

## Index

### **a**

- acetate Mn(I) species 507  
 acetylene-coordinated hydride Ir(I)  
     species 400  
 acetylene-coordinated silyl Ir(III) complex  
     401  
 acetylene insertion 203  
 acetylene moiety 260  
 acetylenes 400  
 acetyl-protected aminoethyl quinoline  
     additive 217  
 $\pi$ -acidic catalyst Pt(II) species 264  
 $\pi$ -acidic compounds 297  
 acidic hydrogen 128  
 activation free energy 66, 83, 101, 104,  
     128, 134, 137, 141, 201, 203, 207  
 $\pi$ -activation of alkynes 586  
 active digold complex 617  
 active hydride ferrous species 432  
 acyl aryl reductive elimination 214  
 3-acyloxy-1,4-enynes 368  
 Ag-catalyzed nitrene transfer 578–580  
 Ag-catalyzed vinylcarbene insertion 573  
 Ag-mediated alkyne activations  
     C—H activation of alkynes 587–588  
      $\pi$ -activation of alkynes 586–587  
     vinyl compounds 585  
 Ag-mediated carbene complex  
     transformation  
     carbene insertion into C—Cl bond  
         572–573  
     carbene insertion into C—H bond  
         574–576  
 carbene insertion into O—H bond 573  
 Fischer-type metallacarbene complex  
     568  
 general mechanism 568  
 nucleophilic attack by carbonyl groups  
     573–574  
 silver–carbene formation 568–572  
 Ag-mediated nitrene transfer reactions  
     577  
 Ag-mediated nitrene transformations  
     nitrene 576–577  
     nucleophilic attack by amines  
         582–583  
     nucleophilic attack by unsaturated  
         bonds 580–582  
     silver–nitrene complex formation  
         577–579  
 Ag-mediated silylene transformations  
     583–585  
 agostic amino borane-ferrous complex  
     437  
 agostic Ru(0) species 459  
 alcohol dehydrogenation 434, 510  
 alcoholate Rh(II) intermediate 467  
 alcohol-coordinated iron(III) complex  
     421  
 alcohol dehydrogenations 473  
 alcohols 405  
 Alder-ene reaction 617  
 alkane-coordinated Ir(III) complex  
     390  
 alkane oxidation 420  
 alkanes 402

- alkene-coordinated cationic Cu(I) species 540  
 alkene-coordinated cationic Rh(I) species 347  
 alkene coordinated Rh(I) species 347  
 alkene diboration 347  
 alkene hydrogenations 464  
 alkene insertion 294  
 alkene oxidations 423  
 alkenes 388, 427  
 alkenes, Cu-catalyzed borylations 551  
 alkenyl-Rh(III) complex 338  
 alkoxy/amino Ir(III) complex 391  
 alkoxy iorn(II) intermediate 432  
 alkoxy Rh(III) intermediate 352  
 alkoxy Mn(I) intermediate 509  
 alkyl arenes 438  
 alkyl aryl iron(0) intermediate 438  
 alkylated bipyridine-coordinated Rh(I)  
     intermediate 334  
 alkylated enamine-coordinated Rh(I)  
     complex 335  
 $\alpha$ -alkylated ketone product 335  
 alkyl bromide 135  
 alkyl copper-carbene species 542  
 alkyl-cuprous intermediate 551  
 $\alpha$ -alkyl elimination 349  
 alkylideneoxindole product 576  
 3-alkylideneoxindoles 569, 575  
 alkyl Ir(III) complex 398  
 alkyl Ir(V) complex 389, 391  
 alkyl Ir(III) intermediate 389  
 alkyl Ir(V) intermediate 388  
 alkyl Ir(V) trihydride intermediate 389  
 alkyl metal compounds 6  
 alkyl Rh(III) intermediate 334, 335, 338,  
     347  
 alkylruthenium intermediate 461  
 alkyne-coordinated Au(I) species 599,  
     601  
 alkyne-coordinated Rh(I) species 351  
 alkyne hydroamination 349  
 alkyne metathesis 484  
 alkynes, Cu-catalyzed borylations 552  
 alkynes, isomerization of 599  
 alkynyl-Au(I) coordinated Au(I) complex 617  
 alkynyl benzaldehyde 601  
 alkynyl-coordinated Cu(I) species 536  
 alkynyl Cu(I) species 535  
 alkynyl Cu(II) species 538  
 alkynyl Cu transformations 536  
 alkynyl-N-propargylanilines 603, 605  
 alkynyl nucleophile 80  
 allene-coordinated hydride-Rh(III)  
     351  
 allene-coordinated Rh(I) intermediate 350  
 allene intermediate 599  
 allene moiety 70  
 allenes, hydroalkoxylation of 610  
 allenes, hydroamination of 610  
 allenyl arene product 507  
 allenylarylimine 507  
 allenyl gold intermediate 599  
 allenyl indole intermediate 603  
 allenyl ketones, cycloisomerization of 613  
 allenyne cycloisomerizations 617  
 allyl ammonium intermediate 610  
 allylic carbon cation intermediate 610  
 allylic ether 611  
 allylic hydrogen 599  
 allylic ions 363  
 allylic Pd complex 234  
     formation, from allene insertion  
         238–239  
     formation, from allylic C—H activation  
         237–238  
     formation, from allylic nucleophilic  
         substitution 236–237  
     formation, from allylic oxidative  
         addition 235–236  
     formation, from nucleophilic attack  
         onto allene 237  
 allylic Ru(II) species 469  
 allylic Rh(III) intermediate 365  
 allylic substitutions 608  
 amide-coordinated aryl-Cu(III) species 528

- amide-directed C—H bond activation 332  
 amination of nitrenes 543  
 amine-coordinated ferrous species 427  
 amine coordinated Ir(I) complex 397  
 amine-*N*-oxide coordinated Au(I) species 601  
 aminimides 582  
 aminocarbonylation 230  
 amino ferrous 441  
 amino ferrous complex 434  
 amino ferrous species 429, 435, 437  
 amino Ir(III) intermediate 406  
 aminomethyl indole 526  
 amino Ru(II) species 474  
 ammonia-borane Lewis acid-base complex 437  
 ammonium iridate species 397  
 amphiphilic palladium acetate 212  
 Amsterdam Density Functional (ADF) 39  
 animo olefin coordinated IrI species 397  
 anionic fluoride Cu(I) species 522  
 anionic sulfonate 197  
 anionic trifluoromethyl group 524  
 $\pi$  antibond 5  
 anti-Markovnikov product 470  
 arene oxidation 422  
 arenes 403, 407  
 arenes/indole derivatives 293  
 arenes, nucleophilic attack by 606  
 aromatic chromenylium 601  
 aromatic fluorocarbons 467  
 aromatic ketones 452  
 aromatic *N*-heterocycles 582  
 arylalkyl Ru(II) intermediate 461  
 arylation of carbenes 357  
 arylation-product-coordinated Rh(I) complex 332  
 aryl boranes 459  
 aryl bromide 459  
 aryl Cu(I) intermediate 527  
 aryl diazonium salts 408  
 $\beta$ -aryl elimination 88, 343  
 aryl halides 457  
 aryl iron(0) intermediate 438  
 aryl-Rh(III) intermediate 332, 337  
 aryl Rh-nitrene complex 361  
 aryl sulfamates 186  
 atom-economical reactions 204  
 atomic orbitals 21  
 Au-catalysis 258  
 Au(I) catalyzed non-redox unsaturated C—C bonds functionalization 597  
 Au-mediated alkene activations  
     allylic substitutions 608–609  
     nucleophilic addition of alkenes 607–608  
 Au-mediated alkyne activations  
     isomerization of alkynes 599  
     nucleophilic attack by arenes 606  
     nucleophilic attack by nitrogen-involved nucleophiles 602–606  
     nucleophilic attack by oxygen-involved nucleophiles 599–602  
     trans-nucleophilic attack 598  
 Au-mediated allene activations  
     cycloisomerization of allenyl ketones 613  
     hydroalkoxylation of allenes 610–612  
     hydroamination of allenes 610  
 Au-mediated enyne transformations  
     allenyne cycloisomerizations 617  
     conjugative enyne cycloisomerizations 617–618  
     1,5-enyne cycloisomerization 614–615  
     1,6-enyne cycloisomerizations 615–616  
 azaindoline 334  
 7-azaindoline cocatalyst 335  
 azaindoline-coordinated Rh(I) complex 334  
 azepanone product 602  
 azide–alkyne cycloadditions 533  
 azide-coordinated alkynyl Ru(II) species 479  
 aziridination of nitrenes 361  
 aziridination of olefins 580

**b**

back-donation bonds 53  
 back-donation  $\pi$ -bond formation 567  
 base-assisted C—H bond cleavage 453  
 base-assisted internal electrophilic-type substitution (BIES) 452  
 benzaldehyde 467  
 benzamides 332  
 benzamide substrate 296  
 benzoate-assisted reductive deprotonation 526  
 benzoic acid-coordinated sextet ferric(III)-hydroperoxo complex 423  
 benzyl alcoholate Ru(II) intermediate 469  
 benzylalcohol product 467  
 B(boryl)-H(hydride) elimination 402  
 biaryl coordinated iron(I) species 441  
 biaryl Cu(III) intermediate 520  
 biaryl moiety 186  
 [2,2,2]-bicyclic intermediate 601  
 bicyclo[3.1.0]hexene 614  
 bidentate olefin ligands 330  
 bidentate phosphine 134  
 bidentate phosphine-amine ligand coordinated amino Mn(I) hydride 508  
 bidentate phosphine ligand 129, 146, 147  
 bifunctionalized carbenoid compound 568  
 bimetallic reductive elimination 75–77  
 bimetallic single-electron reductive elimination mechanism 538  
 binuclear copper catalyzed azide alkyne [3+2] cycloaddition 534  
 binuclear Cu(I) species 543  
 bisaryl-Cu(III) intermediate 551  
 bisaryl Ir(V) intermediate 408  
 bisboryl Rh(III) intermediate 345  
 bisphosphine-coordinated allylic Pd(II) complex 74  
 bisphosphinesilver 584  
 bis-silylation 202

bissilylethane derivatives 202  
 $\pi$ -bonding electrons 4  
 Born–Oppenheimer approximation 20, 22  
 boryl aryl hydride Ir(III) intermediate 403  
 boryl-copper complexes 549  
 boryliminoacyl intermediate 342  
 boryl Ir species 387  
 borylisocyanide-coordinated phenyl Rh(I) complex 342  
 boryl Rh(I) species 342, 343  
 branched allylic ether 611  
 bromamine-T 577  
 Brønsted acid 437  
 Brønsted base-assisted isomerization of alkynes 599  
 butylbenzene-coordinated Ir(III) complex 391

**c**

carbene 82  
 carbene insertion into C—Cl bond 572–573  
 carbene insertion into C—H bonds 261–264, 354–357, 574–576  
 carbene insertion into O—H bond 573  
 carbene insertions 541–542  
 carbenes rearrangement 542  
 carbenoids 332  
 carbonate hydrogenations 508  
 carbonate Ir(III) complex 405  
 carbon-cyano bond activation 342  
 carboncycles 362  
 carbon dioxide 430  
 carbon dioxide hydrogenation 507  
 $\beta$ -carbon elimination 89, 343  
 carbon-halogen bonds 5, 184  
 carbon monoxide 81, 229  
 carbon radical attacks 75  
 carbonyl compounds 5, 80, 391  
 carbonyl-coordinated aryl Rh(I) intermediate 343  
 carbonyl-coordinated five-membered rhoda(III)cycle 349

- carbonyl hydrogenation 465  
 carbonyl insertion 214  
 carbonyl oxygen atoms 573  
 carbonyls 429  
 carbonyls, Cu-catalyzed borylations 553  
 carboxylate-assisted C—H bond activation 128  
 carboxylic anhydrides 184  
 C2-arylated indole intermediate 332  
 catechols 425  
 cationic Au(I) species 613  
 cationic Cp<sup>\*</sup>Rh(III) complex 337  
 cationic ferrous intermediate 429  
 cationic iorn(II) intermediate 429  
 cationic iron(IV)-oxo complex 423  
 cationic oxidant 63  
 cationic quinolinium intermediate 396  
 cationic Rh(I) catalyzed dihydrogenation of alkenes 347  
 cationic Rh(I) species 352  
 cationic Ru(IV) hydride intermediate 464  
 C(aryl)—B reductive elimination 403  
 C(vinyl)—C(vinyl) bond 183  
 C(aryl)—C(alkyl) bond formation 332  
 C—C/C—hetero bonds 329  
 C(aryl)—C(aryl) cross-coupling reaction 408  
 C—C cross-couplings with alkyl halide 441  
 C—C cross-couplings with aryl halide 438  
 C(aryl)—Cl bond 184  
 cesium pivalate 330  
 C—F bond couplings 522  
 C(aryl)—F reductive elimination 524  
 β-C(alkyl)—H activation 408  
 C—H activation of alkynes 587–588  
 C(aryl)—halide bond 519  
 C—H amidations 580  
 C—H aminations 529  
 C—H arylation 527  
 C—H azidations 501  
 C—H bond arylation, Ru-catalyzed 456  
 C—H bond cleavage 330  
 C—H bond oxidative addition 452  
 chelated Rh(I)—NHC complex 334  
 chelation-assisted *meta*-C(aryl)—H activation 214–216  
 chelation-free C(sp<sup>2</sup>)—H activation 208–211  
 chelation-free C(sp<sup>3</sup>)—H activation 206–207  
 C—H etherifications 532  
 C—H halogenations 501  
 C—H hydroxylations 500, 531  
 C—H isocyanations 501  
 chloramine-T 577  
 chloroaryl triflate 184  
 chloronium ylide intermediate 572  
 chloronium ylide moiety 572  
 C—H metalation 223  
 C(alkyl)—H reductive elimination 398  
 click (3+2) cyclization 478  
 C—N bond activation 344  
 C—N bond couplings 520  
 C—N cross-couplings with aryl halide 438  
 cobalt (Co) 289  
 C(arene)—O(oxo) bond 423  
 C—O bond activation 345  
 C—O bond coupling 522  
 C(alkyl)—O(hydroxide) bond formation 420  
 Co-catalysis, theoretical study of  
     co-catalyzed hydroformylation 307  
         direct hydroformylation, by H<sub>2</sub> and CO 308  
         transfer hydroformylation 309–310  
     co-catalyzed hydrogenation 301  
         of carbon dioxide 301–304  
         hydrogenation, of alkenes 304–306  
         hydrogenation, of alkynes 306–307  
     co-mediated carbene activation 310  
         arylation, of carbene 310–312  
         carboxylation, of carbene 312–313  
     co-mediated carbene activation  
         arylation, of carbene 312  
 Co-mediated C—H bond activation 289, 290

- Co-catalysis, theoretical study of (*contd.*)  
 hydroarylation, of alkenes 291–293  
 hydroarylation, of alkynes 294–296  
 hydroarylation, of allenes 293–294  
 hydroarylation, of nitrenoid 296–297  
 oxidative C—H alkoxylation 297  
 Co-mediated cycloadditions 297–298  
 co-catalyzed [2 + 2] cyclizations 300–301  
 co-catalyzed [2 + 2 + 2] cyclizations 299–300  
 co-catalyzed [4 + 2] cyclizations 299  
 Pauson-Khand reaction 298–299  
 co-mediated nitrene activation 313, 314  
 amination, of C—H bonds 315  
 amination, of isonitriles 314–316  
 aziridination, of olefins 314  
 co-catalyzed [2 + 2 + 2] cyclizations 299–301  
 co-catalyzed [4 + 2] cyclizations 299–300  
 complete basis set (CBS) methods 23  
 concerted metalation-deprotonation (CMD) 206, 258, 290, 452, 505  
 concerted oxidative addition 60  
 concerted reductive elimination 71–73  
 conductor-like PCM (C—PCM) 33  
 Conia-ene type addition 367  
 co-nitrene complex 313, 314  
 conjugative diene 599  
 conjugative enyne cycloisomerizations 617–618  
 conjugative insertion 83–85  
 conjugative olefin 469  
 conjugative triene product 617  
 conjugative unsaturated bonds 83  
 conventional organocatalysis 6  
 coordinative chelation-assisted C(sp<sup>3</sup>)—H activation 216, 217  
 copper 517  
 copper-based coupling reactions 518  
 copper catalytic cycle 518  
 copper-catalyzed benzene oxidation reaction 531  
 copper(II) dichloride 537  
 copper-mediated cyclopropanation 540  
 correlation-consistent basis sets 31, 32  
 coupled cluster (CC) methods 39  
 coupled cluster theory 39  
 coupling 183  
 covalent chelation-assisted *ortho*-C(aryl)—H activation 212, 213  
 Cp\*Rh(III)-catalyzed C—H bond alkylations 335  
 CpRh(III) species 361  
 CpRu(II) catalyzed alkyne trimerization 476  
 [CpRu(Py)<sub>2</sub>(PPh<sub>3</sub>)]PF<sub>6</sub> 463  
 CpRu(II) species 475  
 C(aryl)—Rh bond 332  
 C—Rh bond transformation 330  
 cross-coupling reactions 4  
 Cu(I) catalyzed allylic trifluoromethylation 525  
 Cu-catalyzed borylations alkenes 551–552  
 alkynes 552–553  
 carbonyls 553–554  
 Cu(I)-catalyzed [3+2] cycloadditions 533  
 Cu-catalyzed hydrofunctionalizations hydroborylations 547  
 hydrocarboxylations 548–549  
 hydrosilylation 547–548  
 Cu(II) dicarboxylate complex 526  
 Cu-mediated alkyne activations alkynyl Cu transformations 536–539  
 azide–alkyne cycloadditions 533–535  
 nucleophilic attack onto alkynes 535–536  
 schematic of 533  
 Cu-mediated carbene transformations carbene insertions 541–542  
 [2+1] cycloadditions with alkenes 539–541  
 rearrangement of carbenes 542  
 Cu-mediated C—H activations

- C—H aminations 529  
 C—H arylations 527  
 C—H etherifications 532  
 C—H hydroxylation 531  
 Cu-mediated nitrene transformations  
     amination of nitrenes 543–544  
     [2+1] cycloadditions with alkenes 543  
     nitrene insertions 544–545  
 Cu-mediated trifluoromethylations  
     radical type trifluoromethylations 525–527  
     through cross-coupling 524  
     through oxidative coupling 524–525  
 Cu-mediated Ullmann condensation  
     C—F bond couplings 522–524  
     C—N bond couplings 520–522  
     C—O bond coupling 522  
     coupling reaction of aryl halides and nucleophiles 519  
     single electron transfer involving pathway 519  
 cumulene-type Lewis electron structure 569  
 cupric carboxylate 552  
 cuprous borylcarboxylate complex 554  
 cuprous boryl complex 552, 554  
 cuprous borylmethanolate 554  
 cuprous methoxide species 553  
 Curtin–Hammett principle 570  
 cyclopentadiene derivatives 330  
 (2+2+2) cycloadditions 475–478  
 (3+2) cycloadditions 365–367  
 (5+2) cycloadditions 367–369  
 (5+2+1) cycloadditions 369  
 [2+1] cycloadditions with alkenes 539–541, 543  
 cyclobutanol 343  
 cyclobutanolate Rh(I) species 343  
 cyclobutenones 204  
 cyclobutyl substituted 1,5-ene 614–615  
 cycloheptatriene product 369  
 cycloisomerization of allenyl ketones 613  
 cyclometalation intermediate 212  
 cyclopentadiene 617  
 cyclopentadienyl (Cp) ligands 330  
 cyclopentenone derivatives 349  
 cyclopentenone product 478  
 cyclopropanation 266–268  
 cyclopropanation of carbenes 358, 359  
 cyclopropenes 273
- d**
- dearomatic alkyl Cu(III) intermediate 528  
 dearomatized amino Ru(II) intermediate 468  
 decarbonylation 224  
 decarbonylation reaction 90  
 decarboxylation transition state 145  
 dehydrogenative coupling 511  
 density functional theory (DFT) 23, 24, 259, 570  
 Jacob's ladder, of density functionals 25  
     correction, of dispersion 27–29  
     fifth rung 26  
     fourth rung 26  
     second rung 25–26  
     third rung 26  
 deprotonation-metallation mechanism 527  
 dialkylbiarylphosphine ligand 186  
 dialkyl orthoacetate 574  
 diaryl ferric intermediate 441  
 diaryl-Rh(III) complex 332  
 diaryl-Rh(III) intermediate 332  
 diaryl Ru(II) complex 459  
 diazo compound 310  
 diazo compounds 310  
 $\alpha$ -diazonitrile intermediate 542  
 diazonium salt 521  
 diboryl alkane 349  
 dichloromethane (DCM) 572  
 dielectric formulation (D-PCM) 33  
 1,6-diene 484  
 diene insertion 167  
 diethylene-coordinated Pd(0) species 232

- dihalosilanes 583  
dihydride iron(II) intermediate 427  
dihydride Rh(III) intermediate 347, 352  
dihydride Rh(III) species 347, 353  
dihydrogen-coordinated cationic ferrous intermediate 437  
dihydrogen-coordinated cationic Ir(III) complex 396  
dihydrogen-coordinated Ir(III) dihydride catalyst 389  
dihydrogen molecule-coordinated iron(0) complex 427  
dihydroquinoline product 606  
dimeric ferrous complex 438  
dimeric Rh(II) 330  
*N,N*-dimethylformamide (DMF) 532  
diphenylethanimine 395  
(*E*)-1,2-diphenyl-1-propene 389  
diphosphine ligand 304  
diphosphine ligand Xyl-MeO-BIPHEP 403  
dipolar carbonyl ylide 601  
direct hydrogenation 391  
directing group-coordinated Mn(I) species 504  
dirhodium catalyst 361  
dirhodium tetracarboxylate complexes 356  
dispersion effect 35  
dissociative mechanism 57  
distortion-interaction analysis 184  
1,4-disubstituted 1,2,3-triazoles 533  
d orbital 5, 41, 52, 53, 82  
doublet iron(V)-oxo benzoate complex 423  
double-zeta (DZ) basis 30  
Drude oscillators 27
- e**  
effective core potential (ECP) 32  
eight-membered Rhoda(III)cycle 368  
electron-deficient olefins 335  
electronegativity, of carbon atom 206  
electron-electron repulsion 21
- f**  
electron pair filling one  $sp^2$  hybrid orbital 5  
electron-poor phosphine ligand 330  
electron-rich arenes 606  
electrophile 456  
electrophilic carbon subtracts 181  
electrophilic deprotonation 503  
electrophilic proton 397  
electrophilic silver-silylene complexes 583  
 $\alpha$ -elimination 90, 91  
 $\beta$ -elimination 87–89, 91  
enamine type 1,4-dihydrogenated intermediate 396  
enamine type 1,4-dihydroquinoline 396  
enantioselective direct hydrogenation reactions of ketones 391  
6-endo nucleophilic attack 616  
ene-vinylcyclopropane 369  
enolate-Rh(III) complex 335  
enolate tautomer 572  
entropy effect 41  
1,5-ene cycloisomerizations 614  
1,6-ene cycloisomerizations 615  
enynol 365  
equivalent formate Rh(III) hydride complex 353  
ester hydrogenation 466  
ethanol 467  
etherification product coordinated gold complex 608  
ethynylbenzene reactant 262  
ethynyl-benzylalcohol 261, 262  
exact solvation effect 41  
exo-addition vinyl copper intermediate 536  
5-exo alkene 616

- C—N cross-couplings with aryl halide 438–441  
 iron-mediated oxidative coupling 441  
 Fe-mediated dehydrogenations  
   alcohols 434–435  
   ammonia-borane dehydrogenation 437–438  
   formaldehyde 435  
   formic acid 435–437  
 Fe-mediated hydrofunctionalizations  
   hydroamination of allenes 432–434  
   hydrosilylation of ketones 431–432  
 Fe-mediated hydrogenations  
   alkenes 427–429  
   carbon dioxide 430–431  
   carbonyls 429–430  
   imines 430  
 Fe-mediated oxidations  
   alkane oxidation 420–422  
   alkene oxidations 423–425  
   arene oxidation 422–423  
   iron-oxo species 420  
   oxidative catechol ring cleavage 425–426  
   ferric(IV) hydroxide intermediate 420  
 Fischer-type metallacarbene complex 568  
 Fischer type Rh-carbene complex 354, 358, 359  
 five-coordinated Cu(III) species 522  
 five-membered rhoda(III)cycle 344  
 five-membered rhodacycle complex 339  
 five-membered-ring CMD-type transition state 452  
 five-membered ring type allylic carbocation 617  
 formaldehyde-coordinated hydride Ir(III) complex 405  
 formaldehyde dehydrogenation 435, 473  
 formate-coordinated cationic Mn(I) species 508  
 formate-Ru(II) intermediate 474  
 formic acid dehydrogenation 435, 474  
 four-coordinate anionic Rh(I) complex 331  
 four-coordinated Cu(III) intermediate 522  
 four-membered cyclic  $\sigma$ -CAM-type transition state 456  
 four-membered rhodacycle 359  
 free electron gas 24  
 free radical 67  
 frontier molecular orbitals (FMOs) 60  
 fused pyrrole coordinated Au(III) complex 616
- g**  
 gaseous dihydrogen 102, 140, 157, 302, 353, 388, 391, 396  
 Gaussian-*n* methods 23  
 Gaussian-type orbitals (GTOs) 29  
 generalized gradient approximation (GGA) 24  
 Gibbs free energy 55  
 gold-assisted alkyne activations 599  
 Grubbs II type catalyst-mediated intermolecular olefin metathesis 482
- h**  
 Hamiltonian operator 19  
 Hartree–Fock (HF) theory 20–22, 39  
 Hartwig–Buchwald amination reaction 519  
 Heck–Mizokori reaction 183  
 heme iron enzymes 419  
 hetero agostic complex 432  
 $\beta$ -heteroatom 88  
 heteroatoms 265  
 hetero-Diels-Alder [4+2] cycloaddition 601  
 hexenylidene Pt intermediate 267  
 high-spin triplet Rh(III)–nitrene complex 360  
 high spin trispyrazolylborate-coordinated Cu(II)–oxo radical 532  
 high valence transition metal 5  
 H-Ir covalent bond 397  
 Hiyama coupling 183, 190, 192, 193  
 $\eta^6$ -oligoacene coordinated Cr(CO)<sub>3</sub> 54

- $\eta^1$ -oligoacene coordinated intermediate 54  
 $\eta^3$ -oligoacene coordinated transition state 54  
 homogeneous catalytic dehydrogenation of alcohols 472  
 hydride–alkyl reductive elimination 389  
 hydride-coordinated Ru(II) intermediate 474  
 hydride copper 545, 548  
 $\beta$ -hydride elimination 210, 294  
 $\beta$ -hydride elimination yields 227  
 hydride Ir(III) complex 397  
 hydride Rh(III) intermediate 351  
 hydride Ru(II) species 467  
 hydroacetoxylation of alkynes 351  
 hydroacylation of ketones 353  
 hydroacylations 469  
 hydroalkoxylation of allenes 610  
 hydroamination of allenes 610  
 hydroamination reaction 270  
 hydroborations 471  
 hydroborylations 547  
 hydrocarboxylations 470, 548  
 hydrocylation of alkynes 349  
 hydrodefluorination of fluoroarenes 467  
 hydrogenation of alkenes 346  
 hydrogenation of carbon dioxide 353  
 hydrogenation of ketones 352  
 hydrogen-bonded six-membered ring type intermediate 608  
 $\beta$ -hydrogen elimination 78, 88, 268  
 hydrosilylation 547  
 hydrosilylation of ketones 431  
 hydrothiolation of alkynes 351  
 hydrotris(pyrazolyl)borate (Tp<sub>x</sub>) 580  
 hydroxymethanolate anion 473  
 hypervalence silicon intermediate 432
- i*
- imines 5, 393, 430  
 imine type 3,4-dihydroquinoline 396  
 iminium intermediate 601  
 iminoiodinanes 577  
 imino pyrrolone 213
- indolyl gold intermediate 603  
 inert C(sp<sup>3</sup>)—H bonds 500  
 inner-sphere oxidative addition 235  
 insertion reaction 78  
 in-situ generated benzoic acid 471  
 integral equation formalism PCM (IEF-PCM) 33  
 intermolecular hydrogen transfer 156  
 intermolecular olefin metathesis 482  
 intramolecular C—C bond formation 267  
 intramolecular [2+2] cycloaddition 484  
 intramolecular diene metathesis 484  
 intramolecular nucleophilic 5-exo-attack 536  
 intramolecular phenylsulfane oxidative addition 198  
 intramolecular radical type reduction 75  
 intrinsic reaction coordinate (IRC) 260  
 Ir-catalyzed aminations  
 alcohols 405–407  
 arenes 407  
 Ir-catalyzed borylations  
 alkanes 402–403  
 arenes 403–405  
 Ir-catalyzed C—C bond coupling reactions 407  
 Ir-catalyzed hydroamination 397  
 Ir-catalyzed hydroarylations 397–399  
 Ir-catalyzed hydrogenations  
 alkenes 388–391  
 carbonyl compounds 391–393  
 imines 393–396  
 quinolines 396–397  
 Ir-catalyzed hydrosilylation 399–401  
 Ir-C(aryl) bond 398  
 Ir(PHOX) complex 389  
 Ir(III) dihydride complex 389  
 Ir-mediated dihydrogenation 387  
 Ir(III)–nitrene complex 407  
 iron-catalyzed Kumada type coupling reaction 438  
 iron-mediated oxidative coupling 441  
 iron-mediated oxidative *ortho*-hydroxylation of benzoic acid 423

- iron(V)-oxo complex 420  
 iron-oxo species 420  
 Ir-(PHOX)-mediated imine hydrogenation 394  
 Ir(III) trihydride complex 396  
 isocyanatoalkane 502  
 isocyanide 231  
 isocyanide insertion 213  
 isodensity PCM (I-PCM) 33  
 isomerization of alkynes 599  
 isonicotinamide 213  
 isonitrile 213  
 isopropoxy Ru(II) intermediate 460  
 isoquinoline product 507
- k**  
 ketone  $\alpha$ -alkylation reaction 334  
 kinetic isotope effect (KIE) 332  
 Knölker's type iron(0) complex 430, 432, 434  
 Kumada coupling 7, 438
- l**  
 $\beta$ -lactams 344  
 Lewis acid 597  
     additives 142  
     property, of Pt 257  
 ligand-free reaction condition 232  
 linear combination of atomic orbitals (LCAO) theory 21  
 lithium silylphenyl methanolate intermediate 192  
 local-density approximation (LDA) 24  
 local spin density approximation (LSDA) 24
- m**  
 Möbius aromaticity 476  
 manganese 499  
 Markovnikov type adduct 470  
 maximum electron correlation energy 31  
 metalation-deprotonation mechanism 529  
 metal-( $\eta^2$ -silane) interactions 53
- metal-involved intramolecular Alder-ene type reaction 268  
 metallacarbene complexes 82  
 metallacyclobutane intermediate 102, 103, 539, 541  
 metallacyclopentatriene intermediate 476  
 metal-organic bond 84  
 metal-organic cooperative catalysis 334  
 metal-silicon double bond 583  
 metathesis-insertion type Ir(III)oendash Ir(V) catalytic cycle B 390  
 metathesis type C—H bond cleavage 421  
 methanediol 435, 511  
 methanol-assisted H—H bond cleavage 509  
 methanol assisted 1,3-hydrogen transfer 611  
 methanol-coordinated iron(I) complex 421  
 methoxide cationic Ru(II) complex 473  
 methoxy Cu(I)  $\sigma$ -complex 527  
 methoxyethanolate 392  
 methoxy Mn(I) intermediate 509  
 methylene pyridine intermediate 542  
 methylene pyridinide moiety 467  
 methylene-Ru(II) species 484  
 methyl ferric(III) hydroxide intermediate 421  
 8-methylquinolines 337  
 Mg-Fe(-2) species 438  
 minima-energy cross-point (MECP) 68, 75  
 Mizoroki-Heck reaction 79, 87  
 Mn(IV) azide species 501  
 Mn-catalyzed C—H activation-alkylation 503  
 Mn-catalyzed ligand-assisted hydrogenation 508  
 Mn(I)-hydride species 509  
 Mn(IV) hydroxide 500  
 Mn-mediated C—H activations  
     concerted metalation-deprotonation 505–507  
     electrophilic deprotonation 503–504

- Mn-mediated C—H activations (*contd.*)  
 σ-complex assisted metathesis  
   504–505
- Mn-mediated dehydrogenation  
   alcohol dehydrogenation 510–511  
   dehydrogenative coupling 511–512
- Mn-mediated hydrogenations  
   carbonates 508–509  
   carbon dioxide 507–508
- Mn-mediated oxidation of alkanes  
   C—H azidations 501  
   C—H halogenations 501  
   C—H hydroxylations 500–501  
   C—H isocyanations 501–502  
   general mechanism 500  
   modified Chalk-Harrod pathway 398  
   modified Ullmann reaction 519  
   molecular mechanics (MM) force fields  
     27  
   molecular vinylcyclopropane substrate  
     167
- Möller-Plesset perturbation theory 22,  
 23, 39
- monodentate phosphine 147
- monomeric diamino ferrous species 438
- mononuclear Cu(I) acetate complex 535
- muconic acid 426
- n**
- N amidation 580
- naphthaldehyde 601
- N*-aryl-α-diazoamides 569
- N*-bromosuccinimide (NBS) 62, 340
- Negishi coupling 7, 186, 188, 189
- neutral aryl Mn(I) intermediate 504
- neutral/cationic iron(IV)-oxo complex  
   423
- neutral four-membered-ring ruthenacycle  
   464
- neutral gold carbene 613
- neutral Ir(III) hydride complex 394
- neutral Ir(III) trihydride complex 396
- neutral vinyl ferrous species 432
- N—H bond cleavage/formation 392
- NHC-oxazole ligands 390
- N*-hetero carbene IMes<sup>Me</sup> 345
- N-heterocyclic carbene 148, 186
- Ni(0)—carbene catalyzed intramolecular  
 (5+2) cycloadditions of enynes  
   161
- Ni-catalysis, theoretical study of  
   Ni-mediated C—C bond cleavage  
     C=C double bond activation  
       152–153  
     C—C single bond activation  
       151–152
- Ni-mediated C—halogen bond cleavage  
   133  
   by β-halide elimination 137–139  
   concerted oxidative addition of  
     C—Halogen bond 133–135, 137  
   nucleophilic substitution 139  
   radical type substitution, of  
     C—halogen bond 135–137
- Ni-mediated C—H bond activation  
   128
- Ni-mediated aldehyde C—H  
 activation 132–133
- Ni-mediated arene C—H activation  
   128–132
- Ni-mediated C—N bond cleavage  
   148–150
- Ni-mediated C—O bond activation  
   140  
   ester C—O bond activation  
     142–148  
   ether C—O bond activation  
     140–143
- Ni-mediated unsaturated bond  
 activation 153  
 electrophilic addition 156–158  
 nucleophilic addition 159, 160  
 oxidative cyclization 153–155  
 unsaturated compounds insertion  
   157–159
- Ni-catalyzed Negishi type cross-coupling  
 reactions 135, 136, 138
- Ni-catalyzed olefin hydroarylation 129
- nickel catalyst 143
- nickel hydride 159
- Ni-mediated α-aryl elimination 91

Ni-mediated concerted metalation-deprotonation type C—H bond activation 128

Ni-mediated cyclization 160

Ni-mediated cycloadditions 161–164

Ni-mediated ring extensions 166–168

Ni-mediated ring substitutions 163–166

Ni-mediated ring substitutions 164

nine-membered Rhoda(III)cycle 369

*N*-iodosuccinimide (NIS) 340

nitrene 83, 576

nitrene insertion into C—H bonds 360

nitrene insertions 544

nitrenoids 577

nitrogen-involved nucleophiles 602

nonheme cationic ferric(III)–hydroperoxo complex 423

nonheme iron complexes 423

non-redox catalytic cycles 271

non-redox mechanism 304

norbornadiene derivatives 330

*N*-oxide-directed CMD-type C—H bond cleavage 335

*N*-oxide-directed electrophilic deprotonation 10

*N*-oxide moiety 335

Noyori-type catalysis 392

*N*-phenoxyacetamides 339

*N*-propargyl hydrazine 586

nuclear-nuclear repulsion energy 20

nucleophiles 4

nucleophilic addition of alkenes 607–608

nucleophilic attack by amines 582–583

nucleophilic attack by arenes 606–607

nucleophilic attack by carbonyl groups 573

nucleophilic attack by nitrogen-involved nucleophiles 602

nucleophilic attack by oxygen involved nucleophiles 599

nucleophilic attack by unsaturated bonds 580

nucleophilic attack onto alkynes 535

nucleophilic carbon 196

nucleophilic hydride 397

nucleophilic substitution 57

**O**

*o*-alkynylbenzaldehyde derivatives 265

O-atom transfer 335

*o*-azidophenyl methanimine 544

octene-coordinated Ru-carbene complex 482

olefin aziridination 580

olefin-coordinated hydride Ru(II) species 469

olefin-coordinated Ru(II) intermediate 471

olefin coordinated silyl Ir(III) complex 401

olefin insertion 291

olefin metathesis 102

orbital interaction 184

organic azides 313, 339, 577

organometallic chemistry

- computational methods in
- accuracy, of DFT methods 40–41
- basis set 29, 30, 36–37
- computational programs 37–40
- correlation-consistent basis sets 31–32
- density function 34–36
- DFT methods 23–29, 34
- diffuse functions 31
- entropy effect 41
- exact solvation effect 41
- excited state 41
- history of, quantum chemistry 19–21
- mechanism 37
- polarization functions 31
- pople's basis set 30
- post-HF methods 21–23
- pseudo potential basis sets 32
- reaction mechanism 41–42
- coupling reactions 4
- electronegativity, of carbon 4
- history 3, 6–8
- mechanism of, transition metal catalysis 8–12
- synthetic chemistry 3

organometallic chemistry, elementary reactions 51, 52  
 coordination bond 52–55  
 dissociation 55–57  
 ligand exchange 57–59  
 oxidative addition 59, 60  
   concerted 60–63  
   oxidative cyclization 68–70  
   radical type addition 67, 69  
   substitution-type oxidative addition 62–64, 66–68  
 organosilicon compounds 190  
 ortho-alkenylation of arenes 461  
*ortho*-alkenylation 293  
*ortho*-alkylation of arenes 460  
*ortho*-alkynylbenzamides 536  
*ortho*-aminated products 339  
*ortho*-phenylpyridine 292  
 outer-sphere  $\sigma$ -bond metathesis 432  
 oxazinedione 165  
 oxazinoquinolinium-coordinated Rh(I) complex 335  
 oxazolidinone-coordinated Cu(I) complex 75  
 oxidative addition, of C—H bond 259  
 oxidative catechol ring cleavage 425  
 oxidative cyclization 68  
 oxidative Heck-type coupling 335  
 oxime esters 329  
 oxime ethers 329  
 oxiranyl propargylic esters 265  
 $\beta$ -oxoalkyl silver character 572  
 oxonium intermediate 606, 610  
 oxonium ylide intermediate 574  
 oxooxazolidinyl directed arenes and acrylates 462  
 oxygen involved nucleophiles 599

## **p**

*para*-boralated benzene 405  
 Paason–Khand reactions 227, 298  
 Paason–Khand type (2+2+1)  
   cycloadditions 367, 478  
 (Xantphos)Pd(CH<sub>2</sub>NBn<sub>2</sub>)<sup>+</sup> 10  
 Pd-catalysis, theoretical study

Pd-catalyzed cross-coupling reactions 182, 183  
 Heck-Mizokori reaction 192–196  
 Hiyama coupling 190–193  
 Negishi coupling 186–189  
 Stille coupling 189–191  
 Suzuki-Miyaura cross-coupling reaction 183–186  
 Pd-mediated activation, of unsaturated molecules 224  
   alkene activation 225, 227  
   alkyne activation 225–227  
   carbene activation 231–233  
   CO activation 229–231  
   enyne activation 226–228  
   imine activation 229  
   isocyanide activation 231  
 Pd-mediated C—H activation reactions 204, 206  
   C—H bond activation, electrophilic deprotonation 219–221  
   C—H bond activation, oxidative addition 223–224  
   C—H bond activation,  $\sigma$ -complex-assisted metathesis 221–223  
   chelation-assisted *meta*-C(aryl)—H activation 214–216  
   chelation-free C(sp<sup>2</sup>)—H activation 208–211  
   chelation-free C(sp<sup>3</sup>)—H activation 206–208  
   coordinative chelation-assisted C(sp<sup>3</sup>)—H activation 216, 217  
   coordinative chelation-assisted *ortho*-C(aryl)—H activation 210–212  
   covalent chelation-assisted C(sp<sup>3</sup>)—H activation 216–219  
   covalent chelation-assisted *ortho*-C(aryl)—H activation 212–214  
 Pd-mediated C—hetero bond formation 196  
   C—B bond formation 196–197  
   C—I bond formation 200–201

- C—S bond formation 197–200  
 C—Si bond formation 201–204  
 Pd-catalyzed C—H activation, of methane  
     207  
 Pd-catalyzed cross-coupling reactions 60  
 Pd-catalyzed intramolecular carbene  
     insertion 223  
 Pd-catalyzed Negishi coupling 187  
 Pd-catalyzed olefin hydroarylation  
     reaction 225  
 Pd-C bond 181  
 pentafluoropyridine 468  
 Perdew–Burke–Ernzerh (PBE) 26  
 pericyclic process 51  
 peroxy-bridged iron(IV) complex 425  
 peroxy iron(IV) complex 425  
 phenol-coordinated Cu(I) species 522  
 phenyl acetate 143  
 phenylacetylene-coordinated Ru(II)  
     species 471  
 phenyl benzoxazole product 528  
 phenylboronate 148  
 phenylboronic acid 144  
 phenyl bromide 210  
 phenylethane product 429  
 phenylethynyl Ru(II) species 471  
 phenyl iron(IV) intermediate 438  
 2-phenylpyridine 310, 339, 452  
 phenyl pyrrole product 520  
 phenylpyrrolidine 357  
 phenyl-Rh(III) intermediate 331  
 phenyl Ru(II) intermediate 460  
 phenyl(trifluoromethyl)sulfane 135  
 1-phenylvinyl benzoate product 471  
 phenyl yrazole product 521  
 phosphate-assisted intermolecular C—H  
     bond activation 145  
 phosphine-coordinated Ir-catalyzed  
     tetrahydrogenation 396  
 phosphine-coordinated Ru(II)—carbene  
     species 484  
 phosphine ligand 105, 201  
 phosphinite 452  
 phosphinooxazoline ligand 389  
 pincer amino Mn(I) species 511  
 pincer bis[2-(diisopropylphosphino)-  
     ethyl]amine (HPNP) ligand  
     coordinated Ru(II)—hydride  
     complex 472  
 pincer ligand coordinated Ru(II) catalyst  
     466  
 PNP type pincer ligand 427  
 PNP type pincer ligand-coordinated  
     iron(II) species 437  
 porphyrin-coordinated Mn(III) species  
     500  
 porphyrin-coordinated Mn(V) species  
     500, 501  
 post-HF linear variational method 22  
 primary alkyl iodide 63  
 product-coordinated Mn(I) species 504  
 propargylamine 587  
 propargyl ester reactant 507  
 propargylic acetoxyl enyne 617  
 propenaminium 236  
 protocatechuate 3,4-dioxygenase 425  
 proton accepter 221, 434  
 proton concerted electron transfer (PCET)  
     290  
 pseudo potential basis sets 32  
 Pt-catalysis, theoretical study  
     Pt-catalyzed alkene activation 270  
         cyclopropenes, isomerization of  
             273–274  
         hydroamination, of alkenes  
             270–273  
     Pt-catalyzed alkyne activation,  
         mechanism 264  
         cyclopropanation 266–267  
         nucleophilic additions 264–266  
         oxidative cycloaddition 268–270  
     Pt-catalyzed C—H activation,  
         mechanism of 258  
         carbene insertion, into C—H bonds  
             261–264  
         electrophilic dehydrogenation 259,  
             260  
         oxidative addition, of C—H bond  
             259

- Pt-catalyzed cycloisomerization, of enynes 266
- Pt-mediated alkene functionalizations 270
- Pt-mediated C—H activations 258
- pyrazolyl Cu(III) intermediate 521
- pyridinone 165
- pyridotriazole 359
- pyridyl Ru vinylidene 464
- pyrocatechol 425
- pyrrolyl 520
- q**
- quantum chemical computation 10
- quantum chemistry composite methods 22
- quinoline-N-oxide 329, 335
- quinolines 396
- r**
- radical-substitution-type reductive elimination 74–76
- radical type substitution, of C—halogen bond 135–138
- radical type trifluoromethylations 525–527
- rearrangement of carbenes 542, 543
- redox-neutral cross-coupling 4, 329, 330, 457, 524, 527, 533
- redox-neutral process reaction 232, 233
- reductive elimination 70, 198
- α-elimination 90, 91
- β-elimination 86–91
- bimetallic reductive elimination 75–78
- concerted reductive elimination 71–73
- eliminative reduction 77–78
- insertion 78
- conjugative insertion 83–85
- 1,1-insertion 80–84
- 1,2-insertion 79–81
- outer-sphere insertion 84–86
- radical-substitution-type reductive elimination 74–76
- substitution-type reductive elimination 73–75
- reductive elimination yields 135, 139, 140, 150, 161, 166, 167, 183, 188, 196, 219, 222, 224, 228, 232, 300, 342, 345, 351, 478, 519
- regioselectivity 140, 145–147, 184, 185, 214, 216, 334, 470, 573, 598
- relative enthalpy 53, 54, 316, 431
- relative free energy 55, 62, 83, 140, 144–146, 185–186, 214, 220, 261, 311, 343, 349, 369, 397, 456, 463, 521, 524, 543, 554, 571, 578–579, 581–583, 599
- Rh(acac)<sub>3</sub> 332
- Rh-assisted intramolecular cope-type 3,3-sigmatropic migration 367
- Rh-catalyzed addition reactions of carbonyl compounds
- hydroacylation of ketones 353–355
- hydrogenation of carbon dioxide 353–354
- hydrogenation of ketones 352–353
- Rh-catalyzed alkene functionalizations
- alkene diboration 347–349
- hydrogenation of alkenes 346–347
- Rh-catalyzed alkenylation of C—H bond 335–338
- Rh-catalyzed alkyne functionalizations
- alkyne hydroamination 349–351
- hydroacetoxylation of alkynes 351
- hydrocylation of alkynes 349–350
- hydrothiolation of alkynes 351
- Rh-catalyzed amination of C—H bond 338–340
- Rh-catalyzed arylation of C—H bond 330–332
- Rh-catalyzed carbene transformations
- arylation of carbenes 357–358
- carbene insertion into C—H bonds 354–357
- cyclopropanation of carbenes 358–359
- cyclopropenation of carbenes 359
- Rh(I)-catalyzed carbonyl insertion reaction 344

- Rh-catalyzed C—C bond activations and transformations  
 β-carbon elimination 343  
 carbon-cyano bond activation 342–343  
 strain-driven oxidative addition 341
- Rh-catalyzed C—H bond alkylation 332, 335
- Rh-catalyzed cycloadditions  
 (3+2) cycloadditions 365–367  
 (5+2) cycloadditions 367–369  
 (5+2+1) cycloadditions 369  
 Pauson–Khand type (2+2+1) cycloadditions 367
- Rh-catalyzed halogenation of C—H bond 340–341
- Rh(III)-catalyzed intermolecular arene C—H bond amination 339
- Rh-catalyzed nitrene transformations  
 aziridination of nitrenes 361–362  
 nitrene insertion into C—H bonds 360–361
- Rh(III)-catalyzed ortho-bromination/iodination of arenes 340
- Rh(III)-catalyzed oxidative C—H/C—H cross-coupling 332, 333
- Rh(III)-catalyzed oxidative Heck-type coupling reaction 335, 337
- Rh-catalyzed redox-neutral cross-coupling reaction 329
- Rh-C(alkenyl) bond 368
- Rh-C(vinyl) bond 11, 349
- [Rh(cod)<sub>2</sub>Cl]<sub>2</sub>-catalyzed C2-selective arylation of indoles 330
- Rh(III)-hydride intermediate 337
- Rh(III)-hydride species 334
- Rh-mediated C-hetero bond activations  
 C—N bond activation 344–345  
 C—O bond activation 345–346
- Rh(V)-nitrene complex 340
- Rh-nitrene complexes 338, 339
- rhoda(III)cycle 342, 344, 349, 354, 363, 367–369
- ring-expanded [3.3.0]bicyclic product 615
- ring-opened Ru-vinylcarbene complex 484  
 [Ru(NHC)(CO)(H<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>] 468
- Ru-carbene complex 104, 451, 482
- Ru(II)-carbene complex 482, 484
- Ru carbennoid moiety 464
- Ru(II) carboxylate species 460
- Ru-catalyzed acetamide-directed C—H bond alkenylation 454
- Ru-catalyzed cycloadditions  
 click (3+2) cyclization 478  
 (2+2+2) cycloadditions 475–478  
 Pauson–Khand type (2+2+1) cycloadditions 478–479
- Ru-catalyzed hydrofunctionalization  
 hydroacylations 469–470  
 hydroborations 471–472  
 hydrocarboxylation 470–471
- Ru-catalyzed hydrogenations  
 alkenes 464–465  
 carbonyls 465–466  
 esters 466–467  
 hydrodefluorination of fluoroarenes 467–468
- Ru(II) hydride intermediate 460
- Ru-involved hetero-seven-membered cyclic intermediate 461
- Ru-mediated C—H bond activation  
 C—H bond arylation 456–460  
 mechanism 452–456  
 ortho-alkenylation of arenes 461–464  
 ortho-alkylation of arenes 460
- Ru-mediated dehydrogenations  
 alcohols 473, 476  
 formaldehyde 473, 477  
 formic acid 474, 477
- Ru-mediated metathesis  
 alkyne metathesis 484–485  
 intermolecular olefin metathesis 482–484  
 intramolecular diene metathesis 484  
 ruthenabicyclo[3.2.0]heptatriene complex 478
- ruthenacyclobutane intermediate 482, 484

- ruthenacyclobutenone intermediate 478  
 ruthenacyclopentatriene intermediate 476  
 ruthenatriazabicyclo[3.1.0]hexadiene intermediate 479  
 ruthenium dibenzoate species 460  
 Ru(II) vinylidene complex 471
- S**
- $\sigma^*$  antibonding orbital of Si—H 53  
 $\sigma$ -bonding orbital 53  
 $\sigma$ -bond metathesis 223  
 $\sigma$ -CAM-type C—H cleavage 454  
 Schrödinger equation 19, 22  
 $\sigma$ -complex-assisted metathesis ( $\sigma$ -CAM) 452, 504  
 $\sigma$  covalent bond 86  
 selectfluor 63  
 self-consistent IPCM (SCI-PCM) 33  
 seven-membered Rhoda(III)cycle 342, 369  
 sextet iron(IV) species 423  
 silacyclobutanes 204, 205  
 silacyclopropanation 583  
 silacycloprenation 583  
 siliranes 583  
 silver–carbene formation 568–572  
 silver catalysis 567  
 silver–nitrene complex formation 577–579  
 silver–silylene complexes 583  
 silyl 99, 157, 203, 204, 273, 397, 400, 401, 404, 432, 547, 548  
 silylated cyclopropene coordination 273  
 silyl-benzene 403  
 silylenes 583  
 silyl ferrous species 432  
 silyl Ir(III) complex 401  
 silyltriflate-coordinated hydride Ir(III) complex 400  
 single-electron transfer (SET) 289, 290, 297, 313, 451, 518–520, 525  
 single electron transfer involving pathway 519
- single-electron transfer redox process 518  
 singlet cyclohexadienone coordinated Cu(I) species 532  
 singlet Fischer-type Ag-nitrene complex 582  
 singlet Rh-nitrene complex 362  
 six-membered 1,3-acetonium intermediate 608  
 six-membered amino-Rh(III) species 340  
 six-membered rhoda(III)cycle 349  
 six-membered Ru(IV) vinylidene intermediate 479  
 six-membered vinyl silver intermediate 586  
 Slater-type orbital (STO) 21, 29, 30  
 small hindrance bipyridine 403  
 small to medium-sized cyclic organic compounds 362  
 $S_N2$  type substitution transition state 64  
 soft and carbophilic Lewis acid 597  
 solvent coordinated cationic Ru(II) species 472  
 solvent-coordinated hydride Ru(II) species 465  
 solvent effect 33–34, 39  
 split-valence basis sets 30, 31  
 stepwise 1,3-proton transfer 613  
 Stevens type [3,3]-sigmatropic rearrangement 603  
 Stille coupling 7, 189–191, 235  
 Stille–Kosugi–Migita coupling 183  
 Stille type cross-coupling reaction 235  
 strain-driven oxidative addition 341–342  
 styrene 131, 159, 195, 292, 314, 358, 398, 427, 461, 462, 482, 543, 544, 551, 552  
 styrene-coordinated Ru(II)–carbene complex 482  
 1,4-substituted triazoles 479  
 1,5-substituted triazoles 479  
 substitution-type oxidative addition 62–68, 76

substitution-type reductive elimination 73–76  
 substrate-coordinated cationic Cp<sup>\*</sup>Rh(III) acetate complex 335  
 sulfonate-assisted 1,3-proton transfer 606  
 sulfoxide 129, 194, 197–199, 347, 602  
 sulfoximide Cu(II) complex 75  
 Suzuki coupling 7  
 Suzuki–Miyaura coupling 183–186  
 Suzuki–Miyaura cross-coupling reaction 72, 183, 184, 186  
 Suzuki–Miyaura type cross-coupling product 148

**t**

terminal alkynes 261, 294, 470, 471, 479, 524, 526, 533–537, 539, 585, 587  
 terminal vinyl Ru(II) intermediate 471  
 tert-butoxide lithium 201  
 tetracarboxylate ligand 330  
 (*E*)-tetradec-7-ene product 482  
 tetradentate ligated Rh(III) catalyst 360  
 tetrafluoropyridine-coordinated Ru(II) fluoride species 468  
 tetrahydroquinolines 396  
 thermodynamically stable linear isomer 611  
 thiolate Rh(I) species 351  
 thiovinyl hydride Rh(III) species 351  
 Togni's reagent 67, 68, 525–527  
 toluenesulfonate 599  
 total free energy 53, 193  
 tracial Noyori-type hydrogenation 392  
 transfer hydrogenation 388, 391, 393, 405  
 transition metal catalysis 5–13  
 transition-metal-catalyzed hydroformylation, of olefins 272  
 transmetallation process 92, 96, 99, 144, 181  
 concerted ring type 92–98  
 electrophilic substitution 98–100  
 metathesis 100–106

alkyne metathesis 106  
 σ-bond metathesis 100–105  
 stepwise transmetallation 99, 101  
 trans to cis isomerization 58  
 trans-vinyl gold complexes 614  
 triazole-coordinated Ru(II) complex 479  
 triazolyl-copper species 534  
 triazolyl Ru(II) species 479  
 tricyclohexylphosphine (PCy<sub>3</sub>) 184  
 trifluoromethanolate alkyl Pd(IV) complex 78  
 trifluoromethylations through cross-coupling 524–525  
 trifluoromethylations through oxidative coupling 524, 526  
 trifluoromethyl Cu(I) intermediate 524  
 trifluoromethyl silane 524  
 trigonal bipyramidal geometry 54  
 triplet Ag-nitrene complexes 577  
 triplet copper-nitrene complex 543, 545  
 triplet dimeric Cu(II) intermediate 539  
 triplet Mn(V)-oxo complex 500  
 triplet nitrene 577, 580  
 triple zeta (TZ) 30  
 truncated Ir(I)–(PHOX) catalyst 389

**u**

unordinary Mg–Fe complex 438  
 α,β-unsaturated carbonyl compounds 292

**v**

van der Waals density functionals (vdW-DFs) 27  
 vinyl acetate 462  
 vinyl compounds 585  
 vinyl cyclopropane-coordinated Rh(I) species 365  
 vinyl cyclopropanes 167, 363, 365  
 vinylcyclopropanes 368  
 vinyl digold complex 617  
 vinyl gold intermediate 599  
 vinylideneamido Mn(I) intermediate 511  
 vinylidene Pt species 262

- vinylideneruthenium intermediate 463  
vinylideneruthenium species 463  
vinyl Ir(I) complex 401  
vinyl Ir(III) complex 401  
vinyl Mn(I) intermediate 507  
vinyloxysulfonium intermediate 602  
vinyl Rh(III)-hydride complex 334  
vinyl Ru(II) intermediate 462, 463
- W**  
water-assisted 1,2-proton shift 618  
water molecule 149, 225, 303, 423, 511, 574
- weak Brøsted base assisted nucleophilic attack 599
- Z**  
*Z*-configuration ethylenes 400  
*Z*-enisoindolinones 536  
zwitterionic agostic intermediate 467  
zwitterionic gold anion 613  
zwitterionic iminium rhodate intermediate 357  
zwitterionic intermediate 432, 576











