enantioselective addition of dialkylzincs, 564
- Alkenyl–propargyl coupling, Pd-catalyzed, 522
- Alkenylzinc compounds
 - alkyl–Zn exchange dynamics, 200–202
 - Pd-catalyzed cross-coupling, 519, 520
 - trans*-selective monosubstitution, 476
- Alkenylzirconium intermediate, Pd-catalyzed
 - alkynylation, 501, 503
- Alkenylzirconocene chlorides, Pd-catalyzed
 - alkylation, 540
- Alkoxyallylic organozinc reagents,
 - cyclopropanone ketal reactions, 894–896
- β -Alkoxy esters, diastereoselective Reformatsky reaction, 818–819
- Alkyl–alkenyl coupling, Pd- or Ni-catalyzed, 526
- Alkyl–alkyl coupling, Pd- or Ni-catalyzed, 540
- Alkylaluminum, Pd-catalyzed alkynylation, 500–501
- Alkylation
 - Fe-catalyzed, 542
 - Pd- and Ni-catalyzed, 477, 479–480, 524–542
 - alkyl electrophiles, 526, 528, 533, 535, 539–542
 - alkyl halides, 477, 479–480, 528, 533, 535, 539–542
 - counterocations, leaving groups and catalysts, 526–528
 - β -dehydrometalation, 525
 - dialkylation, 533
 - enolate regioselectivity, 513
 - history, 525–526
 - natural product synthesis, 528–538
 - side reactions, 528, 533
- Alkylboron–alkylzinc exchange dynamics, 215–216
- Alkyl bromide alkylation
 - Fe-catalyzed, 542
 - Pd- or Ni-catalyzed, 535, 540, 541
- Alkyl chloride alkylation
 - Fe-catalyzed, 542

- Alkyl chloride alkylation (*continued*)
Pd- or Ni-catalyzed, 535, 540
- Alkyl electrophiles, Pd- or Ni-catalyzed alkylation, 526, 528, 533, 535, 539–542
- Alkyl fluorides, Pd- or Ni-catalyzed alkylation, 535, 540
- Alkyl halides
alkylation
Fe-catalyzed, 542
Pd- or Ni-catalyzed, 477, 479–480, 528, 533, 535, 539–542
electrosynthesis of arylzinc halides, 787
- Alkylidenation, sp^3 -geminated organozinc reagents, 657–659
- Alkylidene malonates
olefination, 909–910
Reformatsky reactions, 829, 831
zinc enolate addition, 956
- Alkyl iodides, Ni-catalyzed alkylation, 533, 539
- Alkylmagnesium compounds, Pd- or Ni-catalyzed alkylation, 525, 527, 528–538, 535, 539, 540
- Alkylmagnesium halides, Ni-catalyzed cross-coupling, 480
- Alkylmetals
alkylation, 526–538
alkynylation, 500
- Alkyl organozinc reagents
reactivity, 865–890
multi-component reactions, 885–890
see also Intermolecular carbozincations;
Intramolecular carbozincations
- Alkylphosphines, Pd and Ni catalysts, 528
- Alkyl tosylates, Ni-catalyzed cross-coupling, 480, 535, 540
- Alkyl(trimethylsilyl)zinc, enantioselective addition, 561
- Alkylzinc alkoxides, structure, 94–95, 100–101, 102–103
- Alkylzinc amides, structure, 116–117
- Alkylzincation
alkenes and alkynes, 471–472
Zn–hydrogen exchange, 470
- Alkylzinc compounds
acylation, 542–544
alkylation, 525, 528–538, 541
alkynylation, 507, 508
- Alkyl–zinc exchange
alkyl group effect on rate, 214–215
aryl, alkenyl and alkynylzinc compounds, 200–202
dialkylzinc compounds, 195–200
organoboranes, 215–216
organometallic compounds, 211–216
organozinc salts, 202–204
zincates, 204–205
see also Inversion
- Alkynes
alkyl-substituted, 501
alkylzincation, 471–472
allylic organozinc reagent reactivity, 936–940
crotylzincation, 471
disubstituted, 901
electron-withdrawing substituents, 501
enantioselective addition of alkynylzincs, 565
homodimerization, 508
hydrozincation, 470–471
hydrozirconation, 510, 564
intermolecular allylzincation
1,1-dimetallated olefins, 614
transition metal-promoted, 901
uncatalyzed, 898–900
intermolecular carbozincations
allenylzinc reagent reactivity, 945–948
metallo-ene reactions, 890–891
transition metal-catalyzed/promoted, 472–473, 878–881
uncatalyzed, 865–866
intramolecular carbozincations
allenylzinc reagent reactivity, 948–950
enone–alkyne reductive cyclization, 886–888
Ni-catalyzed, 472–473
uncatalyzed, 868–870
Zn–alkyne interaction, 870
Zr-promoted, 471–472
metallated, 936–940
terminal, 500, 501, 564, 565, 566
three-component couplings, 888, 889
zinc enolate addition, 956–958
- 2-Alkynes, lithiation–zincation, 521
- Alkynyl–acyl coupling, Pd-catalyzed, 505–506
- Alkynyl–alkenyl coupling
Pd-catalyzed, 504
1,2-dihalo-1-alkenes, 507, 509
1,2-dihaloethylenes, 507–512, 513, 514
- Alkynylalkyl halides, Pd-catalyzed alkynylation, 500
- Alkynylalkylzincs, enantioselective addition, 565
- Alkynyl–alkynyl coupling, Pd-catalyzed, 504, 512
- Alkynyl–allyl coupling, Pd-catalyzed, 519, 520–521
- Alkynyl–aryl coupling, Pd-catalyzed, 504
- Alkynylation
enantioselective, 565–566, 572
Pd-catalyzed, 500–516
 α -alkynylation, 512–516
alkynyl–acyl coupling, 505–506
alkynyl–alkenyl coupling, 504, 507–512, 513, 514

- alkynyl–alkynyl coupling, 504, 512
- alkynyl–aryl coupling, 504
- alkynylmetals, 463, 500
- catalyst poisoning, 503
- electrophiles, 500, 501, 503–507, 512–516, 517
- natural product synthesis, 516, 517, 518
- protocols, 499–503
- Alkynyl–benzyl coupling, Pd-catalyzed, 519, 520–521
- Alkynyl epoxides, Pd-catalyzed coupling reactions, 505
- Alkynylindiums, Pd-catalyzed coupling reactions, 505, 506, 519
- Alkynylmagnesium compounds, Pd-catalyzed alkynylation, 503, 516, 517, 518
- Alkynylmetals
 - allenylzincation, 945–946
 - allylmatalation, 623–627
 - allylzincation
 - alkenyl 1,1-diorganometallic functionalization, 940–945
 - metalated alkynes, 936–940
 - Pd-catalyzed alkynylation, 463, 501, 503–506
 - natural product synthesis, 516, 517, 518
- Alkynylmethylzinc, enantioselective addition to aldehydes, 565
- Alkynylsilanes
 - allenylzinc cyclization, 949–950
 - allylzincation, 900
 - Pd-catalyzed alkynylation, 503
- Alkynyl sulfoxide, methylene homologation, 607, 608–609, 612
- Alkynylzincates, 1,2-migration, 699–705
- Alkynylzinc compounds
 - alkyl–Zn exchange dynamics, 200–202
 - enantioselective addition to aldehydes/ketones, 565–566
 - Pd-catalyzed cross-coupling, 462, 519
 - alkynylation, 501, 503–508, 510, 516, 517, 518, 519
 - trans*-selective monosubstitution, 476
 - thermochemistry, 144
 - Zr-promoted carbocationations, 879
- Allenes
 - 1,1'-disubstituted, 581
 - fluoroalkenylzinc preparation, 730–731
 - from propargylic derivatives, 602
 - methylene homologations, 606–610
 - Zn–ene–allene reactions, 629–633, 950–954
- Allenic alcohols, stereoselective cyclopropanation, 274–275
- Allenic zincs
 - 1,2-migration rearrangements, 602–603
 - alkynylzincates, 700–701
 - zinc–ene–allene reactions, 950–954
- Allenyl–alkenyl coupling, Pd-catalyzed, 522
- Allenyl alkylzinc reagents, preparation, 432–434
- Allenyl–alkynyl coupling, Pd-catalyzed, 522
- Allenyl–allyl coupling, Pd-catalyzed, 521–522
- Allenyl–aryl coupling, Pd-catalyzed, 521–522
- Allenylation
 - Pd- or Ni-catalyzed cross-coupling, 474, 516–524
 - allenyl–aryl(allyl) reactions, 521–522
- Allenyl bromides, Pd-catalyzed cross-coupling, 519, 520
- Allenyl electrophiles
 - alkynylation, 504–505
 - allynylation, 518, 519
- Allenylmetals
 - allylzincation, 932–936
 - Pd- or Ni-catalyzed allenylation, 518
- Allenylpalladium intermediate, palladiozincation, 437
- Allenyl–propargyl metallotropy
 - allenylmetal allylzincation, 933, 934, 945, 945–946
 - C–Zn inversion dynamics, 229–230
- Allenylzinc bromide, coupling with aryl/vinyl halides, 435, 436
- Allenylzinc reagents
 - addition reactions
 - aldehydes, 422–428, 446–447
 - imines, 446–447
 - ketones, 422–428
 - regiochemistry, 425
 - stereochemistry, 425–427
 - sulfoximines, 451
 - transition state calculations, 427–428
 - allenyl alkylzinc reagents, 432–434
 - amine-substituted, 449–451
 - chloroallenylzinc reagents, 451–454
 - configurational stability, 432
 - cyclization to alkynylsilanes, 949–950
 - double diastereoselection, 438–442, 446–451
 - iodoallene-derived, 430–431
 - kinetic resolution, 448–449
 - mechanistic studies, 422–424
 - natural product synthesis, 442–445
 - Pd- or Ni-catalyzed allenylation, 519, 520
 - reactivity, 945–956
 - regioselectivity, 428–429
 - zincation of propargylic bromides, 421–422
- Allenynes, Pd-catalyzed coupling reactions, 504–505
- Allyl alcohols
 - allylzincation, 892
 - Cu(I)-catalyzed substitution, 338
 - cyclopropanation, 762
- Allyl alkenylzinc species
 - chelated, 917, 918, 922

- Allyl alkenylzinc species (*continued*)
Mg-assisted metalla–Claisen rearrangements, 914–915, 922
- Allylation
carbonyl compounds, 766–768
fluorinated vinylzinc reagents, 729
Pd- or Ni-catalyzed cross-coupling, 474, 516–524
molar ratio, 519
Tsuji–Trost reaction, 519
perfluoroalkynylzinc reagents, 738
- Allyl electrophiles
alkynylation, 504–505
allylation, 518–519
- Allyl halides, arylzinc compound reactions, 776–777
- Allylic 1,1-dimetallic reagent, Lewis acid-assisted metalla–Claisen rearrangement, 932–933, 934–936
- Allylic derivatives
leaving groups, 474
stereoselective cyclopropanation, 261–262, 264
- Allylic ethers, zincated, 920–921
- Allylic organozinc reagents, reactivity, 323, 324, 890–945
- π -Allylic palladium complex
alkynylsilanes, 900
Zn–ene reactions, 903–904
- Allylic substitution reactions, Reformatsky reactions, 836
- Allylmetalation
alkenyl metals, 614–623
alkynyl metals, 623–626
reaction mechanism computation, 626–627
- Allylmetals, Pd- or Ni-catalyzed allylation, 519
- Allyl methoxymethyl ether, allylzincation of alkenylmetals, 930, 931
- Allylmethyl ether, organozinc reagent derivation, 920–921
- Allyl silanes, stereoselective cyclopropanation, 263–264
- Allyltins, Pd-catalyzed allylation, 519
- Allyltrimethylsilane, organozinc reagent derivation, 919–920
- Allylzincation
alkenes
dimerization reaction, 892–893
transition metal-catalyzed, 898
uncatalyzed, 891–898
alkenylmetals, 908–932
diastereoselective
mutual, 915–916, 917, 921
substrate-induced, 917–927
gem-diorganometallic species, 908–913, 931, 965, 966
 sp^3 -dimetalated carbon stereocenters, 927–932
theoretical studies, 913–915
alkynes
1,1-dimetalated olefins, 614
transition metal-promoted, 901
uncatalyzed, 898–900
alkynylmetals
alkenyl 1,1-diorganometallic functionalization, 940–945
metalated alkynes, 936–940
allenylmetals, 932–936
1-trimethylsilyl-1-alkynes, 471
see also Zincation
- Allylzinc bromide
activated Zn allylation, 768
allylzincation
dimerization reaction, 892–893
homoallyl alcohols, 892
homoallyl amines, 891–892
- Allylzinc reagents
carbozincation, 471
metallotropic C–Zn exchange dynamics, 205–208
Pd- or Ni-catalyzed allylation, 519, 520
preparation, 317–319, 469, 470
- ALP (alkaline phosphatase), 18–19
- Aluminum, syn-hydrometalation, 463
- α -Amidoalkyl phenyl sulphones, Gilman–Speeter reactions, 820
- Aminals, Gilman–Speeter reactions, 821–822
- Amine-substituted allenylzinc reagents, 449–451
- Amino acids
cyclopropanation using zinc carbenoids, 250
enantioselective asymmetric autocatalysis, 581
Zn(II) phthalocyanine decomposition, 411
- α -Aminoacids, lithiation/transmetalation protocols, 839
- β -Amino alcohol, diethylzinc addition to aldehydes, 557
- Amino alcohols
binaphthyl-based, 565–566
dendrimer bound, 570
 β -Aminocrotonamides, zinc enolate addition, 957
 β -Amino esters, Gilman–Speeter reactions, 799
 β -Aminoketones, Gilman–Speeter reactions, 820
- Aminonitriles, Gilman–Speeter reactions, 826–827
- Aminoamidase (AP), zinc enzyme reactions, 12–14
- α -Amino zinc enolates, intramolecular addition to alkenes, 959
- Ammonium salts, zinc carbenoid reactions, 256

- (+)-Amphidinolide J, Pd-catalyzed synthesis, 529
- Amphidinolide T, Pd-catalyzed acylation, 542, 543
- Angiotensin Converting Enzyme, ⁶⁷Zn NMR spectroscopy, 153
- Angular triquinanes, Zn-ene-allene reactions, 953
- Anionic cyclization
 carbozincation
 alkenes, 872, 874
 alkynes, 869–870
- Anions
 enolate structure, 73–74
 in silico studies, 185
 see also Ions
- Anodes, reactive Zn generation, 759
- Anser anser* (graylag goose) preen gland wax, Pd-catalyzed synthesis, 529, 532
- Antenna systems, photosynthesis, 402
- Anthrax Lethal Factor, ⁶⁷Zn NMR spectroscopy, 153
- Antibiotics (antitumor), Pd-catalyzed synthesis, 493, 495
- Antisense oligodeoxynucleotides, Reformatsky reactions, 833, 834
- Antitumor antibiotics, Pd-catalyzed synthesis, 493, 495
- Ant venom, Pd-catalyzed synthesis, 517, 518
- AP (aminopeptidase), 12–14
- Arene diazonium salts, Zn(II) phthalocyanine dediazonation, 411
- Arene–zinc π -interactions (π -stacking)
 chelation, 960
 substrate-induced diastereoselection, 925–927, 929
- Aromatic halides, electrochemical organozinc reagent synthesis, 771
- Aromatic ketones, electrosynthesis, 791–793
- Arrhenius equation, activation parameters, 232–233
- Arylacetylenes, Ni-catalyzed carbozincations, 879–881
- Aryl–alkenyl coupling
 Pd- or Ni-catalyzed, 487–491
 natural product synthesis, 490–491
- Aryl–alkynyl coupling, Pd-catalyzed, 501
- Aryl–allyl coupling, Pd- or Ni-catalyzed, 519
- Aryl–aryl coupling
 Pd- or Ni-catalyzed, 483–487
 aryl chlorides, 486–487
 biaryl asymmetric synthesis, 487
 heterosubstituted arylzincs, 484–486
- Arylation
 activated olefins, 793–794
 dialkoxyphosphinyl difluoromethylzinc reagents, 746–747
 enolate α -arylation, 513
 α -halozinc esters and amides, 835
- Aryl–benzyl coupling, Pd-catalyzed, 523, 525
- Arylboronic acid, enantioselective aryl transfer, 567
- Aryl chlorides
 Pd- or Ni-catalyzed cross-coupling, 294, 362, 363, 486–490
 alkylation, 528
- Aryl halides
 arylzinc compound electrochemical synthesis, 773–776
 asymmetric biaryl synthesis, 777–779
 cross-coupling reactions, 777–779, 790
- Aryl iodides, Pd-catalyzed allenylation, 521, 522
- Aryl organozinc reagent reactivity, 865–890
 multi-component reactions, 885–890
- Aryl organozinc reagents, see also Intermolecular carbozincations; Intramolecular carbozincations
- Arylphosphines, Pd and Ni catalysts, 528
- 1-Aryl-1-propynes, lithiation–zincation, 521
- Aryl transfer reactions, enantioselective, 566–567
- Arylzincates, 1,2-migration, 705–706
- Arylzinc compounds
 alkyl–Zn exchange dynamics, 200–202
 Co-catalyzed electrosynthesis, 785–790
 reactivity, 790–794
 heterosubstituted aryl–aryl coupling, 484–486
 Ni-catalyzed electrosynthesis, 773–776
 reactivity, 776–781
 Pd-catalyzed cross-coupling, 519
 trans-selective monosubstitution, 476
- Arylzinc iodide, structure, 87, 88
- Asymmetric amplification
 asymmetric autocatalysis, 578–580
 enantioselection addition of organozincs, 556, 570, 573–576
- Asymmetric autocatalysis
 amplification of chirality, 578–580, 584
 chiral initiators, 580–581, 582–583, 584
 circularly polarized light, 581, 583, 585
 consecutive reactions, 583
 dialkylzinc addition to aldehydes, 556, 576–584
 high enantioselectivity, 576–578
 spontaneous absolute asymmetric synthesis, 583–584, 586
- Asymmetric biaryls
 aryl–aryl coupling, 483, 487
 aryl halide reactions, 777–779
- Asymmetric dialkylzincs, Zn–B exchange reactions, 561
- Asymmetric induction, sp³-geminated organozinc reagents, 664

- Asymmetric isopropylation, enantioselective autocatalysis, 577
- Asymmetric phenyl transfer reactions, diphenylzinc, 566
- Ate-complex formation, zincates, 686–689
- Atrazine, Zn(II) phthalocyanine decomposition, 411
- Autocatalysis *see* Asymmetric autocatalysis
- Automultiplication, enantioselective addition of dialkylzincs, 576–577
- Axial coordination, Zn(II) porphyrins, 405
- Aza-allyl vinylzinc intermediate, metalla-aza-Claisen rearrangement, 965, 966
- Aza-crown ethers, diarylmagnesium reactions, 50
- Aza-crowns, dimethylzinc complex structures, 79
- Aza-enolates, reactivity, 956–971
- L-Azatyrosine, Negishi cross-coupling, 365, 366
- Back electron transfer, Zn(II) porphyrins, 404, 409
- Barbier-type reactions
Cu(I)-catalyzed acylation, 349
I₂-Zn exchange, 310
perfluoroalkylzinc reagents, 731, 732, 743
Reformatsky reactions, 799, 800
- Barium, Reformatsky reactions, 806
- Benzaldehyde, enantioselective addition of diethylzinc, 573, 574–575
- Benzyl-alkenyl coupling, Pd- or Ni-catalyzed, 519, 522
- Benzyl-alkynyl coupling, Pd-catalyzed, 522
- Benzyl-allyl coupling, Pd- or Ni-catalyzed, 519
- Benzyl-aryl coupling, Pd- or Ni-catalyzed, 519, 522, 523, 525
- Benzylation
Pd- or Ni-catalyzed cross-coupling, 516–524
catalyst poisoning, 519
- Benzyl-benzyl coupling, Pd- or Ni-catalyzed, 519
- Benzyl electrophiles
alkynylation, 504–505
benzylation, 519
- Benzyl organozinc halides, C-Zn inversion dynamics, 227–228
- Benzylzinc reagents
1,2-migration rearrangements, 604–605
Pd- or Ni-catalyzed benzylation, 519
reactivity, 768–769
synthesis, 469, 470–471
- Benzynes
generation from zincates, 706–707
m-benzyne intermediacy, 707
- Biaryls, asymmetric, 483, 487, 777–779
- Bidentate ligands
catalyst turnover numbers, 476–477
monomeric Zn complex mass spectrometry, 176
Pd or Ni catalysts, 476–477, 519
- (+)-Bilobalide, cyclopentenone precursor, 357–358
- 1,2-Bimetallic zinc/silicon reagent, polyfunctional organozinc halide preparation, 297, 299–300
- 1,1'-Bi-2-naphthol *see* BINOL
- 1,1'-Binaphthyl, enantioselective asymmetric autocatalysis, 581
- Binaphthyl-based amino alcohols, enantioselective phenyl transfer, 566–567
- BINAP-palladium complexes, Reformatsky reactions, 836
- BINOL (1,1'-bi-2-naphthol)
enantioselective additions
alkynylzincs, 565
dialkylzincs, 372, 559
- Binuclear zinc complexes, mass spectrometry, 174–176
- Biohydrogen production, Zn(II) phthalocyanine photovoltaics, 409
- Biomacromolecules
chiral homogeneity, 579, 584, 586
⁶⁷Zn NMR spectroscopy, 150–151, 153–155, 156–158
solid-state, 152–153
- Bipyridine
complex structures, 80–81
electrosynthesis of arylzinc compounds, 774–776
- Bipyridinediol, enantioselective conjugate addition, 568
- γ-Bisabolenes, Pd-catalyzed synthesis, 529, 530
- Bis(benzoylmethane) complex, electron ionization mass spectrometry, 179
- Bischlorins, photosynthetic reaction center models, 402
- Bis(chloromethyl)zinc
cyclopropanation using zinc carbenoids, 252
preparation, 239
structure, 242
- Bis(2,4-dienyl)magnesium compounds, metallotropic C-Zn exchange dynamics, 209–210
- Bis(α,ω-diphenylphosphino)alkanes, Pd or Ni catalysts, 476–477
- 2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), 836
- Bis(1,1-diphenylphosphino)ferrocene (dppf), Pd or Ni catalysts, 476–477, 492, 498, 505, 519

- Bis(*o,o'*-diphenylphosphino)phenyl ether (DPEphos)
 Pd or Ni catalysts, 476–477, 480
 alkenyl–alkenyl coupling, 492, 497–498
 alkynylation, 507
 allylation, 505
 benzylation, 505, 519
 (–)-4,5-Bis[hydroxy(diphenyl)methyl]-2,2-dimethyl-1,3-dioxolane *see* TADDOL
- Bis(iodomethyl)zinc
 DME complex, 273–274
 preparation, 239
 structure, 242, 243
- Bis(iodozinc)iodomethane, as carbenoid, 676–677
- Bis(iodozinc)methane, conjugate addition, 665–667
- 1,1-Bismetallated species, 641–683
 sp^2 -geminated organodizinc reagents, preparation and reactions, 677–680
 sp^3 -geminated organodizinc reagents
 preparation, 642–650
 reactions, 650–677
- Bismetallated reagents, allylmethylation, 615, 616
- Bis(2-methylallyl)zinc, metallotropic C–Zn exchange dynamics, 205–206
- Bis(monothiodibenzoylmethane) complex, electron ionization mass spectrometry, 179
- Bismuth, Reformatsky reactions, 806
- Bis-oxazolines
 lithiated, 570
 Ni-catalyzed alkylation, 541
 Zn complex formation, 896, 897
- Bis(2,4-pentadienyl)zinc compounds, metallotropic C–Zn exchange dynamics, 208–210
- Bis(pentafluorophenyl)zinc, preparation, 732
- Bis(pentamethylcyclopentadienyl)zinc, metallotropic C–Zn exchange dynamics, 210–211
- Bis(perfluoroalkyl)zinc compounds
 electron ionization mass spectrometry, 169–171
 solvation, 739
- Bis(perfluoroorgano)zinc, preparation, 732
- Bisporphyrins, photosynthetic reaction center models, 402
- Bis(pyridine)bis(trifluoromethyl)zinc, thermal decomposition, 187
- Bis(sulfonamides)
 C_2 -symmetric, 559
 chiral Ti complex, 560
 enantioselective reactions, 562, 567
- Bis[2,4,6-tris(trifluoromethyl)phenyl]zinc, electron ionization mass spectrometry, 171
- Blaise reaction
 activated zinc synthesis, 765–766
 Cu(I)-catalyzed acylation, 348
 nitriles, 827, 829
- Blodgett, Langmuir–Blodgett films, 405–406, 411
- Boc-L-proline, enantioselective addition of alkynylzincs, 565
- Bond dissociation energies, mass spectrometry, 178–179, 180–181
- Bond energies
 ‘average’ bonds, 143
 C–Zn, 137, 142–143, 144
 DFT calculations, 142
 dialkylzinc compounds, 142–143
 electron diffraction/photoelectron spectroscopy, 142
 homologous series, 143
 homolytic, 142
 methylzinc radical cations, 144
 monoalkylzinc compounds, 143
 quantum chemical calculations, 142
- Bond-formation reactions
 Pd- or Ni-catalyzed acylation, 542–544
 zincate carbenoids, 694
- Bonding
 multi-centre bonding, 59
 multi-hapto bonded groups, 60–64
- Bonds
 C–C, 542–544, 694, 829–837
 C–F, 733
 C–halogen, 722–732, 733, 798, 799–800
 C–Zn, 137, 142–143, 144, 172–179, 194, 195–215
 Zn–halogen, 85–94
 Zn–heteroatom, 118–123
 Zn–N, 107–118
 Zn–O, 94–107
 Zn–transition metals, 123–126
- Bond strength, monoalkylzinc compounds, 143
- Boron trifluoride, diastereoselective Reformatsky reaction, 818–819
- Boron–zinc exchange reactions
 cyclopropanation using zinc carbenoids, 253–254
 diorganozinc functionalization, 311–316, 560–561
 enantioselective alkenylation, 563
- Borrelidin, Pd-catalyzed synthesis, 529, 531, 538
- α -Borylorganozinc, Zn–Cu transmetalation, 914
- Boryl-substituted *gem*-dizincmethanes, preparation, 646–647, 659, 660, 663–664
- Brevetoxin A, Pd-catalyzed synthesis, 529, 530
- Bromine–zinc exchange reactions, polyfunctional organozinc halides, 296, 299

- 1-Bromo-1-alkynes, Pd-catalyzed alkynylation, 500–501
- 4-Bromo-2-butenic acid, zinc dienolates, 849
- Bromocrotonates, Reformatsky reactions, 825, 853
- 2-Bromo-1,3-dienes, Pd-catalyzed coupling reactions, 498, 499
- 3-Bromo-3,3-difluoropropene, *gem*-difluoroallylic alcohol preparation, 734
- α -Bromo- β,β -difluorostyrenes, preparation, 721, 726
- Bromoynes, four-carbon synthons, 508, 510
- α -Bromoesters, Reformatsky reactions, 766, 808
- (*E*)-1-Bromo-2-iodoethylene, Pd-catalyzed alkynylation–alkenylation, 512, 514
- α -Bromoketones
Gilman–Speeter reactions, 820
Reformatsky reactions, 808
- Bromolysis, organozinc reagents, 322–323
- α -Bromomethylacrylates, imino-Reformatsky reactions, 825
- 4-Bromo-3-methyl-2-butenic acid, zinc dienolates, 849
- α -Bromo- $[\alpha']$ sulphinyl ketone, Reformatsky reactions, 806
- Bromothiophene, electrochemical organozinc reagent synthesis, 772–773
- Bromotrifluoromethane, electrochemical reduction, 762
- cis*-Bupleurynol, Pd-catalyzed synthesis, 493, 495, 517, 518
- trans*-Bupleurynol, Pd-catalyzed synthesis, 493, 495, 512, 514, 517, 518
- Butadiene, Ni–butadiene dimer catalyst, 480, 535, 540
- 1,3-Butadiene
dicrotylzinc allylzincation, 894, 895
uncatalyzed intermolecular carbozincations, 866, 867
- Buttenberg *see* Fritsch–Buttenberg–Wiechell (FBW) rearrangement
- t*-Butyl bromoacetate, Gilman–Speeter reaction, 822, 823
- 2-*t*-Butylethynyl-5-pyrimidyl alkanol, enantioselective asymmetric autocatalysis, 577, 578
- 1-Butyl-3-methylimidazolium hexafluorophosphate, ionic liquid, 656
- 2-Butylzinc bromide, C-Zn inversion dynamics, 223
- C₂-symmetric bis(sulfonamide), enantioselective addition of dialkylzincs, 559
- C_{50/60} fullerenes, photoinduced electron transfer, 399–400, 402
- CA (carbonic anhydrase), 20–22
- CAII (Human Carbonic Anhydrase Isozyme II), 157, 158
- Cadiot–Chodkiewicz reaction, 504, 508
- Calcium, Reformatsky reactions, 805
- Calixarenes, structure, 103–104
- Callipeltoside A, stereoselective cyclopropanation, 274
- (–)-Callystatin A, Pd-catalyzed synthesis, 493, 495, 498, 529, 532, 536
- Calorimetry, enthalpies of formation, 140
- Camphorsulfonamide
enantioselective additions
alkynylzincs, 565
dialkylzincs, 562
- (+)-Cannabisativine, Gilman–Speeter reaction, 822, 823
- Capensifuranone, Pd-catalyzed synthesis, 529, 532
- Carbacyclin, Pd-catalyzed synthesis, 493, 494, 497
- 5-Carbamoyl-3-pyridyl alkanol, asymmetric autocatalysis with amplification, 580
- Carbenes
N-heterocyclic, 475, 480, 540–541
see also Fischer carbene complexes
- Carbenoids
sp³-geminated organodizinc reagents, 676–677
see also Zincate carbenoids; Zinc carbenoids
- Carbinols, perfluoroalkylzinc reactions, 741–742, 743
- Carboalkoxydifluoromethylenezinc reagents, 747–750
- Carboalumination
cross-coupling
iterative, 511, 537–538
Pd- or Ni-catalyzed tandem processes, 526, 527, 537–538
Zr-catalyzed, 368, 369, 464, 466, 471, 527, 537–538
- Carbocupration
acetylenic carbonyl derivatives, 356–360
alkynyl sulfoxide, 607, 608–609, 612
ethyl propiolate, 304–305
Pd-catalyzed alkenylation, 464
- Carbohydrates, stereoselective alkene cyclopropanation, 266, 267
- Carbolithiation, 1,3-enynes, 933–934, 935, 951, 952
- Carbomagnesiation
Cu-catalyzed, 465
Zr-catalyzed, 464
- Carbometalation
Cu-catalyzed, 465

- Pd- or Ni-catalyzed tandem cross-coupling, 461, 463, 471, 526
- sp³-geminated organodizinc preparation, 647–650
- Zr-catalyzed, 464, 466
- Carbonates, perfluoroalkylidene reactions, 742
- Carbon–carbon bonds
- electron-poor double bonds, 829–837
 - Pd- or Ni-catalyzed acylation, 542–544
 - zincate carbenoid reactions, 694
- Carbon dioxide, Ni-promoted three-component couplings, 888, 889
- Carbon–fluorine bonds, Zn insertion, 733
- Carbon–halogen bonds, Zn insertion, 722–732, 733, 798, 799–800
- Carbonic anhydrase (CA), zinc enzyme reactions, 20–22
- Carbonickelation, intermolecular carbозincation of alkynes, 881
- Carbonyl addition, epoxide ring opening, 690
- Carbonyl compounds
- activated Zn allylation, 766–768
 - enantioselective addition
 - diorganozinc catalysis, 556–560
 - organozincs, 560–569
- α -substitution, 512–516
 - α,β -unsaturated, 515, 852
- Carbon–zinc bonds
- bond energies, 137, 142–143, 144
 - exchange dynamics, 194, 195–216
 - inversion dynamics, 194, 217–230
- see also* Zinc–carbon bonds
- Carboxylic acid derivatives, Reformatsky reactions, 827–829
- Carboxypeptidase A (CPA)
- proteolytic activity, 151
 - zinc enzyme reactions, 14–16
- ⁶⁷Zn NMR spectroscopy, 153
- Carbozincations
- alkenes and alkynes, 471–473, 840, 863–978
 - allylzincs, 471
 - definition, 864–865
 - 1,3-dipolar intermediate, 890
 - Pd- or Ni-catalyzed cross-coupling tandem processes, 526, 527
 - Zr-catalyzed, 464, 471–472, 878–879, 884
- see also* Intermolecular carbозincations; Intramolecular carbозincations; Zincation
- L-Carnosine (L-CAZ), ⁶⁷Zn NMR spectroscopy, 158
- β -Carotene, Pd-catalyzed synthesis, 493, 494
- γ -Carotene, Pd-catalyzed synthesis, 493, 495
- Carotenoids, synthesis, 508, 511
- Catalysis
- carbозincations
 - Fe-catalyzed, 881–882
 - Ni-catalyzed, 472–473, 876–878, 879–881, 886–890
 - Pd-catalyzed, 464, 876–878, 882–884
 - Ti-catalyzed, 884–885
 - Zr-catalyzed, 464, 471–472, 878–879, 884
- chiral catalysts, 279–281
- Cu(I) compounds, 333–360
- halides, 746–747
- enantioselective addition
- alkynylzincs, 565–566
 - aryl transfer reactions, 566–567
 - asymmetric amplification, 573–576, 578–580
 - asymmetric autocatalysis, 556, 576–584
 - chiral initiators, 580–581, 582–583, 584
 - consecutive reactions, 583
- dialkylzincs
- chiral ligands, 559, 560, 562–563, 568–572, 574–575
 - to aldehydes, 576–584
 - to carbonyl compounds, 556–560, 562
 - to enones, 568–569
 - to ketones, 561–563
- immobilized catalysts, 556–560
- Lewis base catalysts, 556–560
- Ni-catalysis
- carbозincations, 472–473, 876–878, 879–881, 886–890
 - cross-coupling, 457–553
 - acylation, 542–544
 - thioesters 370, 371
 - alkenyl–alkenyl reactions, 461, 462, 492–499
 - alkenyl–aryl reactions, 461, 462, 487–491
 - alkylation, 477, 479–480, 524–542
 - alkyl electrophiles 526, 528, 533, 535, 539–542
 - alkyl halides 477, 479–480, 528, 533, 535, 539–542
 - history 525–526
 - natural product synthesis 528–538 - alkynylation, 500
 - allylation, 474, 516–524
 - aryl–alkenyl reactions, 487–491
 - aryl–aryl reactions, 483–487
 - aryl chlorides, 294, 362, 363, 486–487
 - benzylation, 516–524
 - catalyst poisoning 519 - carbometalation, 461, 526
 - catalyst poisoning, 519
 - catalysts and ligands, 467, 475–480, 526–528
 - cocatalysts or additives, 467, 481
 - conjugated diene synthesis, 461–462
 - counteractions, 467–473, 526–528

- Catalysis (*continued*)
- cyanation, 544
 - hydrometalation, 461, 526
 - leaving groups, 467, 473–475, 526–528
 - organozincs, 461
 - overview, 467–483
 - solvents, 467, 481–483
 - synergistic effects, 527–528
 - hydrozincation, 316–317, 318
 - Nugent's catalyst, 262
 - Pd-catalyzed cross-coupling, 457–553
 - acylation, 542–544
 - alkenyl–alkenyl reactions, 461, 462, 492–499, 501, 503
 - alkenyl–alkyl reactions, 501
 - alkenyl–aryl reactions, 461, 462, 487–491
 - alkylation, 477, 479–480, 524–542
 - alkyl electrophiles, 526, 528, 533, 535, 539–542
 - alkyl halides, 528, 533, 535, 539–542
 - history, 525–526
 - natural product synthesis, 528–538
 - alkynylation, 500–516
 - α -alkynylation, 512–516
 - alkynyl–acyl reactions, 505–506
 - alkynyl–alkenyl coupling, 504, 507–512, 513, 514
 - alkynyl–alkynyl reactions, 504, 512
 - alkynyl–aryl reactions, 504
 - catalyst poisoning, 503
 - dialkynylation, 514
 - electrophiles, 500, 501, 503–507, 512–516, 517
 - natural product synthesis, 516, 517, 518
 - protocols, 499–503
 - selective monoalkynylation, 501, 508, 512
 - Zn, B and Sn alkynylmetals, 463
 - allenylation, 516–524
 - allenyl–aryl(allyl) reactions, 521–522
 - natural product synthesis, 523, 524
 - allenylzinc bromide reagents, 435, 436
 - allylation, 474, 516–524
 - alkynyl–allyl reactions, 520–521
 - natural product synthesis, 523, 524
 - allylzincation, 904, 911, 933, 934
 - aryl–alkenyl reactions, 487–491
 - aryl–alkynyl reactions, 501
 - aryl–aryl reactions, 483–487
 - arylzinc–aryl halides, 777–779, 790
 - benzylation, 516–524
 - alkynyl–benzyl reactions, 520–521
 - catalyst poisoning, 519
 - heterocycles, 523
 - natural product synthesis, 523, 524
 - carbometalation, 461, 464, 526
 - carbozincation
 - intermolecular, 880, 884
 - intramolecular, 869–870, 948, 949, 953
 - catalyst poisoning, 503, 519
 - catalysts and ligands, 467, 475–480, 526–528
 - classification, 460
 - cocatalysts or additives, 467, 481, 500, 501
 - conjugated diene synthesis, 461–462
 - countercations, 467–473, 526–528
 - cyanation, 544
 - diorganozinc preparation, 313
 - enantioposition-selective cross-coupling, 487, 488
 - fluorinated vinylzinc reagents, 715–722
 - history, 459–467
 - hydrometalation, 461, 463, 465, 470, 526
 - hydrozirconation, 462, 510
 - leaving groups, 467, 473–475, 526–528
 - organoborons, 461, 463
 - organozinc reagents, 361–370, 371, 461, 761
 - overview, 467–483
 - perfluoroalkynylzinc reagents, 737
 - propargylation, 516–524
 - natural product synthesis, 523, 524
 - propargyl–aryl(allyl) reactions, 521–522
 - solvents, 467, 481–483
 - synergistic effects, 527–528
 - zinc enolate addition, 961
- Pearlman's catalyst, 370, 371
- Rh-catalyzed hydroboration, 316
- Ti-catalysis
- carbozincations, 884–885
 - hydromagnesiation, 917, 918
- transition metals
- allylzincation, 898, 901
 - carbozincations, 876–890
 - coupling reactions, 833–837
- Wilkinson's catalyst, 842, 845
- zinc enzymes, 2, 7–22
- Zn(II) porphyrin and phthalocyanines
- photocatalytic oxidation, 411–412
 - photovoltaics, 407, 408, 409, 411
- see also* Cocatalysis; Uncatalyzed . . .
- Catalyst poisoning, 503, 519
- Catenane, Zn(II) porphyrin photonics, 407
- Cations
- heteroleptic monoorganic compounds, 83–85
 - in silico* studies, 184
 - see also* Ions; Radical cations
- Cavitand, Zn(II) porphyrin photonics, 407
- ¹¹³Cd NMR spectroscopy
- chemical shielding anisotropy, 153
 - hetero-TOCSY, 151

- HMQC, 151
surrogate probes, 150, 153
Zn-containing proteins, 150–151
- Cellulose, Zn(II) phthalocyanine reactions, 411
- Chain extension, dicarbonyl derivatives, 250
- Chain growth polymerization, dialkylzinc compounds, 142
- Chamaemelum nobile* L, Pd-catalyzed alkynylation, 501
- Charge separation/recombination, Zn(II) porphyrins, 404, 409
- Charge transfer, medicinal photodynamic therapy, 409
- Chelated allyl alkenylzinc species, substrate-induced diastereoselection, 917, 918, 922
- Chelating phosphines, Pd or Ni catalysts, 476–477, 492, 497–498, 505, 507, 508, 528
- Chelation
diorganozinc *N,N*-chelating ligands, 78–79
Zn(II) porphyrins, 404–405
- π -Chelation, zinc enolate addition to alkenes, 960
- Chemical ionization (CI) mass spectrometry
monomeric Zn complexes, 176
organozinc fragments, 177
self-chemical ionization, 166
- Chemical shielding anisotropy (CSA), ^{113}Cd NMR spectroscopy, 153
- Chemical shift anisotropy (CSA), ^{67}Zn NMR spectroscopy, 155
- Chemoselective reactions
dialkylzinc additions, 561
 sp^3 -geminated organodizinc methylenation, 656–657
- Chiral acetals, chiral auxiliaries, 268, 269
- Chiral alkenes, stereoselective cyclopropanation, 256–266
- Chiral allenylzinc reagents, kinetic resolution, 448–449
- Chiral allylic alcohols, Cu(I)-catalyzed substitution, 338
- Chiral amino alcohols, enantioselective addition of alkynylzincs, 565
- Chiral auxiliaries
allylzincation of alkenylmetals, 923, 924, 925, 926
imino-Reformatsky reactions, 823, 824
 α -methylbenzylamine, 959–960
stereoselective alkene cyclopropanation, 266–273
chiral acetals, 268, 269
- Chiral aziridinyl alcohol, enantioselective addition to imines, 570
- Chiral bis(sulfonamide)-Ti complex, enantioselective addition of dialkylzincs, 560
- Chiral C_2 symmetrical amination, substrate-induced diastereoselection, 923, 924
- Chiral catalysts, stereoselective alkene cyclopropanation, 279–281
- Chiral dihydroxybis(sulfonamide), enantioselective phenyl transfer, 567
- Chiral enamides, stereoselective cyclopropanation, 272
- Chiral epoxides, enantioselective asymmetric autocatalysis, 581
- Chiral initiators, enantioselective asymmetric autocatalysis, 580–581, 582–583, 584
- Chirality
asymmetric amplification, 578–580, 584
circularly polarized light, 581, 583, 585
homogeneity of biomolecules, 579, 584, 586
light-harvesting complexes, 402
- Chirality transfer,
Fritsch–Buttenberg–Wiechell rearrangement, 942–943
- Chiral lactams, Cu(I)-catalyzed addition, 349
- Chiral ligands
dioxaborolane, 273, 275
disulfonamide, 279
enantioselective addition of dialkylzincs
asymmetric amplification, 574–575, 578–580
asymmetric autocatalysis, 576–584
chiral initiators, 580–581, 582–583, 584
automultiplication, 576–577
Lewis acid catalysts, 559, 560, 571–572
to enones, 568–569
to imines, 569–573
to ketones, 562–563
- Chiral olefins
enantioselective asymmetric autocatalysis, 581
photoequilibrium, 581
- Chiral phosphoric acid, stereoselective cyclopropanation, 280, 282
- Chiral physical force, circularly polarized light, 581, 582
- Chiral quaternary centers, Cu(I)-catalyzed substitution, 339–340
- Chiral salen-Ti isopropoxide catalyst, enantioselective addition of dialkyls, 562–563
- Chiral sulfonamide alcohol, enantioselective addition of alkynylzincs, 565
- Chiral Zn(salen) catalyst, enantioselective alkynylation, 565
- Chlorambucil, Reformatsky reaction, 811
- Chloroallenylzinc reagents
additions to aldehydes/imines, 451–454
preparation, 451, 452

- p*-Chlorobenzoic acid,
 tryptamine/*p*-chlorobenzoic acid
 cocrystal, 584
- 1-Chloro-2,2-difluorovinylzinc reagent,
 preparation, 719
- (*E*)-Chloroenynes, Pd-catalyzed synthesis, 508
- α -Chloroesters, electrochemical Reformatsky
 reactions, 804
- α -Chloroketones, Reformatsky reactions, 806
- α -Chloronitrile, electrochemical Reformatsky
 reaction, 804
- α -Chloro propanoate, electrochemical
 Reformatsky reaction, 804
- α -Chlorozinc carbenoids, alkynylmetal
 allylzincation, 942–944
- CHLP protocol, enthalpies of vaporization, 138
- Chodkiewicz, Cadiot–Chodkiewicz reaction,
 504, 508
- Chromium(II) chloride, Reformatsky reactions,
 805
- Cicaprost™ side chain, Cu(I)-catalyzed
 substitution, 342–343
- CI (chemical ionization), 166, 176
- CID (collision-induced dissociation), 172
- Cinchona alkaloids, enantioselective addition
 of alkynylzincs, 565
- Circularly polarized light (CPL),
 enantioselective asymmetric
 autocatalysis, 581, 583, 585
- Claisen rearrangements *see*
 Metalla-aza-Claisen rearrangement;
 Metalla–Claisen rearrangement
- Clusters
 mass spectrometry
 cubane, 172–174
 electron ionization, 178
 Zn–Ni, 124–125
- ¹³C NMR spectroscopy
 halomethylzinc reagents, 244
 Zn(II) organometallic compounds, 148–150
- Cobalt
 catalysis
 allylzincation, 901
 organozinc reagent synthesis, 770–771,
 781–794
 Co–Zn transmetalation, 783
- Cobalt complexes
 catalytic organozinc reactions, 378–379
 Reformatsky reactions, 805
- Cobalt halides
 electrochemical organozinc reagent
 synthesis, 770, 781–794
 aryl- or heteroarylzinc compounds,
 785–790
 electrochemical behavior, 782–785
 reactivity, 790–794
- Cocatalysis
 ethylzincation of alkenes, 471
 Pd- and Zn-catalyzed coupling reactions,
 462, 465–467, 481, 482, 500, 501
- Coenzymes, Pd- or Ni-catalyzed synthesis,
 523, 524, 529, 531, 534
- Collision-induced dissociation (CID), cubane
 clusters, 172
- Computational chemistry
 allylmetalation mechanism, 626–627
 organozinc ion structures, 184
- Computer simulation of molecular structures
 (COSMOS), Zn(II) coordination
 chemistry, 154
- Condensation reactions, Zn-mediated, 105
- Configuration
 C–Zn bond dynamics
 inversion of configuration, 217, 218,
 223–228
 retention of configuration, 198, 216, 217,
 223
- Configurational stability
 allylzinc reagents, 432
 allylzincation of alkenylmetals, 931–932
 vinyl organozinc compounds, 227
- Conjugate addition reactions
 allylzincation
 alkenylmetals, 911
 alkynylmetals, 940–941
 arylzinc compounds, 776, 793–794
 bis(iodozincio)methane, 665–667
 dialkylzincs to enones, 568–569
 enantioselective, 568–569, 576, 798
 α,β -unsaturated compounds, 690–694
 zinc enolates, 798, 958, 964
 see also Addition reactions
- Conjugated dienes, Pd- or Ni-catalyzed
 selective synthesis, 461–462
- Conjugated diynes, Pd-catalyzed
 cross-coupling, 504, 508, 512, 513, 514
- Conjugated enones
 reduction, 513
 zinc dienolates, 852
- Conjugated enynes
 synthesis, 508, 512
 see also Enynes
- Conjugated oligoenes, synthesis, 508, 510
- Conjugated triendynes, synthesis, 512, 514
- Controlled-potential, cobalt halide catalysts,
 783
- Coordination compounds
 intramolecularly coordinating substituents,
 64–70
 zinc enzymes, 2–8
 ⁶⁷Zn NMR spectroscopy, 147–161
- Cope rearrangements, [3,3]-oxy-Cope
 rearrangement, 852
- Copolymers, π -conjugated, 790–791, 792
- Copper
 catalysis

- acylation reactions, 346–349, 505
addition reactions, 349–352
 Michael additions, 344–345, 352–360
alkyl–alkyl coupling, 540
cocatalysts, 500
cyclic anti-carbomagnesiation, 464, 465
enantioselective reactions
 alkynylation, 565
 conjugate addition, 568–569
 organozinc reagents, 333–360
 substitution reactions, 334–346, 347
Reformatsky reactions, 805
Zn–Cu carbenoids, 238, 335, 336
Zn–Cu transmetalation
 allylzincation, 910–911, 914, 927,
 940–941
 carbozincation, 868, 871, 873, 876, 883,
 948–949
 Cu(I) cyanide, 293, 303, 305, 306,
 333–334, 347–348
 perfluoroalkynylzinc reagents, 738
 polyfunctional organozinc halide
 preparation, 293, 295, 303, 305, 306
 zinc enolate addition, 961, 964, 965
Copper(I) cyanide, transmetalation, 293, 303,
305, 306, 333–334, 347–348
Copper(I) halides,
 dialkoxyphosphinyldifluoromethylzinc
 catalysis, 746–747
Copper–zinc superoxide dismutase, structure,
6, 7
Correlation spectroscopy (COSY), 151
Corriu, Kumada–Tamao–Corriu coupling, 459
COSMOS (computer simulation of molecular
structures), 154
COSY, ¹H NMR spectroscopy, 151
Countercations
 Pd- or Ni-catalyzed cross-coupling,
 467–473, 526–528
 synergistic effects, 527
Coupling reactions
 dialkoxyphosphinyldifluoromethylzinc
 reagents, 746
 Gaudemar/Normant coupling, 647–649,
 667–671
 homo-coupling, 293
 transition metal-catalyzed, 833–837
 Wurtz-coupling, 292
 see also Cross-coupling reactions
CP (cross polarization), 153, 156
CPA *see* Carboxypeptidase A
CPL (circularly polarized light), 581, 583, 585
Cross-coupling reactions
 Cu(I)-catalyzed, 344, 346, 347
 Negishi reactions, 288, 361–370, 504, 507
 Ni-catalyzed, 457–553
 acylation, 542–544
 thioesters, 370, 371
 alkenyl–alkenyl reactions, 461, 462,
 492–499
 alkenyl–aryl reactions, 461, 462,
 487–491
 alkylation, 477, 479–480, 524–542
 alkyl electrophiles, 526, 528, 533, 535,
 539–542
 alkyl halides, 477, 479–480, 528, 533,
 535, 539–542
 history, 525–526
 natural product synthesis, 528–538
 alkynylation, 500
 allenylation, 516–524
 allylation, 474, 516–524
 aryl–alkenyl reactions, 487–491
 aryl–aryl reactions, 483–487
 aryl chlorides, 294, 362, 363, 486–487
 benzylation, 516–524
 catalyst poisoning, 519
 carbometalation, 461, 526
 catalyst poisoning, 519
 catalysts and ligands, 467, 475–480,
 526–528
 cocatalysts or additives, 467, 481
 conjugated diene synthesis, 461–462
 countercations, 467–473, 526–528
 cyanation, 544
 double cross-coupling, 488, 490
 Grignard reaction, 459
 hydrometalation, 461, 526
 leaving groups, 11, 473–475, 526–528
 organozincs, 461
 overview, 467–483
 propargylation, 516–524
 solvents, 467, 481–483
Pd-catalyzed, 457–553
 acylation, 542–544
 alkenyl–alkenyl reactions, 461, 462,
 492–499, 501, 503
 alkenyl–alkynyl reactions, 501
 alkenyl–aryl reactions, 1, 461, 462,
 487–491
 alkylation, 477, 479–480, 524–542
 alkyl electrophiles, 526, 528, 533, 535,
 539–542
 alkyl halides, 528, 533, 535, 539–542
 history, 525–526
 natural product synthesis, 528–538
 alkynylation, 500–516
 α -alkynylation, 512–516
 alkynyl–acyl reactions, 505–506
 alkynyl–alkenyl reactions, 504,
 507–512, 513, 514
 alkynyl–alkynyl reactions, 504, 512
 alkynyl–aryl reactions, 504
 catalyst poisoning, 503
 dialkynylation, 514

- Cross-coupling reactions (*continued*)
 electrophiles, 500, 501, 503–507, 512–516, 517
 natural product synthesis, 516, 517, 518
 protocols, 499–503
 selective monoalkynylation, 501, 508, 512
 Zn, B and Sn alkynylmetals, 463
allenylation, 516–524
 allenyl–aryl(allyl) reactions, 521–522
 natural product synthesis, 523, 524
allenylzinc bromide reagents, 436, 436
allylation, 474, 516–524
 alkynyl–allyl reactions, 520–521
 natural product synthesis, 523, 524
allylzincation, 904, 911, 933, 934
aryl–alkenyl reactions, 487–491
aryl–alkynyl reactions, 501
aryl–aryl reactions, 483–487
arylzinc–aryl halides, 777–779, 790
benzylation, 516–524
 alkynyl–benzyl reactions, 520–521
 catalyst poisoning, 503
 heterocycles, 523
 natural product synthesis, 523, 524
carbometalation, 461, 464, 526
carbozincation
 intermolecular, 880, 884
 intramolecular, 869–870, 948, 949, 953
catalyst poisoning, 503, 519
catalysts and ligands, 467, 475–480, 526–528
classification, 460
cocatalysts or additives, 467, 481, 500, 501
conjugated diene synthesis, 461–462
counteractions, 467–473, 526–528
cyanation, 544
diorganozinc preparation, 313
double cross-coupling, 488, 490, 507
enantioselective cross-coupling, 487, 488
fluorinated vinylzinc reagents, 715–722
history, 459–467
hydrometalation, 461, 463, 465, 470, 526
hydrozirconation, 462, 510
leaving groups, 467, 473–475, 526–528
organoborons, 461, 463
organozinc reagents, 361–370, 371, 461, 761
overview, 467–483
perfluoroalkynylzinc reagents, 737
propargylation, 516–524
 natural product synthesis, 523, 524
 propargyl–aryl(allyl) reactions, 521–522
solvents, 467, 481–483
zinc enolate addition, 961
 polyfunctional organozinc halide
 preparation, 300–301
 sp³-geminated organodizinc reagents, 661, 662
 Stille cross-coupling, 904
 zincates, 707–709
 see also Coupling reactions
Cross-homo scrambling, 11.77, Pd- or Ni-catalyzed alkylation, 528
Cross polarization (CP), ⁶⁷Zn QE NMR spectroscopy, 153, 156
Crotylzincation
 alkenes, 893–895
 alkenylmetals, 915, 916, 917–918
 alkynes, 471
 alkynylmetals, 942–943
 kinetic vs thermodynamic control, 938–939
 metallotropic reagent forms, 894, 895, 917
 see also Zincation
Crotylzinc bromide, allylmetalation, 617, 627
Crown ethers
 diarylmagnesium reactions, 50
 diphenylzinc complexes, 75–76
Cryptands, diarylmagnesium reactions, 50
Crystal lattices, ⁶⁷Zn NMR spectroscopy, 152
CSA (chemical shielding anisotropy), 153
CSA (chemical shift anisotropy), 155
Cubane-like zinc-containing clusters
 mass spectrometry, 172–174
 see also Heterocubane
Cyanation, Pd- or Ni-catalyzed, 544
Cyanohydrins, Reformatsky reactions, 827, 829
Cyclic aldimines, enantioselective addition of diorganozincs, 570
Cyclic anhydrides, Ni-catalyzed acylation, 542, 543
Cyclic voltametry
 bipyridine complexes, 775, 782
 cobalt halide reduction, 782
Cyclization
 allenylzincs to alkynylsilanes, 949–950
 carbozincation
 alkenes, 870–876
 alkynes, 868–870, 879
 di(5-hexynyl) metals, 871
 endo-cyclization, 703–704
 enone–alkyne reductive cyclization, 886–888
 exo-cyclization, 703–704
 gem-dialkyl effect, 954
 macrocyclization, 818
 σ-type, 879, 939
 zinc–ene–allene reactions, 629–633, 950–954
 zinc enolates, 633, 959–964, 965
 Zn–Cu transmetalation, 868, 876

- Zn-ene reactions, 901–908, 932, 935–936, 951, 952, 953
- trans*-2-Cyclohexene-1,4-diols, stereoselective cyclopropanation, 259–260
- Cyclohex-2-en-1-one, conjugate addition of arylzinc compounds, 776
- Cyclohexyne, alkynylzincate 1,2-migration, 703–704
- Cyclooctadiene, Ni-catalyzed alkylation, 541
- [η^5]-Cyclopentadienylrhenium tricarbonyl complex, enantioselective aryl transfer, 567
- Cyclopropanation
- Simmons–Smith reactions, 237–238, 288, 842, 844
 - sp³-geminated organodizinc reagents, 671–674
 - zinc carbenoids, 237–286
 - alkene cyclopropanation, 245–281
 - gem*-dizinc carbenoid, 241
 - mechanism, 245–246
 - preparation and structure, 238–245
 - α -substituted, 240–242
 - synthetic scope, 246–281
 - unsubstituted, 238–240
- Cyclopropanes
- allylmetalation of alkenyl metals, 619–620
 - halo-substituted, 251–252
 - 1,2-migration rearrangement, 604
 - sacrificial anode process, 761–762
 - stereoselective cyclopropanation, 275
 - 1,2,3-substituted, 275
- Cyclopropanols
- enolate cyclopropanation, 250
 - enol ester cyclopropanation, 249–250
 - stereoselective cyclopropanation, 271–272
- Cyclopropenes, dicrotylzinc allylzincation, 894, 895
- Cyclopropenone ketals
- allylzincation, 894–898
 - Fe-catalyzed carbозincation, 881–882
 - zinc enolate addition, 968–969
- Cyclopropylamines, stereoselective cyclopropanation, 271
- Cyclopropylboronic acids, stereoselective cyclopropanation, 271–272
- Cyclopropylmethanol, stereoselective cyclopropanation, 262, 273
- Cyclopropylmethylamine, stereoselective cyclopropanation, 271
- Cyclopropylzinc compounds
- cyclopropenone ketal allylzincation, 897–898
 - dicrotylzinc reactions, 894, 895
 - 1,3-elimination, 927–931, 939
 - halo-substituted cyclopropane synthesis, 252–253
 - zinc enolate addition, 968
- Cysteine, Zn(II) tetrapyrrole photosensitizers, 411
- DAIB (3-*exo*-(dimethylamino)isoborneol), 557, 568
- DBNE (*N,N*-dibutylnorephedrine), 557, 566, 569
- Decamethylidzincocene, mass spectrometry, 174
- Degradation, Zn(II) porphyrins and phthalocyanines, 398
- Dehalogenation, perfluoroalkynylzinc reagent preparation, 736–737
- β -Dehydrometalation, Pd- or Ni-catalyzed alkylation, 525
- 6,7-Dehydrostipamide, Pd-catalyzed synthesis, 493, 495, 512, 517, 518
- Delactonmycin, Pd-catalyzed synthesis, 529, 531
- Dendrimer bound amino alcohols, enantioselective addition to imines, 570
- Dendrimers
- zinc enolate synthesis, 837, 838
 - Zn(II) porphyrins, 405
 - fullerenes, 399
- Density functional theory (DFT)
- aminopeptidase reaction mechanisms, 14
 - bond energies, 142
 - C-Zn exchange dynamics, 196, 201, 210, 215
 - dialkylzinc structure, 55
 - Zn(II) coordination chemistry, 154
- Dermostatins A and B, Pd-catalyzed synthesis, 510
- Destannylation, cyclopropanation using zinc carbenoids, 255
- α -Deuteriated chiral primary alcohols, enantioselective asymmetric autocatalysis, 581
- DFT *see* Density functional theory
- Dialkoxyporphinyl difluoromethylzinc reagents, 744–747
- reactivity, 745–747
- Dialkylation, 1-sila-1-zircona-1-alkenes, 533
- gem*-Dialkyl effect, Zn-ene-allene cyclization, 954
- Dialkylphosphines, Pd and Ni catalysts, 477, 478
- Dialkylzinc compounds
- alkyl-Zn exchange dynamics, 195–200
 - bond energies, 142–143
 - chain growth polymerization, 142
 - chemoselective addition, 561
 - enantioselective reactions
 - addition, 556–586
 - asymmetric dialkylzincs, 561
 - conjugate addition, 568–569

- Dialkylzinc compounds (*continued*)
 Reformatsky reactions, 811–815
 enthalpies
 of formation, 138, 140–142, 143
 of isomerization, 141–142
 of vaporization, 138–139
 mass spectrometry, 166–171
 metal exchange reactions, 560
 structure, 53–82
 intramolecularly coordinating substituents, 65–68
 Zr-promoted alkyne carbozincation, 471–472
- Di-*n*-alkylzinc compounds, enthalpies of formation, 140, 141
- Dialkynylation, Pd-catalyzed cross-coupling, 514
- Dialkynylzincs, enantioselective addition, 565
- Diallylmagnesium, metallotropic exchange dynamics, 206
- Diallylzincs
 allylzincation of alkenes, 892–893
 metallotropic C-Zn exchange dynamics, 205–206, 208
- Diarylcarbinols, enantioselective addition of diorganozincs, 375, 377
- Diarylmagnesium, ionic structures, 50
- Diarylzinc compounds, structure, 53–82
- Diastereoselection
 acyclic alkene cyclopropanation, 261–266
 alkenylmetal allylzincation
 A-1,3 strain, 919
 mutual diastereoselection, 915–916, 917, 921
 substrate-induced diastereoselection, 917–927
 allenylzinc reagents, 438–442, 446–451
 allylic zinc reagents, 319, 323, 324
 Reformatsky reactions, 806, 812, 815–819
- Diastereoselective construction, sp^3 -geminated organozinc reagents, 667–671
- Diastereospecificity, pinacolone rearrangement, 674–675
- (-)-Diazonamide A, Pd-catalyzed synthesis, 490–491
- Dibenzylzinc, C-Zn inversion dynamics, 228–229
- Diboration, Pd-catalyzed alkenylation, 465
- 1,1-Dibromoalkenes
 1,2-metallate rearrangements, 597–598
 Pd-catalyzed disubstitution, 536
 trans-selective monosubstitution, 476, 492, 497–498, 507
- Dibromobenzene, electrosynthesis of arylzinc compounds, 787
- 1,1-Dibromocyclopropanes, 1,2-metallate rearrangements, 598–600
- 2,5-Dibromo-3-substituted thiophenes, thienylzinc synthesis, 772–773
- N,N*-Dibutylnorephedrine (DBNE)
 enantioselective reactions
 dialkylzinc addition, 557, 569–570
 phenyl transfer, 566
- Di-*s*-butylzinc, *meso* and *racemic* diastereomers, 199
- Di(*tert*-butyl)zinc
 uncatalyzed intermolecular carbozincations, 865–867
 addition to alkenes, 866–867
 addition to alkynes, 865–866
- Dicarbonyl derivatives, cyclopropanation using zinc carbenoids, 250
- α,α -Dichloroacetate, electrochemical Reformatsky reaction, 804
- 1,1-Dichloro-1-alkenes
 Pd-catalyzed cross-coupling
 double substitution, 492, 507
 Negishi and Sonogashira reactions, 507
- Dichlorobenzene, electrosynthesis of arylzinc compounds, 787
- 1,2-Dichloroethylene alkenylation
 alkynyl–alkenyl coupling, 508, 510
 Sonogashira reaction, 501, 508
- 1,1-Dichloro-1-octene, *trans*-selective monosubstitution, 27, 482
- β,β -Dichlorostyrenes, *trans*-selective monosubstitution, 490
- 2,5-Dichlorothiophene, electrosynthesis of arylzinc compounds, 787
- 1,1-Dichlorotrifluoroethylzinc chloride, 742–743
- Dicrotylzinc, allylzincation of alkenes, 893–894
- gem*-Dicyanoalkenes, Reformatsky reactions, 829, 831
- Dicyclopentadienyl compounds, transition metals, 60, 123–125
- Dicyclopentadienylzinc (zincocene)
 mass spectrometry, 171
 metallotropic C-Zn exchange dynamics, 210–211
 structure, 61–64, 116, 123–125
- Dicyclopropylzinc
 dicrotylzinc reactions, 894, 895
 enantioselective addition, 559
- Diels–Alder reactions, Cu(I)-catalyzed substitution, 344, 346
- Dienes
 conjugated, 461–462
 fluorinated, 717, 727–729
- 1,3-Dienes
 multi-component reactions, 888, 889
 preparation, 663
- 1,5-Dienes, homologation of terpenoids, 534

- 2,4-Dienylzinc compounds, metallotropic C-Zn exchange dynamics, 205, 208–210
- Diethyl bromomalonate, Reformatsky reaction, 829, 830
- Diethyl methylbromomalonate, zinc enolate addition, 956–957
- Diethylzinc
alkyl-Zn exchange dynamics, 203, 214–216
calixarene complex, 104
enantioselective addition
 conjugate addition, 576, 798
 to benzaldehyde, 573, 574–575
 to imines, 570–571
I₂-Zn exchange, 872, 874, 876
mass spectrometry, 167–169, 174
pyrolysis, 185–186
Ni-catalyzed cross-coupling, 477, 479
self-chemical ionization, 166, 167–168, 181
zinc enolate synthesis, 798, 842–854
- gem*-Difluoroallylic alcohols,
 3-bromo-3,3-difluoropropene reaction, 734
- gem*-Difluoroallyl intermediate, fluorinated allylzinc reagent preparation, 734
- gem*-(Difluoroallyl)lithium reagent, allylation, 734
- (Difluoroallyl)silanes, preparation, 735
- α,α -Difluoro- β -amino acids, Gilman–Speeter reactions, 821
- α,α -Difluoro- α -bromoesters, Reformatsky reactions, 809
- 1,1-Difluoro-3-(dimethylphenylsilyl)propene, allylation, 734
- 3,3-Difluoro-3-(dimethylphenylsilyl)propene, allylation, 735
- L-4,4-Difluoroglutamic acid, diastereoselective Reformatsky reaction, 817
- 1,1-Difluoromethylene olefins, preparation, 721–722
- E*- α,β -Difluorostyrenes, stereospecific preparation, 725, 726
- Z*- α,β -Difluorostyrenes, stereospecific preparation, 725
- β,β -Difluoro- α -(trifluoromethyl) styrenes, preparation, 726–727
- 2,2-Difluoro-3-(trimethylsilyl)methyl-3-buten-1-ol derivatives, 735
- α -Difluorovinyl substituted β -hydroxyesters, preparation, 735, 736
- Dihaloalkanes
 sp³-geminated organodizinc preparation, 645–646
 1,1-dihaloalkane preparation, 646
 heteroatom-substituted, 646–647
 α -substituted zinc carbenoid preparation, 240
 triorganozincate rearrangement, 597–598, 600–602
- 1,1-Dihalo-1-alkenes
 double cross-coupling, 488, 490, 507
 Pd-catalyzed alkynylation, 506–507
 triorganozincate rearrangement, 597–598
- 1,2-Dihalo-1-alkenes, Pd-catalyzed alkynylation, 506–507, 509
- Dihaloalkylzinc compounds, mass spectrometry, 166–171
- 1,1-Dihalocompounds, triorganozincate rearrangement, 596–602
- 1,1-Dihalocyclopropanes, triorganozincate rearrangement, 598–600
- 1,2-Dihaloethylenes, Pd-catalyzed alkynylation, 507, 509, 513
- Dihalomethane, sp³-geminated organodizinc preparation, 643–645
- Dihalomethylzinc carbenoids, halo-substituted cyclopropane synthesis, 252
- Di(5-hexynyl) metals, cyclization, 871
- Dihydrooxazoles, stereoselective cyclopropanation, 273
- (–)-4a,5-Dihydrostreptazolin, Pd-catalyzed synthesis, 529, 530
- 1,1-Diiodoalkanes, cyclopropanation using zinc carbenoids, 255
- 1,4-Diiodo-2-methyl-1-butenes, homologation of terpenoids, 534
- Diiodomethane
 cyclopropanation using zinc carbenoids, 250
 I₂-Zn exchange, 309
- Diisopropenylzinc, enantioselective addition, 564
- Diisopropyl tartrate metal alkoxide, enantioselective addition of diorganozincs, 570–571
- Diisopropylzinc, enantioselective asymmetric autocatalysis, 577, 579, 581
- 1,3-Diketone, sp³-geminated organodizinc sequential reactions, 664–665
- Dimeric zinc complexes, mass spectrometry, 174–176
- Dimerization reactions
 allylzincation of alkenes, 892–893
 perfluoroalkylzinc reagent preparation, 739
- Dimetalated carbon stereocenters, alkenylmetal allylzincation, 927–932, 936–937
- 1,1-Dimetallic species
 1,2-metallate rearrangements, 614
 zincated hydrazone and alkenylmetal, 675–676
- Dimethylzinc, allylzincation of alkenes, 893
- Dimethoxyethane (DME), bis(iodomethyl)zinc complex, 273–274
- 3-*exo*-(Dimethylamino)isoborneol (DAIB)
 enantioselective addition of dialkylzincs, 557
 conjugate addition to enones, 568

- Dimethylcadmium, methyl-Zn exchange dynamics, 211–214
- Dimethylformamide (DMF), Pd- and Ni-catalyzed cross-coupling, 481, 483, 505, 544
- N,N*-Dimethylhydrazones, aza-enolate addition, 964, 965, 966
- 1,3-Dimethyl-2-imidazolidinone (DMI), Ni-catalyzed alkylation, 541
- Dimethylmagnesium, alkyl exchange dynamics, 198
- Dimethylmercury, methyl-Zn exchange dynamics, 212
- Dimethylzinc
alkyl-Zn exchange dynamics, 195–199, 211–214, 215–216
electron ionization mass spectrometry, 166–167
pyrolysis mass spectrometry, 185
radical cation thermochemistry, 144
- Dineohexylzinc, C-Zn inversion dynamics, 217–218, 220, 221
- gem*-Diorganometallic species, alkenylmetal allylzincation, 908–913, 931, 965, 966
- Diorganozinc compound structure
donor–acceptor complexes, 70–82
heteroleptic, 57–58
homoleptic, 53–57
intramolecularly coordinating substituents, 64–70
multi-hapto bonded groups, 60–64
- Diorganozinc reagents
alkyl-Zn exchange dynamics, 199
classification, 288–289
electrophile reactivity, 308–309
enantioselection addition
functionalized, 560–561
to carbonyl compounds, 556–561
to imine derivatives, 569–573
to ketones, 561–563
preparation
alkene hydrozincation, 316–317, 318
B–Zn exchange, 311–316
I₂–Zn exchange, 308–311, 312
- Dioxaborolane ligand, stereoselective cyclopropanation, 273, 275
- Dipent-4-enylzinc, metallotropic C-Zn exchange dynamics, 208
- Dipeptides, stereoselective cyclopropanation, 277, 280, 281
- Diphenyl(1-methylpyrrolidin-2-yl)methanol (DPMPM)
enantioselective reactions
dialkylzinc addition, 557
phenyl transfer, 566
- N,N*-Diphenylphosphinylimines, enantioselective addition of diorganozincs, 569–571, 575
- Diphenylzinc
arylacetylene carbozincations, 880
asymmetric phenyl transfer reactions, 566
C–Zn exchange dynamics, 201
enantioselective addition to aldehydes, 566
structure, 59
crown-ether complexes, 75–76
- 1,3-Dipolar intermediate, carbozincations, 890
- Diprenylzinc, allylzincation of alkenes, 893
- Directing metalating group (DMG), *ortho*-metalation, 52
- Discodermolides, Pd-catalyzed synthesis, 493, 529, 533
- Disproportionation, cobalt halide catalysts, 783, 784
- Distannation, Pd-catalyzed alkenylation, 465
- Disubstituted alkynes, transition metal-promoted allylzincation, 901
- 1,1'-Disubstituted allene, enantioselective asymmetric autocatalysis, 581
- Disubstituted 1,1-dibromo-1-alkene, (–)-callystatin A synthesis, 536
- Disulfide–oxazolidine, enantioselective addition of alkynylzincs, 565
- Disulfonamide ligand, stereoselective cyclopropanation, 279
- Divinylzinc
C–Zn exchange dynamics, 201–202
C-Zn inversion dynamics, 227
enantioselective addition to aldehydes, 563
- Diynes, Pd-catalyzed cross-coupling, 504, 508, 512, 513, 514
- 1,3-Diynes, allylzincation, 938
- 1,7-Diynes, allenylzincation, 948–949
- Dizinc compounds
electrosynthesis, 787, 788
see also Geminal bismetallic reagents
- DME (dimethoxyethane), 273–274
- DMF (dimethylformamide), 481, 483, 505, 544
- DMG (directing metalating group), 52
- DMI (1,3-dimethyl-2-imidazolidinone), 541
- DNA
Zn(II) tetrapyrrole photosensitizers, 410–411
⁶⁷Zn NMR spectroscopy, 156
- Domino-Michael addition, Cu(I)-catalyzed, 353, 355
- Donor–acceptor complexes
diorganozinc structure, 70–82
N,N-chelating ligands, 78–79
photoinduced electron transfer, 398–406
axial coordination, 405
chelation, 404–405
light-harvesting complexes, 402
materials and formulations, 405–406
novel acceptor groups, 399–402
reaction center models, 402
synthetic strategies, 402–405

- Double bonds, electron-poor C=C, 829–837
- Double diastereoselection, allenylzinc reagents, 438–442, 446–451
- DPEphos *see*
Bis(*o,o'*-diphenylphosphino)phenyl ether
- DPMPM (diphenyl(1-methylpyrrolidin-2-yl)methanol), 557, 566
- dppf (bis(1,1-diphenylphosphino)ferrocene), 476–477, 492, 498, 505, 519
- Dyes, Zn(II) phthalocyanines, 406
- Dynamic behavior
 organozinc compounds, 193–236
 C–Zn exchange, 194, 195–216
 C–Zn inversion, 194, 217–230
- Dzhemilev ethylmagnesium, 471
- Echo repetitions, solid-state ^{67}Zn QE NMR spectroscopy, 154
- Efavirenz, AIDS drug, 374, 376
- EFG tensors *see* Electric field gradient tensors
- EI *see* Electron ionization mass spectrometry
- Electric field gradient (EFG) tensors
 ab initio calculations, 156
 ^{67}Zn NMR spectroscopy, 151–152, 156
 computation, 152
- Electrochemical generation
 arylzinc compounds, 295, 773–776
 reactivity, 776–781
 highly reactive Zn, 803
 organozinc reagents, 755–796
- Electrochemical Reformatsky reactions, 803–805
- Electrolytic zinc, organozinc reagent generation, 760–765
- Electron carriers, Zn(II) phthalocyanine photovoltaics, 407, 408
- Electron diffraction
 bond energies, 142
 enthalpies of formation, 141
 see also Gas phase electron diffraction
- Electron donors, Zn(II) porphyrin and phthalocyanine photovoltaics, 407, 408, 411
- Electronegativity, enthalpies of formation, 140, 141
- Electron ionization (EI) mass spectrometry
 binuclear Zn complexes, 174
 bis(benzoylmethane) complex, 179
 bis(monothiodibenzoylmethane) complex, 179
 bis(perfluoroalkyl)zinc compounds, 169–171
 bis[2,4,6-tris(trifluoromethyl)phenyl]zinc, 171
 cubane clusters, 173–174
 diethylzinc, 167–168, 174
 dimeric Zn complexes, 174
 dimethylzinc, 166–167
 ferrocenyl-containing Zn complexes, 177–178
 gas phase ion/molecule reactions, 181, 184
 heterometallic compounds, 177–178
 ionization energy measurement, 179
 methylzinc isopropoxide, 172
 monomeric Zn complexes, 176–177
 organozinc fragments, 177–179
 zincates, 178
- Electron-poor carbon-carbon double bonds, Reformatsky reactions, 829–837
- Electron transfer *see* Photoinduced electron transfer; Single-electron transfer
- Electron-withdrawing groups
 electrosynthesis of arylzinc halides, 789
 Pd-catalyzed alkylation, 501
- Electrophiles
 diorganozinc reactivity, 308–309
 organozinc reactivity, 322–323
 Pd-catalysis
 alkylation, 526, 528, 533, 535, 539–542
 alkynylation, 500, 501, 503–507, 512–516, 517
 allylation, 518–519
 benzylation, 519
 propargylation (allenylation), 518, 519
 Reformatsky reagents, 827–837
 sp³-geminated organozinc sequential reactions, 659–667
- Electropositivity, enthalpies of formation, 140, 141
- Electroreduction, reactive Zn generation, 756, 758–759, 762–763, 770
- Electrospray ionization (ESI) mass spectrometry, cubane clusters, 172–173
- Elimination reactions
 1,3-elimination
 allenylzincation, 945, 946
 allylzincation
 alkenylmetals, 927–931
 alkynylmetals, 939
 β-elimination, 528
 elimination–addition, 328, 329
- Enals, 1,2-addition of alkenylalkylzinc, 564
- Enantiomeric excess, asymmetric amplification, 573–576
- Enantioselective asymmetric cross-coupling, 487, 488
- Enantioselective reactions
 addition reactions, 555–593
 alkynylzinc to aldehydes/ketones, 565–566
 asymmetric amplification, 556, 570, 573–576, 578–580
 asymmetric autocatalysis, 556, 576–584
 consecutive reactions, 583
 high enantioselectivity, 576–578

- Enantioselective reactions (*continued*)
spontaneous absolute asymmetric synthesis, 583–584, 586
automultiplication, 576–577
conjugate addition, 568–569, 576, 798
dialkylzincs to carbonyl compounds, 556–569
aldehydes, 97–99, 556–558, 563–564, 576–584
alkenylation, 563–564
aryl transfer, 566–567
asymmetric addition, 560–561, 566–567
enones, 568–569
functionalized, 560–561
ketones, 561–564
Lewis base catalysts, 556–560
diorganozincs to imine derivatives, 569–573
lithium triorganozincate preparation, 321
enantioselective cross-coupling, 487, 488
(+)-ibuprofen synthesis, 339, 340
Reformatsky reactions, 811–812, 813–814
Endo-cyclization, alkynylzincate 1,2-migration, 703–704
Energetics, organozinc ion structures, 179–181, 184
Energy conversion, Zn(II) phthalocyanine photosensitization, 407–409
Energy diagrams, sp^3 -geminated organodizinc carbometalation, 647–648
Enolates
 α -alkynylation, 514
anion structure, 73–74
regioselective alkylation, 513
see also Zinc enolates
Enol esters, cyclopropanation using zinc carbenoids, 249–250
Enol ethers, cyclopropanation using zinc carbenoids, 249, 271
Enones
anionic carbozincations, 872, 874
conjugated, 513, 852
enantioselective dialkylzinc addition, 568–569
enone–alkyne reductive cyclization, 886–888
Pd-catalyzed α -alkynylation, 514, 516
Zn–ene–allene cyclization, 953
Enthalpies of formation, 137
dialkylzinc compounds, 138, 140–142, 143
electron diffraction/photoelectron spectroscopy, 141
homologous series, 140–141
linear regression analysis, 140
methylene increment, 141
monoalkylzinc compounds, 143
quantum chemical calculations, 141
unweighted least squares regression analysis, 141
Enthalpies of isomerization, 141–142
Enthalpies of reaction, 140
Enthalpies of vaporization, 137
CHLP protocol, 138
dialkylzinc compounds, 138–139, 140
homologous series, 138
linear regression analysis, 138
temperature correction, 138
Entropy, C–Zn inversion dynamics, 220
1,3-Enynes
allylzincation
alkynes, 899–900
alkynylmetals, 937–938
allenylmetals, 933–934, 935
carbolithiation, 933–934, 935, 951, 952
uncatalyzed intermolecular carbozincations, 866
1,4-Enynes, allenylzincation, 945–946
1,6-Enynes
cyclization, 953
Ti-catalyzed carbozincations, 884–885
1,7-Enynes
carbozincations
intramolecular, 950–951
Ti-catalyzed, 884–885
Enynoic acids, Pd-catalyzed alkynylation, 501
Enzymes *see* Coenzymes; Zinc enzymes
(1*R*,2*S*)-Ephedrine, chiral auxiliary, 925
Ephedrine–silica hybrid, enantioselective asymmetric autocatalysis, 584
Epiandrosterone, diastereoselective Reformatsky reaction, 817–818
Epothilones A and B, Pd-catalyzed synthesis, 529, 530, 531
Epoxidation, Katsuki–Sharpless, 573
Epoxides
chiral, 581
ring-opening, 328, 330, 337, 690
ESI (electrospray ionization), 172–173
Esters
fluorinated vinylzinc reagents, 716
 sp^3 -geminated organodizinc methylenation, 654–655
Ethyl bromoacetate, Reformatsky reaction, 798
Ethyl bromodifluoroacetate, Reformatsky reaction, 801–802
Ethyl-3-bromodifluoromethyl-3-benzyloxy-acrylate, 735
Ethyl 2-bromo-2-methylpropanoate, Reformatsky reaction, 801–802
Ethylene, Ti(II)–ethylene complex, 885
Ethylene–zirconocene complex, ethylzincation, 884
Ethylmagnesium, Dzhemilev, 471
Ethylzinc alcoholate, structure, 99, 100, 103

- Ethylzinc amide, structure, 115
Ethylzincation
 Zr-catalyzed, 471, 527, 884
 see also Zincation
Ethylzinc diphenylamide, structure, 107–108
Ethylzinc diphenylphosphide, structure, 122–123
Ethylzinc–enamine, ethylzinc–aldolate formation, 78
Ethylzinc enolate, structure, 105
Ethylzinc halides, alkyl–Zn exchange dynamics, 202–203
Ethylnylmetals, Pd-catalyzed alkynylation, 501
Euniconone A, Pd-catalyzed synthesis, 493, 495, 497
Exchange reactions
 Br–Zn, 296, 299
 C–Zn
 alkyl group effect on rate, 214–215
 intermolecular exchange, 195–205
 mechanism, 215
 metallotropic exchange, 205–211
 mixed exchange, 201
 organometallic compounds, 211–216
 halogen–Zn, 430–432, 470, 688–689
 intramolecular carbocation of alkenes, 870–874
 I₂-Zn, 870–875, 876
 Zn–Hg, 870, 871
Excitonic interactions, Zn(II) porphyrin PET, 402–403
Exo-cyclization, alkynylzincate 1,2-migration, 703–704
Eyring equation, activation parameters, 232–233

FAB (fast atom bombardment), 176–177
 α -Farnesene, Pd-catalyzed alkenyl–allyl coupling, 523
Farnesols, Pd-catalyzed synthesis, 529, 531, 535
Fast atom bombardment (FAB) mass spectrometry, monomeric Zn complexes, 176–177
FBW (Fritsch–Buttenberg–Wiechell rearrangement), 627–629, 942–944
N,O-Ferrocene, enantioselective addition of alkynylzincs, 565
Ferrocenyl alkanol, enantioselective asymmetric autocatalysis, 577, 578
Ferrocenyl-containing compounds
 electron ionization mass spectrometry, 177–178
 Pd-catalyzed cross-coupling, 365, 367
Ferrocenyl hydroxy oxazoline, enantioselective aryl transfer, 567
Field sweeping, ⁶⁷Zn NMR spectroscopy, 155
Fischer carbene complexes, diorganozinc addition, 327
Fish deterrents, sporochinol, 339, 341
Fluorinated allylzinc reagents, 733–736
 α -Fluorinated carboethoxy substrates, Reformatsky reactions, 750
Fluorinated 1,2,3-cumulenes, preparation, 728
Fluorinated diene preparation, 717
 stereospecific, 727–729
Fluorinated organozinc reagents, 713–754
Fluorinated polyenes, preparation, 717–718
Fluorinated propargylzinc reagents, 733–734, 736
Fluorinated styrenes, preparation, 720–721, 725–727
Fluorinated vinylzinc reagent preparation
 C–halogen Zn insertion, 722–732
 acylation, 729–730
 allene formation, 730–731
 allylation, 729
 direct, 722
 functionalized CF₃ compounds, 730
 polymer precursors, 731, 732
 stereospecific preparation, 725–729
 fluorinated vinyl halides, 719–722, 723
 vinylithium reagents
 ambient temperature *in situ* capture, 718–722
 low temperature capture, 714–718
Fluorination, Reformatsky reactions, 809–811
Fluoroalkenylzinc reagents, 714–732
Fluoroenynes, preparation, 716–717
 α -Fluorophosphonates,
 dialkoxyphosphinyldifluoromethylzinc reactions, 747
Formic acid, photoreduction of carbon dioxide, 411
Fourier transform–ion cyclotron resonance (FT–ICR)
 diethylzinc, 166, 167–168, 181
 gas phase ion/molecule reactions, 181, 182–183
 Zn(II) cyanide complexes, 179
FR-900848 natural product, stereoselective cyclopropanation, 276
FR-901464 (antitumor antibiotics), Pd-catalyzed synthesis, 493, 495
Freelingyne, Pd-catalyzed synthesis, 501, 517
Frenkel-type excitons, Zn(II) porphyrin PET, 403
Fritsch–Buttenberg–Wiechell (FBW) rearrangement, 627–629
 alkynylmetal allylzincation, 942–944
 migrating abilities, 943, 944
FT–ICR (Fourier transform–ion cyclotron resonance), 166
Fukuyama reaction, Pearlman’s catalyst, 370, 371

- Fullerenes
photoinduced electron transfer, 399–400, 403
fullerene–porphyrin conjugates, 399
Reformatsky reaction, 831–832
- Functionalization
alkenyl 1,1-diorganometallic reagents, 940–945
fluorinated vinylzinc reagents, 730
organozinc compounds
enantioselective asymmetric addition, 560–561
preparation, 288–322
reactions, 322–379
unfunctionalized alkenes, 277
- Furukawa reagent
cyclopropanation, 241, 245
oxidative zincation, 469–470
solution structure, 245
- Gadain, Pd-catalyzed synthesis, 493, 494, 496
- Gas phase electron diffraction,
dicyclopentadienylzinc structure, 62
- Gas phase reactions, ion/molecule, 181–184
- Gas sensors, Zn(II) porphyrins, 412
- Gaudemar/Normant coupling, sp^3 -geminated organodizinc reagents, 647–649, 667–671
- GDH (glucose dehydrogenase), 409
- Geminal bimetallic reagents
allylmetalation, 615, 616
 sp^2 -geminated organodizinc reagents,
preparation and reactions, 677–680
 sp^3 -geminated organodizinc reagents
preparation, 642–650
reactions, 650–677
see also Dizinc compounds
- Geranyl acetate, Pd-catalyzed alkynylation, 506
- (2*E*,6*Z*,10*E*)-Geranylgeraniols, Pd-catalyzed synthesis, 529, 531, 535
- Germanium, Reformatsky reactions, 805
- α -Germylcyclopropylzinc, cyclopropanone ketal allylzincation, 898
- Germyl-substituted *gem*-dizincmethanes,
preparation, 646–647, 659, 660, 663, 664
- Gilman–Speeter reactions
zinc enolates, 799, 819–827
see also Reformatsky reactions
- Glucose dehydrogenase (GDH), NADH regeneration, 409
- Glucosides, stereoselective alkene cyclopropanation, 266, 267
- Glyceraldehyde, stereoselective cyclopropanation, 265
- L-Glyceraldehyde acetonide, diastereoselective Reformatsky reaction, 816
- (+)-Goniobutenolide A, Pd-catalyzed alkynylation, 501
- Graphite *see* Potassium–graphite
- Graylag goose preen gland wax, Pd-catalyzed synthesis, 529, 532
- Grignard reagents
alkenylmetal allylzincation, 908–909
alkyl-Zn exchange dynamics, 203–204
cross-coupling reactions
Ni-catalyzed, 459, 539, 540
Pd-catalyzed, 463
Cu(I)-catalyzed addition, 351
Fe-catalyzed alkylation, 542
Grignard-type protocol, Reformatsky reaction, 799
- Hahn, Hartman–Hahn matching field, 157
- Half-band widths, ^{67}Zn NMR spectroscopy, 150
- Half-integer spins, ^{67}Zn , 153
- Haloalkylzinc compounds, structure, 80
- Haloboration, Pd-catalyzed alkynylation, 464
- α -Halo- β,β -difluorostyrenes, preparation, 720–721
- α -Haloenones, Pd-catalyzed α -alkynylation, 512–516
- α -Haloesters, C-halogen Zn insertion, 798, 799–800
- 2-Halogenopyridine, arylzinc compound reactions, 780–781
- Halogen–zinc exchange reactions
iodoallenes, 430–432
mixed zincate preparation, 688–689
Pd- or Ni-catalyzed alkylation, 528, 533
see also Carbon–halogen bonds;
Zinc-iodine exchange reactions
- Halometalation, Pd-catalyzed alkynylation, 463, 464
- Halomethylzinc alkoxides, structure, 242, 244
- Halomethylzinc carbenoids, zinc carbenoid preparation, 238–242
- Halomethylzinc reagents, solid and solution structures, 242–245
- Halo-substituted cyclopropanes, zinc carbenoid synthesis, 251–252
- (*Z*)-3-Halo-1-trimethylsilyl-3-en-1-yne,
Pd-catalyzed cross-coupling, 508
- β -Halo- α,β -unsaturated esters,
propargylation–allynylation, 522
- Hartman–Hahn matching field, ^{67}Zn NMR spectroscopy, 157
- Harveynone, Pd-catalyzed synthesis, 514, 515, 516, 517
- Heat of formation *see* Enthalpies of formation
- Heck alkynylation, 500
- Helical silica, enantioselective asymmetric autocatalysis, 581, 584

- [6]Helicene, photosynthesis, 581
Helicenes, enantioselective asymmetric autocatalysis, 581
Hennoxazole A, Pd-catalyzed alkenyl–allyl coupling, 523
Heteroarylalkynes, Ni-catalyzed carbozincations, 881
Heteroarylzinc compounds, Co-catalyzed electrosynthesis, 785–790
Heterocubane
 electrospray ionization mass spectrometry, 172–173
 structure, 96, 100–102, 117
Heterocycles
 fluorinated vinylzinc reagents, 715
 Pd-catalyzed benzylation, 523
 Pd–*N*-heterocyclic carbene–naphthaquinone complexes, 540–541
 Zn–ene–allene cyclization, 954–956
N-Heterocyclic carbenes (NHC), Ni-catalyzed cross-coupling, 475, 480, 498
Heteroleptic compound structure
 diorganozinc compounds, 57–58
 monoorganozinc compounds, 82–123
 triorganozincates, 47–53
Heterometallic compounds, electron ionization mass spectrometry, 177–178
Heteronuclear multiple-quantum coherence (HMQC), 151
Heterosubstituted arylzincs
 Pd- or Ni-catalyzed cross-coupling, 484–486
 five-membered rings, 485–486
 six-membered rings, 486
 one heteroatom, 485, 486
 two heteroatoms, 486
 γ -Heterosubstituted organozinc reagents, substrate-induced diastereoselection, 917
Hetero-TOCSY, Cd(II) coordination chemistry, 151
Heterozincate structure, 45–46
 ortho-metalation, 51–53
Hexaalkynyl benzene, Pd-catalyzed alkynylation, 504
5-Hexyn-1-yl metals
 intramolecular carbocation
 alkenes, 870–871
 alkynes, 868
HMQC, Cd(II) coordination chemistry, 151
¹H NMR spectroscopy
 halomethylzinc reagents, 244
 Zn(II) organometallic compounds, 148–150
 COSY, 151
 hetero-TOCSY, 151
 HMQC, 151
 modified probe, 157
 paramagnetic doping, 157
Hollow fiber membranes, Zn(II) porphyrin PET, 406
Homoallyl alcohols
 activated Zn synthesis, 767
 allylzincation, 892
Homoallyl amines, allylzincation, 891–892
Homobenzylation, Pd-catalyzed natural product synthesis, 529
Homo-coupling, polyfunctional organozinc halide preparation, 293
Homodimerization, alkynes, 508
Homoenolates, formation, 698–699
Homoleptic diorganozinc compounds, structure, 53–57
Homoleptic triorganozincates, structure, 41–46
Homologation
 methylene, 605–614
 polymethylene, 305
 reduced polypropionates, 537
 silylated lithium carbenoids, 305
 terpenoids, 534
 zincates, 698–699
Homologous series
 bond energies, 143
 enthalpies of formation, 140–141
 enthalpies of vaporization, 138
Homolytic bond energies, dialkylzinc compounds, 142
Homopropargylation, Pd-catalyzed natural product synthesis, 529
Homopropargylic alcohol, iodoallene halogen–metal exchange, 430
Homopropargylic amine, allylzincation, 899
Homopropargylic compounds
 1,2-migration rearrangements, 602–604
 zinc enolate addition, 956–957
Human Carbonic Anhydrase, ⁶⁷Zn NMR spectroscopy, 156
Human Carbonic Anhydrase Isozyme II (CAII), ⁶⁷Zn NMR spectroscopy, 157, 158
Hydrazone
 zincated, 675–676
 see also SAMP hydrazone
Hydrazone zinc enolates, intermolecular carbocation, 300, 301, 840
Hydroalumination–cross-coupling tandem process, Pd- or Ni-catalyzed, 526, 527
Hydroboration
 diorganozinc preparation, 312–316
 Rh-catalyzed, 316
Hydrogenase, Zn(II) porphyrin and phthalocyanine catalysis, 409, 411
Hydrogen bonding, Zn(II) porphyrins, 405
Hydrogen generation, Zn(II) porphyrin and phthalocyanine photovoltaics, 407–409
Hydrolases, zinc enzyme reactions, 12–20
Hydromagnesiation, Ti-catalyzed, 917, 918

- Hydrometalation
 anti-hydrometalation, 463
 cyclic, 465
 Pd- or Ni-catalyzed cross-coupling, 461, 463, 465, 470, 526
 syn-hydrometalation, 463
- Hydroperoxides, Zn(II) phthalocyanine
 photosensitization, 407
- Hydroquinone, Zn(II) phthalocyanine
 reactions, 411
- Hydroxycarboxylic acids, enantioselective
 addition of dialkylzincs, 559, 560
- β -Hydroxy esters
 α -difluorovinyl substituted, 735, 736
 Reformatsky reaction, 799
- Hydroxyproline, enantioselective addition of
 dialkylzincs, 562–563
- β -Hydroxysulfoximines
 enantioselective conjugate addition, 568
 stereoselective cyclopropanation, 269
- Hydrozincation, alkenes, 316–317, 318, 470–471
- Hydrozirconation
 Pd-catalyzed cross-coupling, 462, 510
 Schwartz' reagent, 692
 terminal alkynes, 564
 Zr–Zn transmetalation, 265–266
- Hyperconjugation, β -dehydrometalation, 525
- (+)-Ibuprofen, enantioselective synthesis, 339, 340
- IE (ionization energy), 179–181
- Imines
 allenylzinc reagent addition, 446–447
 chloroallenylzinc reagent addition, 453–454
 diorganozinc enantioselective addition, 569–573
 methylene homologation, 611–614
- Iminophosphines, zinc enolate synthesis, 848
- Imino-Reformatsky reactions, 823, 824–825, 850–852
- Immobilized catalysts, enantioselective
 alkenylation, 556–560
- Immobilized zincates, preparation, 322
- Indium
 anti-hydrometalation, 463
 Reformatsky reactions, 805–806
- Indium(III) halides, catalysts, 480, 481, 482, 492
- 3-Indolepropionic acid/phenanthridine
 cocrystal, enantioselective asymmetric
 autocatalysis, 584
- Inducers, enantioselective asymmetric
 autocatalysis, 580–581, 582–583, 584
- Insertion reactions
 polyfunctional organozinc halide
 preparation, 293–295, 296, 308
 Zn into C–halogen bonds, 722–732, 733, 798, 799–800
 In silico studies, organozinc ion structures, 184–185, 186
 Insulin, ^{67}Zn NMR spectroscopy, 153
 Integer nuclei, ^{67}Zn , 153
 Intercalation, Zn(II) tetrapyrrole
 photosensitizers, 410
 Intermediates, C–Zn exchange dynamics, 197, 198, 200, 203, 205, 212, 215–216
 Intermolecular addition reactions, zinc enolates
 and alkenes, 964–971
 Intermolecular allylzincation
 transition metal-catalyzed
 alkenes, 898
 alkynes, 901
 uncatalyzed
 alkenes, 891–898
 alkynes, 898–900
 Intermolecular carbon–zinc exchange
 dynamics, 195–205
 Intermolecular carbocationizations
 allenylzinc reagents, 945–948
 alkenylmetal addition, 947–948
 alkynylmetal addition, 945–946
 di(*tert*-butyl)zinc, 865–867
 hydrazone zinc enolates, 300, 301, 840
 transition metal-catalyzed/promoted
 alkenes, 881–885
 alkynes, 472–473, 878–881
 uncatalyzed
 alkenes, 866–867
 alkynes, 865–866
 Interpulse acquisition periods, solid-state ^{67}Zn
 QE NMR spectroscopy, 154
 Intersystem crossing, Fe(II) porphyrin PET,
 402
 Intramolecular addition reactions, zinc enolates
 and alkenes, 959–964, 965
 Intramolecular carbocationizations
 alkenes, 950–956
 alkynes, 472–473, 948–950
 Cu(I)-catalyzed, 353
 ω -iodo-1-alkenes, 472, 473
 Pd- and Ni-catalyzed, 876–878, 886–890
 uncatalyzed, 868–876
 unsaturated zinc enolates, 841
 Zn–ene reactions, 901–908, 932, 935–936
 Intramolecular charge-separation, Zn(II)
 porphyrin PET, 402
 Intramolecularly coordinating substituents,
 diorganozinc structure, 64–70
 Intramolecular Reformatsky reactions, Sm(II)
 iodide-promoted, 806–807
 Inversion
 C–Zn bond dynamics, 194, 217–230
 alkyl carbon
 primary, 217–222

- secondary, 222–227
 - allylic and propargylic carbon, 229–230
 - benzylic carbon, 227–229
 - mechanisms, 218–219
 - vinyl carbon, 227
- Iodide ions, Reformatsky reactions, 808
- Iodine–zinc exchange reactions
- diorganozinc functionalization, 308–311, 312, 560
 - intramolecular carbozincation of alkenes, 870–875, 876
 - light initiation, 309
- (*Z*)- β -Iodoacrylic acid, Sonogashira alkylation, 501
- ω -Iodo-1-alkenes, intramolecular cyclic carbozincation, 472, 473
- 1-Iodo-1-alkynes, Pd-catalyzed alkylation, 500–501
- Iodoallenes, allenylzinc reagent preparation, 430–431
- γ -Iodo allylic amines, substrate-induced diastereoselection, 923, 924, 925
- δ -Iodo allylic ethers, substrate-induced diastereoselection, 921
- γ -Iodo allylic ethers, substrate-induced diastereoselection, 917, 918–919, 921
- γ -Iodo allylic sulfides, substrate-induced diastereoselection, 923, 924
- (*E*)-1-Iodo-2-bromoethene, Pd-catalyzed monosubstitution, 481, 482
- (*E*)-1-Iodo-2-bromoethylene, Pd-catalyzed alkylation, 501, 508
- (*E*)-1-Iodo-2-chloroethylene, Pd-catalyzed alkylation, 508
- 1-Iodo-2,2-difluoroethylene, 2,2-difluorostyrene preparation, 726
- Iodoform, halomethylzinc preparation, 241
- α -Iodoketones, zinc enolate synthesis, 842, 844
- Iodolysis, organozinc reagents, 322–323
- 3-Iodomethyl prolines, synthesis, 841
- Iodomethylzinc diphenylphosphate, structure, 242
- Iodomethylzinc iodide
- preparation, 238, 240
 - structure, 242
- Iodomethylzinc phosphates, stereoselective cyclopropanation, 278
- α -Iodo- α,β -unsaturated carbonyl compounds, Pd-catalyzed cross-coupling, 515
- α -Iodovinylzinc reagents, preparation, 721
- α -Iodozinc carbenoids, alkynylmetal allylzincation, 944
- Ion cyclotron resonance, Fourier transform–ion cyclotron resonance, 166
- Ionic liquids, 1-butyl-3-methylimidazolium hexafluorophosphate, 656
- Ionization energy (IE), mass spectrometry, 179–181
- Ionization potential (IP), mass spectrometry, 179
- Ionomycin, Pd-catalyzed synthesis, 529, 532, 537
- Ion structure and energetics, 179–185
- computational chemistry, 184
 - gas phase reactions
 - ion/dipole complexes, 181, 184
 - ion/molecule mass spectrometry, 181–184
 - in silico* studies, 184–185, 186
 - isomers, 185, 186
 - photodissociation, 179–181
- IP (ionization potential), 179
- Iron
- catalysis
 - alkylation, 542
 - carbozincations, 881–882
 - Reformatsky reactions, 805
 - Zn–Fe transmetalation, 881–882
- Iron complexes
- catalytic organozinc reactions, 378
 - pentadienyliron, 341, 342
- Iron(III) porphyrins, photoinduced electron transfer, 400, 402
- Irradiation, I₂–Zn exchange, 309
- IR spectroscopy, metallotropic C–Zn exchange dynamics, 208
- Isoelectronic alkynylzinc compounds, Zn(II) cyanide complexes, 144
- Isokinetic relationships, C–Zn inversion dynamics, 220
- Isomerization enthalpies, dialkylzinc compounds, 141–142
- Isomers, organozinc ion structures, 185, 186
- Isoprenylation, aldehydes/ketones, 760
- Isopropylation, asymmetric, 577
- Isopropylzinc alkoxide, asymmetric autocatalysis with amplification, 580
- Isotopic composition, Zn, 165
- Isotropic chemical shifts, ⁶⁷Zn NMR spectroscopy, 153
- Iterative cross-coupling
- carboalumination, 511, 537–538
 - homologation
 - reduced polypropionates, 537
 - terpenoids, 534
 - hydrozirconation, 510
- Jackson reagent, Negishi cross-coupling, 361–362
- Katsuki–Sharpless epoxidation, asymmetric amplification, 573
- β -Keto amides, cyclopropanation using zinc carbenoids, 250
- α -Ketoesters
- enantioselective addition

- α -Ketoesters (*continued*)
alkynylzincs, 566
dialkylzincs, 562–563
- β -Ketoesters, Blaise reaction, 766
- Ketones
activated Zn allylation, 768
activated Zn synthesis, 767
allenylzinc reagent addition, 422–426
aromatic electrocatalysis, 791–793
enantioselective reactions
alkenylation, 563–564
alkynylzinc addition, 565–566
diorganozinc addition, 561–563
fluorinated vinylzinc reagents, 716
isoprenylation, 760
propargylation, 760
sp³-geminated organozinc reactions, 654, 664–665
unsaturated, 716, 767
- β -Ketophosphonates, cyclopropanation using zinc carbenoids, 250
- Kinetic resolution, chiral allenylzinc reagents, 448–449
- Knight shift, ⁶⁷Zn NMR spectroscopy, 155
- Kumada coupling, 459
- Kumada–Tamao–Corriu coupling, 459
- LA (laser ablation), 179
- β -Lactamase, zinc enzyme reactions, 16–18
- β -Lactams, Reformatsky reaction, 802, 824–825
- Lactic acid, Zn(II) tetrapyrrole photochemistry, 411
- Lactones, Sonogashira alkynylation, 501
- Lactonization, Pd-catalyzed, 501
- Langmuir–Blodgett films, Zn(II) porphyrins, 405–406, 411
- Laser ablation (LA), Zn(II) cyanide complexes, 179
- L-CAZ (L-carnosine), 158
- Leaving groups
1,2-metallate rearrangements, 596, 602–605
Pd- or Ni-catalyzed cross-coupling, 467, 473–475, 526–528
synergistic effects, 527–528
reactivity order, 473
- Leucine, racemic, 581
- Lewis acids
chiral acid–ligand system, 559, 560, 571–572
 α -C-glycoside formation, 330
metalla–Claisen rearrangements, 915, 916, 932–933
Reformatsky reactions, 808, 818–819
zinc bromide, 784
- Lewis base catalysts
enantioselective addition
to carbonyl compounds, 556–560
to imines, 572, 573
formation, 559
- Ligands
diorganozinc *N,N*-chelation, 78–79
I₂–Zn exchange, 310, 312
Pd- or Ni-catalyzed cross-coupling, 467, 475–480, 519
binary ligand combinations, 480
synergistic effects, 527–528
zinc enzymes, 2–5
see also Bidentate ligands; Chiral ligands
- Light-harvesting complexes, Zn(II) porphyrin PET, 402
- Lindskog mechanism, carbonic anhydrase, 21, 22
- Linear regression analysis
enthalpies of formation, 140
enthalpies of vaporization, 138
- Linear triquinanes, Zn–ene–allene reactions, 953
- Lipid bilayers, Zn(II) porphyrins, 406
- Lipscomb mechanism, carbonic anhydrase, 21, 22
- Liquid crystals, Zn(II) porphyrin PET, 406
- Lissoclinolide, Pd-catalyzed synthesis, 493, 494
- Lithiated bisoxazolines, enantioselective addition of diorganozincs, 570
- Lithiation–zincation, 2-alkynes, 521
- Lithium
Li–Zn transmetalation
carbozincations, 947–948, 949, 950–951
polyfunctional organozinc halide preparation, 297, 299–300
zinc enolates, 798, 837–842, 959
- Lithium alkoxides, *N*-methylephedrine, 563
- Lithium carbenoids, silylated homologation, 305
- Lithium enolates, homologation, 698–699
- Lithium naphthalenide, highly reactive Zn preparation, 803
- 1,3-Lithium shifts, Pd-catalyzed propargylation, 521
- Lithium tetramethylzincate, alkyl–Zn exchange dynamics, 205
- Lithium triorganozincates, preparation, 319–322, 323
- Lyases, zinc enzyme reactions, 20–22
- Macrocyclization, diastereoselective Reformatsky reaction, 818
- Magic-angle spinning (MAS), ⁶⁷Zn NMR spectroscopy, 155
- Magnesium
metalla–Claisen rearrangement, 914–915, 922

- Mg–Zn transmetalation, 903, 905–907, 913–914
organomagnesium compounds, 50, 198, 206, 209–210
Reformatsky reactions, 805
Magnesium–ene reactions, intramolecular carbocation, 903, 905–907
Magnetogyric ratio, ^{67}Zn , 150
Manganese, Reformatsky reactions, 805
Manganese complexes, catalytic organozinc reactions, 379
MAS (magic-angle spinning), 155
Massive zinc
 organic halide reactions, 765
 organozinc reagent generation, 757, 765–769
Mass spectrometry (MS)
 binuclear Zn complexes, 174–176
 bond dissociation products, 178–179
 decamethylidzinocene, 174
 dialkylzinc compounds, 166–171
 dihaloalkylzinc compounds, 166–171
 dimeric Zn complexes, 174–176
 electrospray ionization, 172
 fast atom bombardment, 176
 Fourier transform–ion cyclotron resonance, 166
 gas phase ion/molecule reactions, 181–184
 ion structure and energetics, 179–185
 molecular ions, 166–167, 171, 174, 178
 monomeric Zn complexes, 176–177
 organometallic vapor phase epitaxy, 187
 organozinc compounds, 163–192
 photodissociation, 181
 pyrolysis of Zn-containing species, 185, 187
 Zn–C bond complexes, 172–179
 see also Electron ionization mass spectrometry
Materials
 photoinduced electron transfer, 405–406
 solid-state ^{67}Zn NMR spectroscopy, 155–156
MD (molecular-dynamics calculations), 16, 17
Medicinal photodynamic therapy, Zn(II)
 porphyrins and phthalocyanines, 409–411
Membranes, hollow fiber, 406
Menaquinone-3, Pd- or Ni-catalyzed synthesis, 523, 524, 529, 531
Mercury, Zn–Hg exchange, 303, 870, 871
Metal alkoxides, diisopropyl tartrate, 570–571
Metalation
 directing metalating group, 52
 ortho-metalation, 51–53, 483
 perfluoroalkynylzinc reagent preparation, 737–738
 zincate preparation, 51–53, 687–688
Metal chelation, Zn(II) porphyrins, 404–405
Metal complexes, topologically chiral, 581
Metal exchange reactions
 dialkylzinc preparation, 560
 intramolecular carbocation of alkenes, 870–872
Metalla-aza-Claisen rearrangements, 965, 966
Metalla–Claisen rearrangements
 allylmetalation, 614–615, 617, 622
 Lewis acid-assisted, 915, 916, 932–933
 Mg-assisted, 914–915, 922
1,2-Metallate rearrangements, 596–614
 allylzincation
 alkenylmetals, 912
 alkynylmetals, 942
 1,1-dihalocompounds and triorganozincates, 596–602
 1,1-dimetallic species, 614
 I₂-Zn exchange, 874
 methylene homologations, 605–614
 1,2-migration with loss of leaving group, 596, 602–605
Metallo-ene reactions
 alkenylmetal allylzincation, 914
 allylic organozinc carbocationations, 890–891
 intramolecular, 901–902
Metallometalation, Pd-catalyzed alkenylation, 463–465
Metalloproteins
 ^{113}Cd NMR spectroscopy, 150–151
 ^{67}Zn NMR spectroscopy, 150–151, 153–155, 156–158
Metalloprotein equilibrium
 allenic organozinc reagents, 945–948
 C-Zn exchange dynamics, 195, 205–211
 allylzinc compounds, 205–208
 2,4-dienylzinc compounds, 205, 208–210
 zincocene, 210–211
 C-Zn inversion dynamics, 229–230
 mutual diastereoselection, 915
Metalloprotein forms, crotylzinc reagents, 894, 895, 917
Metalloprotein rearrangements
 C-Zn exchange dynamics, 206, 207, 209
 [1,3]-rearrangement, 206, 207
 [1,5]-rearrangement, 209, 211
 C-Zn inversion dynamics, 229–230
Metal–olefin interaction, intramolecular carbocationations, 870, 871
Metalorganic chemical vapor deposition (MOCVD), 187
Metathesis, perfluoroalkylzinc reagents, 741
2-Methylallylzinc chloride, metalloprotein C-Zn exchange dynamics, 208
 α -Methylbenzylamine, chiral auxiliary, 959–960
Methyl bromoacetate, Reformatsky reaction, 798–799
Methyl 2-bromo-2-methyl propanoate, Reformatsky reaction, 808, 809

- Methylenation
sp³-geminated organozinc reagents, 643, 651–657
aldehydes, 651, 652
ionic liquid stabilization, 656
- Methylene
homologations
aldehyde and imine reactions, 611–614
allene and olefin synthesis, 606–610
organometallic reagents, 605–606
- (Methylene)cyclopropanes, alkynylzincate
1,2-migration, 703, 704
- Methylenecyclopropanone ketal, 1,3-dipolar
intermediate carbozincation, 890
- Methylene increment, enthalpies of formation, 141
- α -Methylene- γ -lactones, activated Zn
synthesis, 767
- (-)-Methylenolactocin, preparation, 296, 298
- N*-Methylephedrine, lithium alkoxide, 563
- N*-Methylimidazole (NMI), Pd- and
Ni-catalyzed cross-coupling, 481, 483, 539, 540
- cis*-Methyl jasmonate, preparation, 296, 298
- N*-Methyl-2-pyrrolidone (NMP), Pd- and
Ni-catalyzed cross-coupling, 481, 483, 539, 540, 541
- 3-Methylthiophene, polymerization, 779
- Methyl vinyl acetate, electrosynthesis of
arylzinc halides, 789
- Methylviologen, porphyrin–viologen systems, 409, 411
- Methylzinc alkoxide, structure, 101–102
- Methylzinc *tert*-butyl sulfide, structure, 119, 120
- Methylzinc carboxylate, structure, 95
- Methylzinc guanidinate, structure, 115
- Methylzinc iminophosphorane, structure, 109–110
- Methylzinc isopropoxide, electron ionization
mass spectrometry, 172
- Methylzinc radical cation, thermochemistry, 144
- Methylzinc thiolate, structure, 118, 119, 120
- Micelles, Zn(II) porphyrins, 406
- Michael additions
Cu(I)-catalyzed, 344–345, 352–360
domino-Michael addition, 353, 355
polyfunctional organozinc halide
preparation, 291
 α,β -unsaturated compounds, 331, 332
- Microwave heating, Reformatsky reactions, 802
- 1,2-Migration
alkynylzincates, 699–705
arylzincates, 705–706
1,2-metallate rearrangements, 596, 602–605
benzylic substrates, 604–605
propargylic/homopropargylic substrates, 602–604
zincate carbenoids, 694–699, 700
- Minimal DNA Binding Domain of Human
Nucleotide Excision Repair Protein XPA,
⁶⁷Zn NMR spectroscopy, 156
- Mixed diorganozinc reagents
alkyl-Zn exchange dynamics, 199
I₂-Zn exchange, 310
- Mixed zincates
enantioselective alkenylation, 563
preparation
halogen-Zn exchange reactions, 688–689
metalation, 687–688
three-component coupling, 691–692
- MM *see* Molecular mechanical methods;
Quantum mechanical/molecular
mechanical methods
- MNDO calculations, organozinc ion isomers, 185, 186
- MOCVD (metalorganic chemical vapor
deposition), 187
- Modhephene, Pd-catalyzed alkynylation, 505, 506
- Modified neglect of diatomic overlap
(MNDO), 185, 186
- Molar ratio, Pd- or Ni-catalyzed allylation, 519
- Molecular-dynamics (MD) calculations, zinc
enzyme reaction mechanisms, 16, 17
- Molecular ions, mass spectrometry, 166–167, 171, 174, 178
- Molecular mechanical methods (MM)
phospholipase C reaction mechanisms, 19–20
see also Quantum mechanical/molecular
mechanical methods
- Molecular structure, COSMOS, 154
- Molybdenum complexes,
pentadienylmolybdenum, 341, 342
- Monoalkylzinc compounds
bond strength, 143
thermochemistry, 143
- Monoalkynylation, Pd-catalyzed
cross-coupling, 501, 508, 512
- Monomeric zinc complexes, mass
spectrometry, 176–177
- Mononuclear ligand-stabilized complexes, Pd
or Ni catalysts, 475
- Monoorganic compounds
cations, 83–85
halides, 85–94
heteroleptic, 82–123
Zn–heteroatom bonds, 118–123
Zn–N bonds, 107–118
Zn–O bonds, 94–107

- 2-Morpholino-1-phenylpropanol,
enantioselective addition of diethylzinc,
575
- Mössbauer measurements, ^{67}Zn NMR
spectroscopy, 155
- Motuporin, Pd-catalyzed synthesis, 493, 495
- (-)-Mucocin, enantioselective addition
synthesis, 373–374, 375
- Multi-centre bonding, diphenylzinc, 59
- Multi-component reactions, alkyl and aryl
organozinc reactions, 885–890
- Multi-coupling reagents
allylzincation
alkenylmetals, 910, 912
allenylmetals, 933, 934
- Multi-hapto bonded groups, diorganozinc
structure, 60–64
- Murisolin, Pd-catalyzed synthesis, 529, 532
- Musccone, stereoselective cyclopropanation,
259
- Mycolactones A and B
Pd-catalyzed cross-coupling, 529, 530
side chains, 507, 509, 517, 518, 529
- Mycotricins A and B, Pd-catalyzed synthesis,
510
- Myrcin, stereoselective cyclopropanation, 258
- NAD/NADH, Zn(II) phthalocyanine catalysis,
409
- Nakienone A and B, Pd-catalyzed synthesis,
493
- Naphthalene, active Zn generation, 759, 761
- Naphthalenediimide, Zn(II) porphyrin PET,
400
- Naphthalocyanines, photochemical stability,
398
- Naphthaquinone, Pd-*N*-heterocyclic
carbene–naphthaquinone complexes,
540–541
- Natural abundance, ^{67}Zn , 150, 156
- Natural products
palladiozincation, 442–445
Pd-catalysis
alkenyl–alkenyl coupling, 492–497
alkenyl–allyl coupling, 523
alkylation, 528–538
homopropargylation and
homobenzoylation, 529
alkynylation, 516, 517, 518
allylation, benzoylation and propargylation,
523, 524
aryl–alkenyl coupling, 490–491
- Nef reaction, Cu(I)-catalyzed, 355–357
- Negishi cross-coupling reactions
organozinc transmetalation, 288
Pd-catalyzed, 361–370
alkynylation, 504, 507
- Neopentyl-type iodides, Ni-catalyzed Grignard
reactions, 539
- NER (nucleotide excision repair), 156
- Neryl acetate, Pd-catalyzed alkynylation, 506
- NHC (*N*-heterocyclic carbenes), 475, 480, 498
- Nickel
catalysis
allylzincation, 898
carbozincations, 876–878, 879–881
alkynes and alkenes, 472–473
multi-component reactions, 886
cross-coupling, 457–553
acylation, 542–544
thioesters 370, 371
alkenyl–alkenyl reactions, 461, 462,
492–499
alkenyl–aryl reactions, 461, 462,
487–491
alkenylation, 489
alkylation, 477, 479–480, 524–542
alkyl electrophiles 526, 528, 533,
535, 539–542
alkyl halides 477, 479–480, 528,
533, 535, 539–542
history 525–526
natural product synthesis 528–538
alkynylation, 500, 507
allylation, 516–524
alkynyl–allyl reactions 521
aryl–alkenyl reactions, 487–491
aryl–aryl reactions, 483–487
aryl chlorides, 294, 362, 363, 486–487
benzylation, 516–524
alkynyl–benzyl reactions 521
catalyst poisoning 519
carbometalation, 461, 526
catalyst poisoning, 519
catalysts and ligands, 467, 475–480,
526–528
cocatalysts or additives, 467, 481
conjugated diene synthesis, 461–462
counteractions, 467–473, 526–528
cyanation, 544
Grignard reactions, 459, 539, 540
hydrometalation, 461, 526
leaving groups, 467, 473–475,
526–528
organozinc, 461
overview, 467–483
propargylation (allenylation), 516–524
solvents, 467, 481–483
thioester acylation, 371
electrochemical Reformatsky reaction,
804
hydrozincation, 316–317, 318
organozinc reagents
reactions, 362, 363, 371, 776–781
synthesis, 770, 771–780
- Ni–Zn transmetalation, 775, 881, 886, 887
- Zn–Ni cluster structures, 124–125

- Nickel–butadiene dimer complex, catalyst, 480, 535, 540
- Nickel–phosphine complexes, catalysts, 475–480, 528
- Nitriles, Reformatsky reactions, 827, 829
- Nitroalkenes, Reformatsky reactions, 829, 831
- Nitrones
 enantioselective addition
 alkynylation, 572
 diethylzinc, 570–571
- NMI (*N*-methylimidazole), 481, 483, 539, 540
- NMP (*N*-methyl-2-pyrrolidone), 481, 483, 539, 540, 541
- NMR spectroscopy
 activation parameter determination, 230–232
 ¹³C NMR spectroscopy, 148–150
 ¹¹³Cd NMR spectroscopy, 150–151
 ¹H NMR spectroscopy, 148–150
 ¹⁵N NMR spectroscopy, 151
 ⁶⁷Zn NMR coordination chemistry, 147–161
 ¹⁵N NMR spectroscopy, HMQC, 151
- Noncovalent interactions, Zn(II) porphyrins, 404–405
- Nonlinear optical response, Zn(II) porphyrins and phthalocyanines, 407
- Norborylzinc, mass spectrometry, 171
- Nor-ephedrine, chiral auxiliary, 925
- Norethandrolone, diastereoselective Reformatsky reaction, 817–818
- Normant, Gaudemar/Normant coupling, 647–649, 667–671
- Nornicotines, Reformatsky reactions, 809, 810
- NQCC (nuclear quadrupole coupling constant), 155
- NQR (nuclear quadrupole resonance), 155
- Nuclear quadrupole coupling, ⁶⁷Zn NMR spectroscopy, 155, 156
- Nuclear quadrupole coupling constant (NQCC), ⁶⁷Zn NMR spectroscopy, 155
- Nuclear quadrupole resonance (NQR), ⁶⁷Zn NMR spectroscopy, 155
- Nucleophilic cyclopropanation, sp³-geminated organozinc reagents, 671–674
- Nucleotide excision repair (NER), ⁶⁷Zn NMR spectroscopy, 156
- Nugent's catalyst, stereoselective cyclopropanation, 262
- Nysted reagent, sp³-geminated organozinc, 643
- 2-Octylzinc bromide, C–Zn inversion dynamics, 227
- Okinonellin B, Pd-catalyzed synthesis, 493, 494
- Oleandolide, Pd-catalyzed synthesis, 529, 531
- Olefination, alkenylmetal allylzincation, 909–910, 917, 925–927
- Olefins
 chiral, 581
 methylene homologations, 606–610, 614
- Oligoenes, conjugated, 508, 510
- Oligonuclear ligand-stabilized complexes, Pd or Ni catalysts, 475
- OMCVD (organometallic chemical vapor phase epitaxy), 187
- Oncology, Zn(II) tetrapyrrole photosensitizers, 409
- One-pot Barbier-type protocol, Reformatsky reaction, 799, 800
- Orbital energies, ionization energies, 180
- Orbital symmetry rules, metalotropic C–Zn exchange dynamics, 205, 210
- Organic halides, massive Zn reactions, 765
- Organoboranes, alkyl–Zn exchange dynamics, 215–216
- Organoborons, Pd-catalyzed cross-coupling, 461, 463, 465
- Organomagnesium compounds
 C–Zn exchange dynamics, 198, 206, 209–210
 diarylmagnesium reactions, 50
- Organomercurials, polyfunctional organozinc halide preparation, 303
- Organometallic chemical vapor phase epitaxy (OMCVD), mass spectrometry, 187
- Organometallic compounds
 alkyl–Zn exchange dynamics, 211–216
 enantioselective addition to imines, 569
 methylene homologations, 605–606
 Pd-catalyzed cross-coupling, 463–466
- Organotin compounds, polyfunctional organozinc halide preparation, 302–303
- Organozinc alkoxides, structure, 94–95, 100–103, 117
- Organozinc amides, structure, 111–115
- Organozinc arsenides, structure, 121, 122
- Organozincates
 alkyl–Zn exchange dynamics, 204–205
 preparation, 319–322, 323, 686–689
 reactions, 685–686, 690–709
 structure, 34–53
 spirocyclic, 37–40
 see also Tetraorganozincates;
 Triorganozincates; Zincates
- Organozinc bromide, structure, 89–90
- Organozinc carboxylates, structure, 106–107
- Organozinc compounds
 acylation, 542–544
 cyclopropanation, 237–286
 dynamic behavior, 193–236
 exchange, 194, 195–216
 inversion, 194, 217–230
 enantioselective addition, 555–593

- enthalpies of formation, 140
Fe-catalyzed alkylation, 542
functionalized, 287–393
ion structures
 energetics and photodissociation, 179–181
 gas phase ion/molecule reactions, 181–184
 in silico studies, 184–185, 186
 mass spectrometry, 163–192
 methylene homologations, 605–606
Pd- or Ni-catalyzed cross-coupling, 461, 462
 alkylation, 477, 479–480, 539
 transmetalation, 468–469
rearrangement reactions, 595–639
structure, 31–135
 Zn–transition metal bond, 123–126
 thermochemistry, 137–145
 ⁶⁷Zn NMR spectroscopy, 147–161
 see also Organozinc reagents
Organozinc β -diketoiminates, structure, 108–109
Organozinc enolates, structure, 105–106
Organozinc fluoride, structure, 94
Organozinc halides
 alkyl–Zn exchange dynamics, 202–203
 classification, 288–289
 heteroleptic monoorganozinc formation, 83
 polyfunctional preparation
 oxidative addition to Zn, 289–296
 transmetalation reactions, 296–308
 structure, 85–94
Organozinc phosphides, structure, 121–123
Organozinc reagents
 allylmethyl ether, 920–921
 allyltrimethylsilane, 919–920
 electrochemical generation, 755–796
 Co catalysis, 770–771, 781–794
 Ni catalysis, 770, 771–780
 mechanism, 773–776
 reactivity, 776–781
 reactive Zn, 758–769
 sacrificial anode process, 756, 761–763, 785
 fluorinated, 713–754
 γ -heterosubstituted, 917
 polar solvent reactivity, 331
 reactions, 758–769
 Co, Fe and Mn complexes, 378–379
 Cu(I)-catalyzed, 333–360
 Ni-catalyzed, 362, 363, 371, 776–781
 Pd-catalyzed, 361–370, 371
 Ti(IV) and Zr(IV) complexes, 370–378
 uncatalyzed, 322, 323–333
 see also Organozinc compounds
Organozinc rhodium compounds, structure, 125
Organozinc salts, alkyl–Zn exchange dynamics, 202–204
Organozinc selenides, structure, 121
Organozinc sulfides, structure, 119, 120
Organozinc tantalum compounds, structure, 126
Organozinc thiolates, structure, 118–119, 120
Organozinc tungsten compounds, structure, 123, 124
Oxabicyclic alkenes, Pd-catalyzed carbocationations, 882–884
1,3-Oxazolindines, imino-Reformatsky reactions, 825
Oxazolidinone, Reformatsky reaction, 805, 806
Oxidation
 alkenylmetal allylzincation, 910, 912
 Zn at electrodes, 773–774
 Zn(II) phthalocyanines, 411–412
Oxidative addition
 cobalt halide catalysts, 783
 leaving group reactivity order, 473
 Pd to alkenyl and allyl electrophiles, 473–475
 polyfunctional organozinc halide preparation, 289–296
 Zn activation, 801
Oxidative zincation, Pd- or Ni-catalyzed cross-coupling, 469–470
Oxidoreductases, zinc enzyme reactions, 8–10
(13*E*,15*E*,18*Z*,20*Z*)-4-Oxopentacosan-13,15,18,20-tetraen-11-yn-1-yl acetate, 518
[3,3]-Oxy-Cope rearrangement, zinc dienolates, 852
Oxygen, phthalocyanine photosensitization, 407
Ozonolysis, Cu(I)-catalyzed substitution, 339, 340
 π -bonds, Ni-catalyzed cross-coupling, 479
 π -conjugated copolymers, electrosynthesis, 790–791, 792
 π -interactions
 alkenes, 925–927, 929
 arenes, 925, 927, 929, 960
 π -stacking
 chelation, 960
 substrate-induced diastereoselection, 925–927, 929
2-Pallada-1,3-dienes, stereoisomerization, 498, 499
Palladiozincation
 natural product synthesis, 442–445
 propargylic mesylates, 435–437, 442
Palladium
 catalyzed cross-coupling, 457–553
 acylation, 542–544

- Palladium (*continued*)
- alkenyl-alkenyl reactions, 461, 462, 492–499, 501, 503
 - alkenyl-alkynyl reactions, 501
 - alkenyl-aryl reactions, 461, 462, 487–491
 - alkenylation, 463–467, 489
 - alkylation, 477, 479–480, 524–542
 - alkyl electrophiles, 526, 528, 533, 535, 539–542
 - alkyl halides, 528, 533, 535, 539–542
 - history, 525–526
 - natural product synthesis, 528–538
 - alkynylation, 500–516
 - α -alkynylation, 512–516
 - alkynyl-acyl coupling, 505–506
 - alkynyl-alkenyl coupling, 504, 507–512, 513, 514
 - alkynyl-alkynyl reactions, 504, 512
 - alkynyl-aryl coupling, 504
 - catalyst poisoning, 503
 - dialkynylation, 514
 - electrophiles, 500, 501, 503–507, 512–516, 517
 - natural product synthesis, 516, 517, 518
 - protocols, 499–503
 - selective monoalkynylation, 501, 508, 512
 - Zn, B and Sn alkynylmetals, 463
 - allenylation, 516–524
 - allenyl-aryl(allyl) reactions, 521–522
 - natural product synthesis, 523, 524
 - allenylzinc bromide reagents, 435, 436
 - allylation, 516–524
 - alkynyl-allyl reactions, 520–521
 - natural product synthesis, 523, 524
 - allylzincation, 904, 911, 933, 934
 - aryl-alkenyl reactions, 487–491
 - aryl-alkynyl reactions, 501
 - aryl-aryl reactions, 483–487
 - arylzinc-aryl halides, 777–779, 790
 - benzylation, 516–524
 - alkynyl-benzyl reactions, 520–521
 - catalyst poisoning, 519
 - heterocycles, 523
 - natural product synthesis, 523, 524
 - carbometalation, 461, 464, 526
 - carbozincation
 - intermolecular, 880, 884
 - intramolecular, 869–870, 948, 949, 953
 - catalyst poisoning, 503, 519
 - catalysts and ligands, 467, 475–480, 526–528
 - classification, 460
 - cocatalysts or additives, 467, 481, 500, 501
 - conjugated diene synthesis, 461–462
 - countercations, 467–473, 526–528
 - cyanation, 544
 - diorganozinc preparation, 313
 - enantioselective cross-coupling, 487, 488
 - fluorinated vinylzinc reagents, 715–722
 - history, 459–467
 - hydrometalation, 461, 463, 465, 470, 526
 - hydrozirconation, 462, 510
 - leaving groups, 467, 473–475, 526–528
 - organoborons, 461, 463
 - organozinc reagents, 361–370, 371, 461, 761
 - overview, 467–483
 - perfluoroalkynylzinc reagents, 737
 - propargylation, 516–524
 - natural product synthesis, 523, 524
 - propargyl-aryl(allyl) reactions, 521–522
 - solvents, 467, 481–483
 - zinc enolate addition, 961
 - catalyzed/promoted carbozincations, 876–878, 882–884
 - catalyzed Zn-ene reactions, 903–905, 907–908
 - oxidative addition to alkenyl and allyl electrophiles, 473–475
 - Pd-Zn transmetalation, 877–878, 903–904
- Palladium complexes
- alkene π -complexes, 519
 - π -allylic, 900, 903–904
 - BINAP, 836
 - Pd-*N*-heterocyclic carbene-naphthaquinone, 540–541
 - Pd-phosphine catalysts, 475–480, 492, 497–498, 505, 507, 508, 528
- Papulacandin D, Pd-catalyzed synthesis, 493
- [2.2]Paracyclophane
- chiral *N,O*-ligand, 572, 573
 - enantioselective addition
 - alkynylzincs, 565
 - asymmetric autocatalysis, 581
 - dialkylzincs, 557, 558
 - to imines, 572, 573
- Paramagnetic doping, ¹H NMR spectroscopy, 157
- Pearlman's catalyst, thioester acylation, 370, 371
- Pencillamine, ⁶⁷Zn NMR spectroscopy, 153
- Penicillin derivative, Cu(I)-catalyzed substitution, 344, 345
- Pentadienyliron, Cu(I)-catalyzed substitution, 341, 342
- Pentadienylmolybdenum, Cu(I)-catalyzed substitution, 341, 342
- Penta-2,4-dienylzinc systems, metallotropic C-Zn exchange dynamics, 208–209
- Pentafluoropropen-2-ylzinc reagent, tetrafluoroallene preparation, 730–731

- 1-Pentyl-2-anilinomethylpyrrolidine, enantioselective conjugate addition, 568
- Peptide-derived ligands, enantioselective addition of diorganozincs, 572
- Peptides, stereoselective cyclopropanation, 277, 280, 281
- Perfluoroalkylations, Zn-mediated, 741–742
- Perfluoroalkylodides, perfluoroalkylzinc reagent reactions, 739, 741, 742
- Perfluoroalkylzinc reagents, 738–744
metathesis, 741
- Perfluoroalkynylcopper reagents, 738
- Perfluoroalkynylzinc reagents, 736–738
- Perfluoroaryl zinc reagent preparation, 732–733
Zn insertion into C–fluorine bonds, 733
- Perfluorocarboxylic acids, perfluoroalkylidide reactions, 742
- Persistent organometallic radicals, structure, 81–82
- Perylene monomimide, photosynthesis antenna systems, 402
- Perylenes, Zn(II) porphyrin and phthalocyanine PET, 400, 401
- PES *see* Photoelectron spectroscopy
- PET *see* Photoinduced electron transfer
- Phenanthridine, 3-indolepropionic acid/phenanthridine cocrystal, 584
- Phenols, halomethylzinc preparation, 239, 248
- 1-Phenyl-2-propylzinc bromide, C–Zn inversion dynamics, 223
- 4-Phenylpyridines, electrosynthesis, 791
- Phenyl transfer reactions
diphenylzinc, 566
enantioselective, 566–567
- Phosphine complexes, Pd or Ni catalysts, 475–480, 492, 497–498, 505, 507, 508, 528
- Phospholipase C (PLC)
zinc enzyme reactions, 19–20
⁶⁷Zn NMR spectroscopy, 153
- Phosphonate, zincated, 334, 335
- Phosphonium ylides, zinc carbenoid reactions, 256
- Phosphoramidite
Cu-catalyzed enantioselective conjugate addition, 568
zinc enolate synthesis, 846–847
- Phosphoric acids
chiral, 280, 282
halomethylzinc preparation, 239–240
- Phosphorus(III) compounds, Reformatsky reactions, 833, 834
- Photocatalytic oxidation, Zn(II) phthalocyanines, 411–412
- Photochemistry
organozinc ion structure, 181
stability and degradation, 398, 409
Zn(II) phthalocyanines, 395–419
Zn(II) porphyrins, 395–419
- Photodissociation, organozinc ions structure, 181
- Photodynamic therapy, Zn(II) porphyrins, 409–411
- Photoelectrochemical cells, Zn(II) phthalocyanines, 407–409
- Photoelectron spectroscopy (PES)
bond energies, 142
enthalpies of formation, 141
ionization energy determination, 179–180
- Photoequilibrium, chiral olefins, 581
- Photoinduced electron transfer (PET)
donor–acceptor compounds, 398–406
axial coordination, 405
chelation, 404–406
light-harvesting complexes, 402
materials and formulations, 405–406
novel acceptor groups, 399–402
reaction center models, 402
synthetic strategies, 402–405
- Fe(III) porphyrins, 400, 402
intersystem crossing, 402
intramolecular charge-separation, 402
photosynthesis, 398, 402, 407
reorganization energy, 398
Zn(II) porphyrins and phthalocyanines, 398–406, 407
see also Single-electron transfer
- Photoionization, ionization energies, 179, 181
- Photoisomerization, stilbene, 412
- Photolysis, racemic leucine, 581
- Photomedicine, Zn(II) porphyrins and phthalocyanines, 409–411
- Photonics materials, Zn(II) porphyrins and phthalocyanines, 407
- Photosensitizing Zn(II) porphyrins and phthalocyanines
charge transfer, 409
chemical uses, 411–412
generation, 406
medicinal photodynamic therapy, 409–411
photosensitization reactions, 407–412
photostability, 398, 406, 409
photovoltaics, 407–409, 411
- Photosynthesis
antenna systems, 402
circularly polarized light, 581
electron transfer, 398
formic acid production, 411
[6]helicene, 581
photosensitization reactions, 407
reaction center models, 402
- Photovoltaic devices, Zn(II) phthalocyanine photosensitization, 407–409
- Phthalimides, Zn(II) porphyrin PET, 400
- Phthalocyanine photochemistry, 395–419

- Phthalocyanine photochemistry, (*continued*)
 medicinal photodynamic therapy, 409–411
 nonlinear optical response, 407
 photocatalytic oxidation, 411–412
 photoinduced electron transfer, 398–406,
 407
 photonics materials, 407
 photosensitization reactions, 407–412
 photovoltaic applications, 407–409, 411
 pigments and dyes, 406
 reverse saturable absorption, 407
 singlet oxygen generation, 410
- Pigments
 photosynthesis antenna systems, 402
 Zn(II) phthalocyanines, 406
- Pinacolone rearrangement, sp^3 -geminated
 organodizinc reagents, 674–675
- Piperidines
 type II Zn–ene reaction, 907
 zinc enolate addition, 961–962
- Pitamide A, Pd-catalyzed synthesis, 493, 494
- PLC *see* Phospholipase C
- Polaprezinc (L-CAZ), ^{67}Zn NMR
 spectroscopy, 158
- Polarized light, enantioselective asymmetric
 autocatalysis, 581, 583, 585
- Polar solvents, zinc organometallic reactivity,
 331
- Polydentate ligands, monomeric Zn complex
 mass spectrometry, 176–177
- Polyenes
 fluorinated, 717–718
 stereoselective cyclopropanation, 274–275
- Polyfunctional organozinc reagent preparation
 allyl zinc reagents, 317–319
 diorganozincs, 308–317
 lithium triorganozincates, 319–322, 323
 organozinc halides, 289–308
- Polyfunctional zinc–copper reagents,
 organozinc halide preparation, 305, 306
- Polymerization
 chain growth polymerization, 142
 fluoroalkenylzinc reagents, 731, 732
 3-methylthiophene, 779
- Polymethylene, homologation, 305
- Polyoxygenated metabolites of unsaturated
 fatty acids, Cu(I)-catalyzed addition, 351
- Polypropionates, homologation, 537
- Porphyrazines, photochemistry, 396, 397, 398
- Porphyrin photochemistry, 395–419
 back electron transfer, 409
 charge separation/recombination, 404
 chemical uses, 411
 excitonic interactions, 402–403
 fullerene–porphyrin conjugates, 399
 medicinal photodynamic therapy, 409–411
 multiporphyrin arrays, 403
 nonlinear optical response, 407
 photoinduced electron transfer, 398–406
 photonics materials, 407
 photosensitization reactions, 407–412
 porphyrin–viologen systems, 407, 409, 411
 reverse saturable absorption, 407
- Potassium, highly reactive Zn preparation, 802
- Potassium–graphite
 highly reactive Zn preparation, 803
 oxidative zincation, 470
- Powders, Zn activation techniques, 801–803
- Powder X-ray diffraction, Zn(II) coordination
 chemistry, 155
- Preen gland wax of graylag goose,
 Pd-catalyzed synthesis, 529, 532
- Prenyl transferases, zinc enzyme reactions,
 10–12
- Preparative electrolyses, cobalt halide
 catalysts, 783
- (+)-Preussin, lithiation/transmetalation
 protocols, 837, 838
- Primary/secondary (tertiary) isomerization
 enthalpy, dialkylzinc compounds, 142
- Prolines, zinc enolate addition, 960–961, 962
- 3-Prolinoglutamic acid, synthesis, 841
- Propargyl–alkenyl coupling, Pd-catalyzed, 522
- Propargyl–alkynyl coupling, Pd-catalyzed, 522
- Propargyl–allenyl metallotropy
 allenylmetal allylzincation, 933, 934, 945,
 945–948
 C–Zn inversion dynamics, 229–230
- Propargyl–allyl coupling, Pd-catalyzed,
 521–522
- Propargyl–aryl coupling, Pd-catalyzed,
 521–522
- Propargylation
 aldehydes/ketones, 760
 Pd- or Ni-catalyzed cross-coupling, 474,
 516–524
 propargyl–aryl(allyl) reactions, 521–522
- Propargyl bromides
 Pd-catalyzed cross-coupling, 519, 520
 zincation, 421–422
- Propargyl compounds
 allylzincation, 936–937, 940, 941,
 943–944, 945
 1,2-migration rearrangements, 602–604
 zinc enolate addition, 956–957
- Propargyl electrophiles
 Pd-catalysis
 alkynylation, 504–505
 propargylation (allenylation), 518, 519
- Propargyl halides
 Cu(I)-catalyzed substitution, 337–338
 fluorinated propargylzinc reagents, 736
- Propargyl mesylates, palladiozincation,
 435–437, 442
- Propargylmetals, Pd- or Ni-catalyzed
 propargylation, 518

- Propargyl sulfonates, Cu(I)-catalyzed substitution, 338
- Propargylzinc bromide, regioselectivity, 429
- Propargylzinc reagents
Pd- or Ni-catalyzed propargylation, 520
uncatalyzed reactions, 323–324
- Prostaglandins
Cu(I)-catalyzed Michael addition, 353, 354
side chain synthesis, 372–373
three-component coupling synthesis, 691
- Proteins
¹¹³Cd NMR spectroscopy, 150–151
⁶⁷Zn NMR spectroscopy, 150–151, 153–155, 156–158
XPA protein, 156, 157
- Proto-destannylation, cyclopropanation using zinc carbenoids, 255
- (+)-Pumiliotoxins A and B, Pd-catalyzed synthesis, 529, 530
- Purines, Negishi cross-coupling, 365, 366
- Pyrethroid, synthesis, 730
- Pyridine
electrosynthesis of arylzinc compounds, 774–776, 782–783, 786–789
Pd- and Ni-catalyzed cross-coupling, 481, 483, 541
- Pyridinofullerenes, Zn(II) porphyrin PET, 399–400
- 3-Pyridyl alkanol, enantioselective asymmetric autocatalysis, 577
- 5-Pyrimidyl alkanols, enantioselective asymmetric autocatalysis, 577, 578
- Pyrolysis, mass spectrometry, 185, 187
- Pyromellitimide, Zn(II) porphyrin PET, 400
- Pyrrroles, aza-enolate addition, 966, 967
- Pyrrolidines
zinc enolate alkene addition, 959–960
Zn-ene–allene cyclization, 955
- QCPMG NMR, ⁶⁷Zn NMR spectroscopy, 154
- QE *see* Quadrupolar echo
- QM *see* Quantum-mechanical methods
- QM/MM *see* Quantum mechanical/molecular mechanical methods
- Quadrupolar echo (QE)
solid-state ⁶⁷Zn NMR spectroscopy, 153–154
cross polarization, 153, 156
echo repetitions, 154
interpulse acquisition period, 154
pulse sequence, 156
spin-echo sidebands, 154, 156
- Quadrupolar nuclei, ⁶⁷Zn, 150, 153
- Quadrupole coupling, ⁶⁷Zn NMR spectroscopy, 153, 156
- Quadrupole moments, ⁶⁷Zn NMR spectroscopy, 153
- Quadrupole relaxation, ⁶⁷Zn NMR spectroscopy, 150, 153
- Quantum chemical calculations
bond energies, 142
enthalpies of formation, 141
- Quantum-mechanical methods (QM)
 β -lactamase reaction mechanisms, 16–17
⁶⁷Zn NMR spectroscopy, 151–152
- Quantum mechanical/molecular mechanical methods (QM/MM)
zinc enzyme reaction mechanisms, 13, 14, 16
see also Molecular mechanical methods
- Quantum yield
Zn(II) phthalocyanines
singlet oxygen generation, 410
triplet lifetimes, 410
- Quartz, enantioselective asymmetric autocatalysis, 581, 584
- Quinine alkaloid derivative, Cu(I)-catalyzed substitution, 336
- o*-Quinones, Zn(II) porphyrin PET, 400
p-Quinones, Zn(II) porphyrin PET, 400
- Racemic leucine, photolysis, 581
- Racemic reactions, Reformatsky reactions, 808–811
- Radical cations, methylzinc, 144
- Radical cyclization
carbozincations
alkenes, 872, 873
alkynes, 868–870
Pd- and Ni-catalyzed, 877–878
- Radicals, persistent organometallic radicals, 81–82
- Reaction center models, Zn(II) porphyrin PET, 402
- Reactive zinc
aldehyde/ketone reactions, 760
allylation of carbonyl compounds, 766–768
benzylic zinc synthesis, 768–769
Blaise reaction, 765–766
electrochemical generation, 756–757, 758–759, 760, 765
organozinc reagent synthesis, 760–769
Reformatsky-type reactions, 766
- Reactivity
alkyl organozinc reagents, 865–890
allenylzinc reagents, 945–956
allylic organozinc reagents, 890–945
aryl organozinc reagents, 865–890
Co-catalyzed preparation, 790–794
Ni-catalyzed preparation, 776–781, 876–878, 879–881, 886
aza-enolates, 956–971
leaving groups, 473
organozinc reagents, 758–769

- Reactivity (*continued*)
zinc dienolates, 848–854
zinc enolates, 797–848, 886, 887, 956–971
zinc enzymes, 1–29
- Rearrangement reactions, 595–639
allylmetalation of alkenyl/alkynyl metals, 614–627
Fritsch–Buttenberg–Wiechell, 627–629, 942–944
metalla-aza-Claisen rearrangements, 965, 966
metalla–Claisen rearrangements
allylmetalation, 614–615, 617, 622
Lewis acid-assisted, 915, 916, 932–933
Mg-assisted, 914–915, 922
1,2-metallate rearrangements, 596–614, 874, 912, 942
[3,3]-oxy-Cope rearrangement, 852
pinacolone rearrangement, 674–675
1-trimethylsilyl-2-propenylzinc reagents, 634–636
triorganozincates, 596–602
see also Metallotropic rearrangements
- Redistribution reactions, dialkylzinc compounds, 143
- Reduction
cobalt halide catalysts, 784
conjugated enones, 513
electrochemical generation of reactive Zn, 756, 758–759, 762–763, 770
polypropionates, 537
Zn(II) phthalocyanines, 411–412
- Reformatsky reactions
alternative metals, 805–808
 α -bromoesters, 766
C-halogen Zn insertion, 798, 799–800
Cu(I)-catalyzed addition, 351
diastereoselective, 296, 812, 815–819
diethyl zinc conjugate addition, 798
electrochemical, 803–805
electrophiles
carboxylic acid derivatives, 827–837
electron-poor C=C, 829–837
phosphorus(III) compounds, 833, 834
enantioselective, 811–812, 813–814
Grignard-type protocol, 799
heteroleptic monoorganozinc formation, 82, 91–92
imino-Reformatsky reactions, 823, 824–825, 850–852
intramolecular, 806–807
lithium enolate transmetalation 18.21, 837–842
microwave-promoted, 802
organozinc compounds, 288
racemic reactions, 808–811
rate-determining step, 627, 628
regioselective, 836–837
transition metal-catalyzed coupling, 833–837
ultrasound-promoted, 801–802
vinylogous, 839, 850, 854
Zn activation techniques, 800, 801–808
Zn–Cu/Ag couples, 801
see also Gilman–Speeter reactions
- Reformatsky reagents
carboalkoxydifluoromethylenezinc, 747–750
structure, 92, 93
zinc enolates, 798, 963
- Regiochemistry
allenylzinc additions to aldehydes/ketones, 425
zinc dienolates, 848–854
- Regioselectivity
allenylzinc reagents, 428–429
enolate alkylation, 513
Reformatsky reactions, 836–837
- Relaxation times, ^{67}Zn NMR spectroscopy, 153
- Retinoids, synthesis, 508, 511
- Reveromycin B, Pd-catalyzed synthesis, 493, 494
- Reverse saturable absorption, Zn(II) porphyrins and phthalocyanines, 407
- Rhamnose, stereoselective alkene cyclopropanation, 266, 267
- Rhenium carbonyl
[η_5]-cyclopentadienylrhenium tricarbonyl complex, 567
Zn(II) porphyrins, 404
- Rhodium
catalyzed hydroboration, 316
organozinc compound structures, 125
Wilkinson's catalyst, 842, 845
- Rieke barium, Reformatsky reactions, 806
- Rieke germanium, Reformatsky reactions, 805
- Rieke manganese, Reformatsky reactions, 805
- Rieke zinc
intramolecular carbocation of alkenes, 871, 875
oxidative addition to functionalized organic halides, 290
- Ring contraction, stereoselective alkene cyclopropanation, 266, 267
- Ring-opening reactions, epoxides, 328, 330, 337, 690
- RK-397, Pd-catalyzed synthesis, 510
- Roseofungin, Pd-catalyzed synthesis, 510
- Rotaxane
diorganozinc structures, 76–77
photoinduced electron transfer, 399
- Rubrolides A, C, D and E, Pd-catalyzed alkynylation, 501
- σ -cyclization
alkynylmetal allylzincation, 939
Zr-promoted carbocationations, 879

- Sacrificial anodes
 organozinc reagent generation, 756,
 761–763, 785
 Reformatsky reactions, 803–805
(–)-Salicylhalamides A and B, Pd-catalyzed
 synthesis, 517, 518
Samarium/diodomethane, enolate
 cyclopropanation, 250
Samarium(II) iodide, Reformatsky reactions,
 806–807
SAMP hydrazone, zinc enolate addition,
 968–969
Savinin, Pd-catalyzed synthesis, 493, 494, 496
Schiff bases
 diarylzinc addition, 327, 328
 zinc dienolates, 852
Schlenk equilibrium
 alkyl-Zn exchange dynamics, 203–204
 heteroleptic monoorganozinc compounds, 83
Schwartz' reagent, hydrozirconation, 692
Scyphostatin, Pd-catalyzed synthesis, 529, 532
Self-assembly, Zn(II) porphyrins, 403, 406
Self-chemical ionization, diethylzinc, 166,
 167–168, 181
Semiconductors, organometallic vapor phase
 epitaxy, 187
Semiempirical calculations, carboxypeptidase
 reaction mechanisms, 14–16
Sequential reactions
 hydrozirconation/Zr–Zn transmetalation,
 265–266
 sp³-geminated organodizinc reagents,
 659–667
SET *see* Single-electron transfer
Sharpless, Katsuki–Sharpless epoxidation, 573
Side chains, mycolactones A and B, 507, 509,
 517, 518
Silaboration, Pd-catalyzed alkenylation, 465
1-Sila-1-zircona-1-alkenes, Pd-catalyzed
 dialkylation, 533
Silica
 ephedrine–silica hybrid, 584
 helical, 581, 584
Silicon
 1,2-bimetallic Zn/Si reagent, 297, 299–300
 syn-hydrometalation, 463
 in silico organozinc ion studies, 184–185,
 186
Silicon (Si100), Zn(II) porphyrins, 407
Silsesquioxane, enantioselective asymmetric
 autocatalysis, 584
Silver, Zn–Ag couples, 801
Silylated lithium carbenoids, homology,
 305
 α -Silylcyclopropylzinc, cyclopropanone ketal
 allylzincation, 898
Silyl enol ethers, cyclopropanation using zinc
 carbenoids, 249
Silyl-substituted *gem*-dizincmethanes,
 preparation, 646–647, 659, 660, 663, 664
Silylzincate, conjugate addition to
 α,β -unsaturated compounds, 693–694
Simmons–Smith reagent
 cyclopropanation, 288
 heteroleptic monoorganozinc formation, 82
 oxidative zincation, 469–470
 structure, 87–88
 zinc enolate synthesis, 842, 844
Single-electron transfer (SET)
 intramolecular carbozincation of alkynes,
 869
 perfluoroalkylzinc reagents, 741
 see also Photoinduced electron transfer
Singlet oxygen generation
 Zn(II) phthalocyanines, 410
 Zn(II) porphyrins, 405
Siphonarienal, Pd-catalyzed synthesis, 529,
 532
Siphonarienolone, Pd-catalyzed synthesis, 529,
 532
Siphonarienone, Pd-catalyzed synthesis, 529,
 532
Slip sandwich structure, substituted
 cycloopenadienyl compounds, 63
Smith *see* Simmons–Smith reagent
S_N2'-mechanism
 Cu(I)-catalyzed substitution, 334–335
 polyfunctional organozinc halide
 preparation, 291, 292
SOD *see* Superoxide dismutase
Sodium bromate, enantioselective asymmetric
 autocatalysis, 581, 584
Sodium chlorate, enantioselective asymmetric
 autocatalysis, 581, 584
Sodium iodide, Reformatsky reactions, 805
Sodium naphthalenide, highly reactive Zn
 preparation, 803
Solar energy conversion, Zn(II) phthalocyanine
 photosensitization, 407–409
Solid-state ⁶⁷Zn NMR spectroscopy
 coordination chemistry tool, 152–153
 materials, 155–156
 QCPMG NMR, 154
 quadrupolar echo, 153–154, 156
Solutions
 halomethylzinc reagent structures, 242–245
 sp³-geminated organodizinc structure, 644
Solvent exchange, bis(perfluoroalkyl)zinc
 reagent preparation, 739
Solvents
 cyclopropanation using zinc carbenoids,
 246–247
 Pd- or Ni-catalyzed cross-coupling, 467,
 481–483, 539, 540
 polar, 331
Sonochemistry, Zn activation, 801

- Sonogashira reactions
alkynylation, 500, 501, 504, 507, 508
Pearlman's catalyst, 370, 371
- sp^2 -geminated organodizinc reagents,
preparation and reactions, 677–680
- sp^3 -dimetalated carbon stereocenters
alkenylmetal allylzincation, 927–932, 965,
966
1,3-elimination, 927–931
- sp^3 -geminated organodizinc reagents
alkenyl–silane/germane/borane synthesis,
659, 660
alkylidenation, 657–659
as carbenoid, 676–677
diastereoselective construction, 667–671
1,1-dimetal species from zincated hydrazone
and alkenylmetal, 675–676
Gaudemar/Normant coupling, 647–649,
667–671
methylenation, 643, 651–657
aldehydes, 651, 652
nucleophilic cyclopropanation, 671–674
pinacolone rearrangement, 674–675
preparation
carbometalation, 647–650
dihaloalkane and zinc, 645–646
heteroatom-substituted, 646–647
dihalomethane and zinc, 643–645
reactions, 650–677
sequential reaction with two electrophiles,
659–667
structure of solution, 644
- Speeter *see* Gilman–Speeter reactions
- Spingofungin F, Pd-catalyzed synthesis, 529,
531
- Spin-echo sidebands, ^{67}Zn NMR spectroscopy,
154, 156
- Spin–spin relaxation times, ^{67}Zn NMR
spectroscopy, 153
- Spirocyclic organozincates, structure, 37–40
- Spiropentane, stereoselective cyclopropanation,
274–275
- Spiro-products, carbocupration homologation,
305
- Spontaneous absolute asymmetric synthesis,
enantioselective autocatalysis, 583–584,
586
- Sporochinol, fish deterrent, 339, 341
- α -Stannylocyclopropylzinc, cyclopropanone
ketal allylzincation, 898
- α -Stannyloorganozinc reagents, configurational
stability, 931, 932
- Stereochemistry, allenylzinc reagent additions,
425–427
- Stereoinversion, Pd-catalyzed cross-coupling,
497–499
- Stereoisomerization
allylpalladium derivatives, 498, 499
Pd-catalyzed alkynyl–alkenyl coupling, 507
- Stereoselectivity
alkene cyclopropanation
A-1,3-strain, 259, 262–263, 264
acyclic alkenes, 261–266
allylic strain, 262, 264
chiral alkenes, 238–266
chiral auxiliaries, 266–273
chiral catalysts, 279–281
cyclic alkenes, 257–260
ring contraction, 266, 267
stoichiometric chiral reagents, 273–278
allylic zinc–aldehyde reaction, 317,
318–319
Pd-catalyzed alkynylation, 501
- Stereospecificity
fluorinated diene preparation, 727–729
fluorinated styrene preparation, 725–727
- Stilbene, photoisomerization, 412
- Stille cross-coupling, Pd-catalyzed, 904
- Stoichiometric chiral reagents, stereoselective
alkene cyclopropanation, 273–278
- Stored waveform inverse Fourier transform
(SWIFT), 166
- Structure
dialkyl- and diarylzinc compounds, 53–82
donor–acceptor complexes, 70–82
heteroleptic, 57–58
homoleptic, 53–57
intramolecularly coordinating substituents,
64–70
multi-centre bonding, 59
multi-hapto bonded groups, 60–64
slip sandwich structure, 63
halomethylzinc reagents, 242–245
monoorganozinc compounds
cations, 83–85
halides, 85–94
heteroleptic, 82–123
Zn–heteroatom bonds, 118–123
Zn–N bonds, 107–118
Zn–O bonds, 94–107
organozincates, 34–53
tetraorganozincates, 35–41, 45
spirocyclic, 37–40
triorganozincates
heteroleptic, 47–53
homoleptic, 41–46
organozinc compounds, 31–135
ions, 179–185
Zn–transition metal bond, 123–126
 sp^3 -geminated organodizinc solution, 644
zinc enzymes, 2–7
 ^{67}Zn NMR spectroscopy, 152
- Styrenes
electron-deficient, 533, 539
fluorinated, 720–721, 725–727
- Substitution

- α -carbonyl compounds, 512–516
alkyl-substituted alkynes, 501
allylic Reformatsky reactions, 836
amine-substituted allenylzinc reagents,
449–451
Cu-catalyzed reactions, 334–346, 347
1,1-dibromo-1-alkenes, 476, 492, 497–498,
536
2,5-dibromo-3-substituted thiophenes,
772–773
1,1-dichloro-1-octene, 482
 α -difluorovinyl substituted β -hydroxyesters,
735, 736
1,1'-disubstituted allene, 581
halo-substituted cyclopropanes, 251–252
heterosubstituted arylzinc cross-coupling,
484–486
 γ -heterosubstituted organozinc
diastereoselection, 917
intramolecularly coordinating substituents,
64–70
(E)-1-iodo-2-bromoethene, 481, 482
piperidines, 961–962
prolines, 960–961, 962
silyl/germyl/boryl-substituted
gem-dizincmethanes, 646–647, 659,
660, 663, 664
 S_N2' -selectivity, 334–335
1,2,3-substituted cyclopropane, 275
trans-selective monosubstitution, 476, 482,
483, 490, 492, 497–498, 507
trimethylsilyloxy-substituted alkene
cyclopropanation, 249
Sulfinimines, Gilman–Speeter reactions, 821
Sulfonium ylides, zinc carbenoid reactions,
256
Sulfonyl chlorides, perfluoroalkylidide
reactions, 742
Sulfoximine, stereoselective cyclopropanation,
260
Superoxide dismutase (SOD)
Cu–Zn enzyme
reaction mechanisms, 9–10
structure, 6, 7
Superoxides, Zn(II) phthalocyanine
photosensitization, 407
Surgumycin, Pd-catalyzed synthesis, 510
Surrogate probes, NMR spectroscopy, 150, 153
Suzuki couplings
1,1-difluoromethylene olefin preparation,
721–722
Pearlman's catalyst, 370, 371
SWIFT (stored waveform inverse Fourier
transform), 166
TADDOL
chiral auxiliaries, 272
enantioselective reactions
dialkylzinc addition, 370–372, 559, 563
phenyl transfer, 566
Ti–TADDOL, 280, 281, 566
Tamao, Kumada–Tamao–Corriu coupling, 459
Tandem reactions
carbon–carbon bond formation, 694
Pd-catalyzed cross-coupling, 461, 462, 471,
510–511, 526, 527
Tantalum
organozinc compound structure, 126
Reformatsky reactions, 806
Tartaric acid, cyclopropylmethanol preparation,
273
Taxusin, stereoselective cyclopropanation, 258
TDAE (tetrakis(dimethylamino)ethylene), 735,
736
TDPAC (time differential perturbed angular
correlation), 155
Tebbe-type reagent, sp^3 -geminated
organodizinc, 644
Temperature
cyclopropanation using zinc carbenoids,
246–247
enthalpies of vaporization, 138
vinyl lithium reagent capture
ambient temperature, 718–722
low temperature, 714–718
Terminal alkynes
enantioselective addition of alkynylzincs,
565, 566
hydrozirconation, 564
Pd-catalyzed alkynylation, 500, 501
Terpenoids, homologation, 534
Tertiary diarylcarbinols, enantioselective
addition of diorganozincs, 375, 377
5,10,15,20-Tetraazaporphyrins *see*
Porphyrazines
Tetraordinated zincates, preparation, 687
Tetrafluoroallene, fluoroalkenylzinc
preparation, 730–731
Tetrahydrofurans
Pd- and Ni-catalyzed cross-coupling,
481–483, 505, 539, 540
zinc enolate alkyne addition, 958
Zn–ene–allene cyclization, 954–955
Tetrahydropyrans, type II Zn–ene reactions,
906
Tetrakis(dimethylamino)ethylene (TDAE),
gem-difluorinated δ -hydroxyesters, 735,
736
Tetraorganozincates, structure, 35–41, 45
Tetrapyrroles
photochemistry, 395–419
see also Phthalocyanines; Porphyrins
TFP (tris(2-furyl)phosphine), 476, 480, 492
Thermal decomposition
mass spectrometry, 185, 187

- Thermal decomposition (*continued*)
perfluoroalkylzinc reagents, 740
- Thermal ene–allene reactions, intramolecular
alkene carbocation, 950
- Thermal stability
dialkoxiphosphinyldifluoromethylzinc
reagents, 745
perfluoroalkylzinc reagents, 740
perfluoroalkynylzinc reagents, 736
- Thermochemistry
bond dissociation energies, 180–181
computational chemistry, 184
organozinc compounds, 137–145
- Thermolysis
¹¹³Cd NMR spectroscopy, 151
zinc enzyme reactions, 16, 17
⁶⁷Zn NMR spectroscopy, 153
- Thermometric titration, Zn(II) cyanide
complexes, 244
- Thermoneutrality, dialkylzinc bond energies,
142–143
- THF *see* Tetrahydrofurans
- Thienylzinc, electrochemical synthesis,
772–773
- Thioaldehydes, Reformatsky reactions, 829
- Thioesters, Pd-catalyzed acylation, 370, 371
- Thioketones, Reformatsky reactions, 829
- Thiolactone, Ni-catalyzed addition, 370, 371
- Thiophenelactone, Pd-catalyzed alkylation,
501
- Thiophosphoramidate, enantioselective
addition of dialkylzinc, 559, 560
- Three-component coupling
mixed zincates, 691–692
Ni-promoted, 888, 889
- Time differential perturbed angular correlation
(TDPAC), ⁶⁷Zn NMR spectroscopy, 155
- Tin
syn-hydrometalation, 463
Pd-catalysis
alkynylation, 463
allylation, 519
transmetalation, 302–303
- Tin(II) chloride, Reformatsky reactions, 805
- Titanium
catalysts
asymmetric amplification, 573
carbocationations, 884–885
Ti(II)–ethylene complex, 885
chiral salen-Ti isopropoxide, 562–563
hydromagnesiation, 917, 918
Ti-TADDOL, 280, 281, 566
chiral bis(sulfonamide)-Ti complex, 560
Zn–Ti transmetalation, 885, 911
- Titanium chlorides, Reformatsky reactions,
805, 818–819
- Titanium(III) chloride, sp³-geminated
organodizinc methylenation, 653–657
- Titanium(IV) complexes, catalytic organozinc
reactions, 370–377
- Titanium tetraisopropoxide
enantioselective reactions
alkynylzinc addition, 565
dialkylzinc addition, 559
phenyl transfer, 567
Lewis acid catalyst formation, 559
- Titration *see* Thermometric titration
- TOCSY (total correlation spectroscopy), 151
- TON (turnover numbers), 476–477, 505
- Topologically chiral metal complexes,
enantioselective asymmetric
autocatalysis, 581
- Total correlation spectroscopy (TOCSY), 151
- Transferases, zinc enzyme reactions, 10–12
- Transition metal catalysis
allylzincation of alkenes, 898
carbocationations
intermolecular, 472–473, 878–885
intramolecular, 876–878
coupling reactions, 833–837
see also specific metals
- Transition metal–zinc bonds, organozinc
compound structures, 123–126
- Transition states
allenylzinc reagent additions, 427–428
C–Zn exchange dynamics, 196–199,
200–201, 203, 212
Zn–ene–allene reactions, 951, 952
- Transmetalation
Co–Zn, 783
Hg–Zn, 303
Li–Zn
carbocationation, 947–948, 949, 950–951
polyfunctional organozinc halide
preparation, 297, 299–300
zinc enolates, 798, 837–842, 959
Mg–Zn, 903, 905–907, 913–914
Ni–Zn, 775, 881, 886, 887
Pd- or Ni-catalyzed cross-coupling,
468–469
Pd–Zn, 877–878, 903–904
polyfunctional organozinc halide
preparation, 296–308
three-component reaction, 301–302
Sn–Zn, 302–303
Zn–Cu
allylzincation, 910–911, 914, 927,
940–941
carbocationation, 868, 871, 873, 876, 883,
948–949
Cu(I) cyanide, 293, 303, 305, 306,
333–334, 347–348
perfluoroalkynylzinc reagents, 738
polyfunctional organozinc halide
preparation, 293, 295, 303, 305, 306
zinc enolate addition, 961, 964, 965

- Zn–Fe, 881–882
Zn–Ti, 885, 911
Zr–Zn, 265–266, 884
Trialkylaluminums, alkyl exchange dynamics, 198–199
Trialkylphosphines, Pd or Ni catalysts, 477, 478–479, 498, 507, 508, 539, 540
Triarylphosphines, Pd or Ni catalysts, 476
Triarylzincates, structure, 46
Trichloronitromethane, Reformatsky reaction, 805
Trichlorophenol, cyclopropanation of achiral alkenes, 248
Tricholomenyn A, Pd-catalyzed synthesis, 514, 516, 517
Tridentate chiral ligands, enantioselective addition of dialkylzincs, 559
Triendynes, conjugated, 512, 514
Triethylaluminum, cinchona alkaloid systems, 565
Triethylboron, alkyl–Zn exchange dynamics, 215
Trifluoroacetic acid, halomethylzinc preparation, 239
Trifluoroacetic anhydrides, arylzinc compound reactions, 777
Trifluoromethyl alcohols, activated Zn synthesis, 764
Trifluoromethylation, perfluoroalkylzinc reagents, 741
Trifluoromethylzinc, preparation, 740
Trifluoromethyl zinc bromide, electrochemical organozinc reagent generation, 763–765
Trifluoroprenyl bromide, allylation of aldehydes, 767–768
Trifluoropropynylzinc, preparation, 736–737
1,2-Trifluorostyrenes, commercial preparation, 720
1,1,2-Trifluoro-2-trimethylsilylethylene, preparation, 727
Trifluorovinyl ketones, trifluorovinylzinc acylation, 729
Trifluorovinylzinc reagent acylation, 729 preparation, 719–720
Triisopropylsilyl chloride, enantioselective addition of diethylzinc, 571
Trimethylaluminum, alkyl exchange dynamics, 198–199, 211
Trimethylboron, alkyl–Zn exchange dynamics, 215–216
Trimethylindium, methyl–Zn exchange dynamics, 214
Trimethylsilyl 3-butenolate, synthesis, 852
Trimethylsilyloxy-substituted alkenes, cyclopropanation, 249
1-Trimethylsilyl-2-propenylzinc reagents, rearrangement, 634–636
 β -Trimethylstannylethylenetriphenylphosphorane, allylation, 734
Triorganozincates
1,1-dihalocompound rearrangement, 596–602
Pd-catalyzed cross-coupling, 367–368
preparation, 319–322, 323
structure
heteroleptic, 47–53
homoleptic, 41–46
Triphenylboron, enantioselective aryl transfer, 567
Triphenylphosphine
Pd or Ni catalysts, 475–476
Reformatsky reactions, 808
Triplet lifetimes, Zn(II) phthalocyanines, 410
Triquinanes, Zn–ene–allene reactions, 953
Tris(2-furyl)phosphine (TFP), Pd or Ni catalysts, 476, 480, 492
Tris(pyrazolyl)hydroborato, structure, 2, 80–1
Tris(*o*-tolyl)phosphine (TTP)
Pd or Ni catalysts, 476
Reformatsky reactions, 808
Trost, Tsuji–Trost reaction, 519
Tryptamine/*p*-chlorobenzoic acid cocrystal, enantioselective asymmetric autocatalysis, 584
Tsuji–Trost reaction, Pd-catalyzed allylation, 519
TTP *see* Tris(*o*-tolyl)phosphine
Tungsten, organozinc compound structure, 123, 124
Tungsten pentacarbonyl, Zn(II) porphyrins, 404
Turnover numbers (TON), bidentate ligand Pd catalysts, 476–477, 505
Two-step Grignard-type protocol, Reformatsky reaction, 799
U-106305 natural product, stereoselective cyclopropanation, 276
UB-165 natural product, Pd-catalyzed synthesis, 490–491
Ultrasound
perfluoroalkylation, 741
polyfunctional organozinc halide preparation, 291, 292
Reformatsky reactions, 801
Umpolung, allylic system reactivity, 318
Uncatalyzed reactions
allylzincation
alkenes, 891–898
alkynes, 898–900
carbozincations
intermolecular
addition to alkenes, 866–867
addition to alkynes, 865–866

- Uncatalyzed reactions (*continued*)
di(*tert*-butyl)zinc, 865–867
intramolecular
alkenes, 870–876
alkynes, 868–870
organozinc reagents, 322, 323–333,
346–347
- Unfunctionalized alkenes, stereoselective
cyclopropanation, 276
- α,β -Unsaturated compounds
epoxides, 337
esters and ketones, 522, 716
 β -halo- α,β -unsaturated esters, 522
 α -iodo carbonyl compounds, 515
Michael acceptors, 331, 332
zincate conjugate addition, 690–694
zinc dienolate reactions, 852
 β -zinc- α,β -unsaturated esters, 522
- Unsaturated fatty acids, polyoxygenated
metabolites, 351
- Unsaturated ketones, activated Zn synthesis,
767
- Unsymmetric ... *see* Asymmetric ...
- Unweighted least squares regression analysis,
enthalpies of formation, 141
- Valence isoelectronic compounds, Zn(II)
cyanide complexes, 144
- Vanadium(VI) chloride, Reformatsky reactions,
805
- Vaporization *see* Enthalpies of vaporization
- Vapor pressures, dialkylzinc compounds, 138
- Vesicles, Zn(II) porphyrins, 406
- Vinyl acetate, electrosynthesis of arylzinc
halides, 789
- Vinylalanes, cyclopropanation using zinc
carbenoids, 254
- Vinylation, Pd-catalyzed carboalumination
tandem processes, 527, 537
- Vinylboronates, cyclopropanation using zinc
carbenoids, 254
- E*-Vinyl chloride, stereoselective
cyclopropanation, 265
- Vinylgermanes, cyclopropanation using zinc
carbenoids, 254, 255
- Vinylidene chloride, Pd-catalyzed
monoalkynylation, 512
- Vinyl lithium reagents
ambient temperature *in situ* capture,
718–722
low temperature capture, 714–718
- Vinylogous Reformatsky reactions, zinc
dienolates, 839, 850, 854
- Vinyl organozinc halides
C-Zn inversion dynamics, 227
fluorinated vinylzinc reagent preparation,
719–722, 723, 726–727
- Vinylphosphonates, cyclopropanation using
zinc carbenoids, 254, 255
- Vinylsilanes
aza-enolate addition, 966
cyclopropanation using zinc carbenoids,
254, 255
- Vinylstannanes
aza-enolate addition, 966, 967
cyclopropanation using zinc carbenoids,
254, 255, 256
- Vinylzinc reagents
cyclopropanation using zinc carbenoids, 254
enantioselective addition, 564
- Viologen, porphyrin–viologen systems, 407,
409, 411
- Wannier-type excitons, Zn(II) porphyrin PET,
403
- Wiechell *see* Fritsch–Buttenberg–Wiechell
(FBW) rearrangement
- WIEN code, electric field gradient
calculations, 156
- Wilkinson's catalyst, zinc enolate synthesis,
842, 845
- Wires, Zn(II) porphyrins, 402–403
- Wurtz-coupling, polyfunctional organozinc
halide preparation, 292
- Xerulin, Pd-catalyzed synthesis, 493, 494, 501,
503, 508, 517
- Xerulinic acid, Pd-catalyzed synthesis, 493,
495
- XPA protein, ^{67}Zn NMR spectroscopy, 156,
157
- X-ray crystal structure, halomethylzinc
reagents, 242–244
- X-ray diffraction, Zn(II) coordination
chemistry, 155
- 5-Yn-2-enoic esters, Pd-catalyzed
propargylation, 522
- ZACA reaction (Zr-catalyzed asymmetric
carboalumination), 464, 537–538
- Zaragozic acid C, Pd-catalyzed synthesis, 493,
496
- Zeeman energy levels, ^{67}Zn NMR
spectroscopy, 150
- Zinc
acidic cleaning, 801
activation, 758–769, 800, 801–808, 868
chemical/physical activation, 290,
801–802
electrolytic zinc, 760–765
highly reactive Zn, 290, 801, 802–803
massive zinc, 757, 765–769
Reformatsky reactions, 799, 801–808

- Zn anode oxidation, 759
dust, 289–290
foil, 289
syn-hydrometalation, 463
insertion
 into C–halogen bond, 722–732, 733, 798, 799–800
 polyfunctional organozinc halide
 preparation, 293–295, 296, 308
isotopic composition, 165
metalation
 mixed zincate preparation, 687–688
 perfluoroalkynylzinc reagent preparation, 737–738
oxidative addition to functionalized organic halides, 289–296
Pd cocatalyzed cross-coupling, 462, 465–467, 481, 482, 501
perfluoroalkylzinc Zn-mediated reactions, 741, 742
transmetalation
 Co–Zn, 783
 Hg–Zn, 303
 Li–Zn, 798, 837–842, 947–948, 949, 950–951, 959
 carbozincation, 947–948, 949, 950–951
 polyfunctional organozinc halide
 preparation, 297, 299–300
 zinc enolates, 798, 837–842, 959
Mg–Zn, 903, 905–907, 913–914
Ni–Zn, 775, 881, 886, 887
Pd–Zn, 877–878, 903–904
Sn–Zn, 302–303
Zn–Cu
 allylzincation, 910–911, 914, 927, 940–941
 carbozincation, 868, 871, 873, 876, 883, 948–949
 Cu(I) cyanide, 293, 303, 305, 306, 333–334, 347–348
 polyfunctional organozinc halide
 preparation, 293, 295, 303, 305, 306
 zinc enolate addition, 961, 964, 965
 Zn–Fe, 881–882
 Zn–Ti, 885, 911
 Zr–Zn, 265–266, 884
⁶⁷Zn, 150, 153, 156
 Zn–Ni cluster structures, 124–125
 see also ⁶⁷Zn; ⁶⁷Zn NMR spectroscopy
Zinc acetate dihydrate, thermal decomposition, 187
Zinca–ene–allene reactions
 cyclization, 629–633
 intramolecular carbozincations, 950–954
Zinc–alkene interaction, intramolecular
 carbozincations, 870, 871, 872
Zinc–alkyne interaction, intramolecular
 carbozincations, 870
Zincate carbenoids, 1,2-migration, 694–699, 700
Zincated allylic ether, mutual
 diastereoselection, 920–921
Zincated hydrazone, sp³-geminated
 organodizinc reaction, 675–676
 β -Zincated phosphonate, Cu(I)-catalyzed
 substitution, 334, 335
Zincates
 alkyl–Zn exchange dynamics, 204–205
 electron ionization mass spectrometry, 178
 preparation, 686–689
 I₂-Zn exchange, 874
 lithium triorganozincates, 319–322, 323
 immobilized zincates, 322
 Pd-catalyzed carbozincations, 883
 reactions, 690–709
 benzyne generation, 706–707
 carbonyl addition/epoxide ring opening, 690
 conjugate addition to α,β -unsaturated
 compounds, 690–694
 cross-coupling reactions, 707–709
 tetracoordinated, 687
 see also Mixed zincates; Organozincates;
 Tetraorganozincates; Triorganozincates
Zincation
 allenyl alkylzinc reagents, 432–434
 lithiation–zincation of 2-alkynes, 521
 oxidative, 469–470
 palladiozincation of propargylic mesylates, 435–437, 442
 propargylic bromides, 421–422
 see also Allylzincation; Carbozincations;
 Crotlylzincation; Ethylzincation
Zinc–boron exchange reactions
 cyclopropanation using zinc carbenoids, 253–254
 diorganozinc functionalization, 311–316, 560–561
 enantioselective alkenylation, 563
Zinc carbenoids
 alkene cyclopropanation
 achiral alkenes, 247–256
 mechanism, 245–246
 reaction solvent, additives and
 temperature, 246–247
 stereoselective
 acyclic alkenes, 261–266
 chiral alkenes, 256–266
 chiral auxiliaries, 266–273
 chiral catalysts, 279–281
 cyclic alkenes, 257–260
 ring contraction, 266, 267
 stoichiometric chiral reagents, 273–278
 N-substituted alkenes, 250–251

- Zinc carbenoids (*continued*)
synthetic scope, 246–281
allylzincation
alkenylmetals, 912
alkynylmetals, 942–944
gem-dizinc carbenoid, 241
1,2-migration, 694–699, 700
preparation
 α -substituted halomethylzinc carbenoids,
240–242
unsubstituted halomethylzinc carbenoids,
238–240
zinc enolate synthesis, 842, 844
Zn–Cu carbenoids, 238, 335, 336
- Zinc–carbon bonds
bond energies, 137, 143–144, 144
mass spectrometry
bond dissociation products, 178–179
complexes, 172–179
see also Carbon–zinc bonds
- Zinc complexes
bis-oxazolines, 896, 897
COSMOS, 154
density functional theory, 154
enzymes, 2–7
Zn-finger protein domains, 6, 7
 ^{67}Zn NMR spectroscopy, 147–161
- Zinc–copper couples
intramolecular carbozincation of alkynes,
868, 869
iodomethylzinc iodide preparation, 238
Reformatsky reactions, 801
- Zinc–copper reagents, polyfunctional, 305
- Zinc(II) cyanide
complexes
laser ablation, 179
thermochemistry, 144
Pd- or Ni-catalyzed cyanation, 544
- Zinc dienolates, reactivity, 848–854
- Zinc enamides, addition to alkenes, 969–971
- Zinc–ene reactions
alkynylsilanes, 900
allylzincation, 319, 914, 932, 936
intramolecular carbozincation, 901–908
allenylzinc reagent reactivity, 948,
950–954
Pd-catalyzed, 903–905, 907–908
type I, 902–905, 906
type II, 902, 905–908, 936
zinc–ene–allene reactions, 950–954
- Zinc enolates
alkyne addition reactions, 956–958
anion structure, 73–74
cyclization, 633
diethylzinc reactions, 842–848
Gilman–Speeter reactions, 819–827
lithiation/transmetalation protocols,
837–842
reactivity, 956–971
multi-component reactions, 886, 887
Reformatsky reactions, 798–837
applications, 808–819
electrophiles, 827–837
Zn metal activation, 801–808
- Zinc enzymes
hydrolases, 12–20
lyases, 20–22
oxidoreductases, 8–10
reaction mechanisms, 1–29
general mechanisms, 7–8
structural aspects, 2–7
polynuclear Zn sites, 3, 4, 5
Zn-finger protein domains, 6, 7
transferases, 10–12
 ^{67}Zn QCPMG NMR spectroscopy,
154
- Zinc(II) halides, cocatalysts, 481
- Zinc–hydrogen exchange reactions,
alkynylzinc preparation, 470
- Zinc–iodine exchange reactions
alkylzinc preparation, 470
diorganozinc functionalization, 308–311,
312, 560
intramolecular carbozincation of alkenes,
870–875, 876
see also Halogen–zinc exchange reactions
- Zinc malonates, Cu(I)-catalyzed Michael
addition, 358, 360
- Zinc–mercury exchange reactions,
intramolecular carbozincation of alkenes,
870, 871
- Zincocene
mass spectrometry, 171
metallotropic C–Zn exchange dynamics,
210–211
structure, 61–64, 116, 123–125
- β -Zinco- α,β -unsaturated esters,
propargylation–allenylation, 522
- Zinc(II) phthalocyanines
photochemistry, 395–419
medicinal photodynamic therapy,
409–411
nonlinear optical response, 407
photocatalytic oxidation, 411–412
photoinduced electron transfer, 398–406,
407
photonics materials, 407
photosensitization reactions, 407–412
photovoltaic applications, 407–409, 411
pigments and dyes, 406
reverse saturable absorption, 407
singlet oxygen generation, 410
- Zinc(II) porphyrazines, photochemistry, 396,
397, 398
- Zinc(II) porphyrins
photochemistry, 395–419

- back electron transfer, 409
- charge separation/recombination, 404
- chemical uses, 411
- excitonic interactions, 402–403
- medicinal photodynamic therapy, 409–411
- multiporphyrin arrays, 403
- nonlinear optical response, 407
- photoinduced electron transfer, 398–406
- photonics materials, 407
- photosensitization reactions, 407–412
- reverse saturable absorption, 407
- synthesis, 402–406
- wires, 402–403
- Zinc/silicon reagent, polyfunctional organozinc halide preparation, 297, 299–300
- Zinc–silver couples, Reformatsky reactions, 801
- Zinc(II) tetrapyrroles
 - photochemistry, 395–419
 - see also* Zinc(II) phthalocyanines; Zinc(II) porphyrins
- Zinc–transition metal bonds, organozinc compound structures, 123–126
- Zirconacycles, Zn–ene–allene cyclization, 953
- Zirconium
 - alkenylzirconium intermediate, 501, 503
 - catalysis
 - allylzincation, 901
 - carboalumination, 368, 369, 464, 466, 471, 527, 537–538
 - carbomagnesium, 464
 - carbozincations, 464
 - alkenes, 471–472, 884
 - alkynes, 878–879
 - crotylzincation, 471
 - syn-hydrometalation, 463
 - Zr–Zn transmetalation, 265–266, 884
 - Zirconium-catalyzed asymmetric carboalumination (ZACA reaction), 464, 537–538
 - Zirconium(IV) complexes, catalytic organozinc reactions, 377–378
 - Zirconocene complexes, 1,6-enyne cyclization, 953
 - Zirconocene dihalides
 - intermolecular alkyne allylzincation, 901
 - intermolecular carbozincation
 - alkenes, 884
 - alkynes, 879
 - ⁶⁷Zn
 - half-integer spins, 153
 - magnetogyric ratio, 150
 - natural abundance, 150, 156
 - quadrupolar nucleus, 150, 153
 - ⁶⁷Zn NMR spectroscopy, 147–161
 - ab initio* calculations, 156, 157
 - applications, 156–158
 - biomacromolecules, 150–151, 153–155, 156–158
 - chemical shift anisotropy, 155
 - coordination chemistry tool, 147–161
 - cross polarization, 153, 156
 - crystal lattices, 152
 - electric field gradient tensors, 151–152, 156
 - field sweeping, 155
 - half-band widths, 150
 - Hartman–Hahn matching field, 157
 - isotropic chemical shifts, 153
 - Knight shift, 155
 - magic-angle spinning, 155
 - materials, 155–156
 - metalloproteins, 150–151, 153–155, 156–158
 - Mössbauer measurements, 155
 - nuclear quadrupole coupling, 155, 156
 - nuclear quadrupole resonance, 155
 - QCPMG NMR, 154
 - quadrupolar echo, 153–154
 - quadrupole moment, 153
 - quadrupole relaxation, 150, 153
 - quantum-mechanical calculations, 151
 - relaxation times, 153
 - solid-state NMR, 152–156
 - surrogate probes, 150, 153
 - theory, 151–152
 - time differential perturbed angular correlation, 155
 - Zeeman energy levels, 150

With kind thanks to Caroline Barlow for creation of this index.