

Subject Index

A

- Absorption spectra, mercury
 photosensitization, 199
- Acetaldehyde, 329
- Acetic acid
 formation during catalysis, 330
 rate of dihydrogen evolution, 345
- Acetic anhydride, commercial process,
 377–378
- Acetyl complexes, 328–330
- Acetyl iodide
 activation, 389–390
 reductive elimination, 330
- Acetyl ligand, conversion to acetaldehyde,
 329
- Acetylenes
 C–H oxidative addition, 189
 cycloisomerizations and macrocyclizations,
 470–472
- N*-Acetylglycine, synthesis, 236–237*t*
- Acid–base properties, soluble ruthenium
 hydrocarbonylation catalysts, 321
- Acrylate dimerization studies, 484–487
- Activation energy
 calculation, 89
 hydroformylation process, 90
 olefin insertion, 90
- Acyl complexes
 decarbonylation process, 85
 oxidative addition to form dihydride, 87
- Acyl intermediates, interaction with
 incoming H₂ molecule, 86–87
- Agglomeration, Pt particles, 546, 548*f*
- Agostic interaction, β -hydrogen and vacant
 metal center, 80
- Alcoholysis, silsesquioxanes in toluene
 reaction solution, 559–560*f*
- Aldehydes
 formation, 85
 hydrogen-induced elimination, 85–89
 product selectivity at increased CO partial
 pressures, 412–417
 reaction with CoH(CO)₄, 303–305
 reduction
 in the presence of CO, 373–374
 mechanism, 374–375
 photoreduction, 193
 supposed intermediates, 297
 selectivity
 phosphite ester ligands, 414–415*t*
 PPh₃-to-catalyst ratio, 357
 synthesis, 185–189
- Aldehydic intermediate, amination of
 ethylene glycol, 439
- Alkanes
 cross-dimerization, 201
 dehydrogenation, 190–194
 dimerization, mercury photosensitization,
 203–204
 functionalization, product volatility, 199
 oxidative addition, catalytic organic
 synthesis, 182
 oxidative addition process, 211
 product ratio, 206–207
 productive functionalization, 183
 reactivity, 181
 selectivity, 203
 types of activation, 222–223
- Alkenamides, intramolecular
 amidocarbonylation, 283–289
- Alkenes
 formed in alkane dimerization, 203
 substrate reactivity pattern, 204–205
- Alkenyl chain-growth reaction, tests of
 mechanism, 571–573
- Alkyl
 migratory insertion into Co–CO bond,
 81–85
 1,2 shift reaction, 83
- Alkyl complexes
 isolation, 370
 linear isomers, 371
- Alkyl sarcosinate, synthesis, 238–239*f*
- Alkyldiarylphosphine complexes, steric
 crowding, 398
- Alkyldiphenylphosphine–rhodium
 complexes, rhodium hydroformylation
 catalysts, 398
- Alkylidenes, production, 599–601*f*
- Allyl oxides and aryl oxides, deoxygenation
 by CO, 515–528
- Allyl systems, transition metal controlled
 behavior, 476
- Allylation mechanism, proposed, 533–535
- Allylic alcohol derivatives, hydroboration,
 167–175
- Allylic alkylation, macrocyclization, 464–469
- Allylic amine derivatives, hydroboration,
 175*t*
- Allylic and homoallylic alcohols, asymmetric
 hydrogenation, 131–133
- Allyloxycarbonyl complexes, β -allyl
 migration–decarboxylation, 520
- Allylpalladium carboxylate, identification,
 538
- Allylpalladium complexes, synthesis,
 537–538
- Aluminum, Ziegler polymerization catalysts,
 575–590

- Aluminum halides, soluble promoters, 310–314
- Aluminum hydroxide, insoluble promoter, 313–314
- Amido acids
from functionalized olefins, 246*t*
from other olefins, 244*t*
synthesis, 235–236, 239–240*f*
- Amidocarbonylation
advantages, 244–246
N-alkenylamides, 278–283
applications, 242–243
catalyst, reaction scope, and industrial application, 235–247
rhodium-catalyzed sequential double carbonylation, 279–280
- Amination of ethylene glycol
selectivity control, 433–442
selectivity of ruthenium–phosphine catalyst, 439*t*
- Annulation method, hydrocarbonylation, 283
- Anti* selectivity, hydroborations, 174
- Antifragmentation, polyphosphine ligand, 351
- Antiphase polarization
multiplet effect, 49
³¹P resonances, 67, 68*f*
- Argon, dimerization reaction of rhodium(I) phosphine intermediates, 108
- Aryloxycarbonyls, orthometallation, 521
- Asymmetric catalytic synthesis of C–C bonds, hydroformylation of olefins, 267
- Asymmetric hydrogenation
catalytic, 123–142
catalyzed by cationic complexes, 135*t*
olefinic substrates, 129–133
stereoselectivities, 137*t*
- Asymmetric induction, formation of γ -lactones, 459
- Asymmetric synthesis, synthetic and industrial chemistry, 141
- Autocatalytic behavior, Co₂(CO)₈
concentration, 301, 303
- Autoclaves, CIR reactors, 4
- Autoxidation
cyclohexanone, 100
feedback, 96
halogen-free, 102–103
hydrocarbon, 95
oscillating behavior, 95–96
- B**
- Back bonding, coordination of an alkene to a transition metal, 170*f*
- Back donation, stability, 409
- Back migration, methyl, 83
- Base-catalyzed deuterium exchange, kinetics, 338
- Benzaldehyde
O₂ oxidation, 96–99
oscillations in redox potential, 97*f*
stages in oxidation reaction, 97
- Benzene, carbonylation, 185–189
- Benzoyl radicals, mechanism of benzaldehyde oxidation, 98–99
- Benzyne intermediate, deoxygenation of phenols, 522–525
- Bidentate phosphines, accelerating effect on hydroformylation, 368
- Bifunctional catalyst species, cobalt, 273
- Bimetallic catalyst
selectivity, 362
steric and electronic factors, 363
- Bimetallic hydroformylation
chemistry, 355–364
proposed mechanism, 360, 361*f*
selectivity, 361–362
- Bimetallic rhodium–eLTP complexes, synthesis, 354
- Bimetallic system
catalytic activity, 357
comparison to commercial rhodium catalyst system, 357
- Binap, structure, 124
- Binap–Ru(II) complexes
structural parameters, 126*t*
synthesis and structures, 124–129
- Binding energy, Hg*, 201
- Binucleating ligand system
polyphosphine, 351
tetraphosphine, 352–353
- Bis(aryloxycarbonyls), formation, 522
- Bis(triarylphosphine) ligands, synthesis, 138–140
- Bond angles, hyperconjugation, 578
- Bond energies
C–H oxidative addition, 213
ligand steric requirements, 258
- Bond homolysis, low-energy pathway, 257
- Bond length, titanium–methylene, 587
- Bond strength
catalyst systems containing dicarbonylhydridorhodium complex, 404
electronic and steric properties of the phosphorus ligand, 402*f*
organic compounds with functional groups, 207
- Branched-chain acyls, hydrosilation reactions, 493
- Bridging ligands, drawbacks, 351
- Bromide ion in benzaldehyde oxidation reaction, 96–98
- 1-Butanol, carbonylation–homologation, 310–321
- Butene isomerization, triphenyl phosphite, 414

C

- ¹³C NMR studies
 carbonylhydridorhodium complexes, 408
 equilibrium at two CO pressures, 408*f*
Cage structure, polysilsesquioxanes, 554–555
Carbene addition, aromatic ring, 450
Carbene insertion, substitution by an ether
 or ester oxygen, 457
Carbenoid intermediates, generation, 482
Carbenoid reactions
 active intermediates, 444
 insertion, conformational preferences, 451
Carbocyclic rings, regioselectivity, 467–468
Carbon–carbon bonds, formation reactions, 567
Carbon dioxide, reduction of methanol, 507–513
Carbon–hydrogen activation
 Rh(I) photocatalysis, 110*f*
 trimethylphosphine complex, 108
Carbon–hydrogen bond(s), activation in
 alkanes and other organic molecules, 211–220
Carbon–hydrogen bond functionalization,
 mercury-photosensitized, 197–210
Carbon–hydrogen insertion reactions
 catalytic intramolecular, 443–461
 cyclopentanones, 445–448
 diastereoselectivity, 446
 lactams, 448–455
 lactones, 455–458
 regioselectivity, 446
Carbon–hydrogen oxidative addition
 homogeneous catalysis, 182
 preferred active species, 186
Carbon monoxide
 activation by metalloradicals, 249–259
 monomeric tetramesitylrhodium(II)
 complex, 254
 one-electron activation, 250
 problems with spectroscopy, 25
 rhodium complexes, 25–28
Carbon–oxygen bonds
 activation, 515–528
 bond energy, 516
 methods for cleavage, 516
Carbonyl
 decay kinetics, 115
 dissociation energies, 78
 dissociation from HCo(CO)₄, 77–78
 energy of dissociation from CoH(CO)₄, 305
 energy profile for insertion into Co–CH₃
 bond, 84*f*
 formation of basic magnesium iodides, 317
 π-acceptor ligands, 87–88
 reversible migratory insertion into
 alkyl–metal bond, 112
 Carbonyl complexes
 infrared spectroscopic data, 299*f*,*t*
 spectral data, 300*t*
 Carbonyl compounds, reduction, 193*t*
 Carbonyl dissociation, carbonyl-free
 rhodium hydrides, 406
 Carbonyl exchange
 radical mechanism, 38
 rate constants, 37–39
 temperature stability under pressure, 38
 Carbonyl ligands, catalyst function, 399–400
 Carbonyl photodissociation
 laser flash photolysis, 113
 methane matrix, 114
 Carbonyl stretching frequencies, rhodium
 and cobalt complexes, 27–28
 Carbonylation
 benzene, 185–189
 C–H bond of hydrocarbons, 185–189
 catalyzed by transition metal complexes,
 277–296
 diversion to reductive carbonylation, 324
 lithium-promoted, 384–390
 mechanism, 325*f*
 methanol, mechanism, 382*f*
 methyl acetate
 kinetics, 378–380*f*, 385–389
 rhodium-catalyzed, 377–394
 methyl acetate and methanol, parameters,
 393*t*
 methyl acetate to acetic anhydride,
 proposed mechanism, 392*f*
 reduction of CH₃OH by Co(CO)₄[−], 509
 sodium-promoted, 390
 temperature dependence, 381
 yields of secondary reactions of aldehydes,
 188*t*
 Carbonylation–homologation, 1-butanol and
 ethanol, 310–321
 Carbonylmanganese compounds,
 unsaturated mononuclear, 112–117
 Carbonyl(methoxycarbonyl)cobalts,
 formation and thermal decomposition,
 510
 Carbonylrhodium, intensity of IR bands, 12
 Carbonylruthenium species
 CO stretching frequencies, 315*f*
 interaction of clusters with metal oxide
 surfaces, 313
 oxides as heterogeneous promoters,
 309–321
 Carbonyltriruthenium clusters
 infrared difference spectrum of transients,
 111*f*
 laser flash photolysis, 110–112
 reactions, 113*f*
 reactivities, 109–112
 Carboxylic acids
 asymmetric hydrogenation, 130–131
 role in catalytic reaction, 375

- Catalysis
 electrogenerated species
 cobalt, 272–273
 platinum, 262–266
 rhodium, 266–272
 high-velocity, 529–540
 selectivity of aldehydes, 412–417
 triethylphosphine ligand concentrations, 410–412
- Catalyst(s)
 composition, hydroformylation, 368–369*t*
 detection by CIR technique, 12
 function, carbonyl ligands, 399–400
 performance, difficulties, 324
 real-time observation, 17
 regeneration, proposed mechanism, 360
- Catalyst combinations, activity–selectivity behavior, 28
- Catalyst complexes
 NMR studies, 404–408
 synthesis, 403–404
- Catalyst precursor, palladium, 532–533
- Catalytic activity
 correlations with spectroscopic data, 29
 hydrosilation, 497–499
 nature of phosphine ligands, 190
- Catalytic cycle
 cytochrome P-450, 155*f*
 lithium-catalyzed conversion of acetyl iodide to methyl iodide, 391–393
 reaction steps, 332–334
 schematic, 333*f*
 silylformylation, 293
 turnovers, 202
- Catalytic reactions
 carbonylation, CO atmosphere, 330
 dimerization of methyl acrylate, synthesis of fine chemicals, 479–480
 hydroformylation reactions, 368–370
 model systems, 565–574
 synthesis of polymethylsilsequioxanes, 553–563
 transformations of diazoamides
 lactam products, 453
 manipulation of product distribution, 453
- Catalytically active intermediates, identification, 20
- Cation reactivity, water–gas shift, 340
- Cationic promoters
 carbonylation, 390
 catalyst activity, 384–385
 comparison of rates, 385*t*
- Ceramic crystal
 CIR reactors, 3
 fragility, 5–6
- Ceramic products, apparent compositions, 562
- Ceramic yield, polysilazane oligomers, 560
- Chaotic dynamics, O₂ oxidations, 95–104
- Chelate ring, puckering, 148–150
- Chelating ligands, diols, 439
- Chelation control, hydrocarbons, 277–296
- Chemical shifts
 function of donor or polar character of solvent, 587
 interaction of Cp₂Ti(Cl)CH₂SiMe₃ with Me_nAlCl_{3–n}, 584*t*
 ion-pair formation, 586
 solvent dependence, 583*t*
 solvent polarity, 581
- Chemical trapping, structure identification, 576–577
- Chiral allylic alcohol(s), *anti* selectivity, 174
- Chiral allylic alcohol derivatives, hydroboration, 167–175
- Chirality
 LTTP system, 352
 optical isomers, 123
- Chloride, suppression of Pt deposition, 226
- Chloroplatinum salts, hydroxylation of water-soluble organic compounds, 221–232
- Chromatographic procedures, siloxyalkyl complexes, 492
- Chromium, metal–metal bonds between octahedral ions, 595
- Chromium catalysts
 active oxidation state, 591, 598–599
 cyclic voltammogram and molecular structure, 600*f*
 homogeneous, 591–602
 molar magnetic susceptibility and effective magnetic moment, 594*f*
 molecular structures, 596*f*
 presumed active site, 593*f*
 synthesis, 592–595
 unanswered questions, 592
- Chromium–chromium pairs, cooperative interactions between neighboring metal atoms, 593
- CIR, *See* Cylindrical internal-reflectance reactors
- Classic process chemistry, new science and new applications, 479–489
- Cluster catalysts, advantages and problems, 350
- Cluster species, hydrocarbonylation conditions, 321
- Cobalt
 bifunctional catalyst species, 273
 converting internal alkenes to terminal hydroformylation products, 367
 electrogenerated catalyst species, 272–273
 rac- and *meso*-M₂(LTTP) binuclear systems, 354

- Cobalt—*Continued*
reduction of methanol, 507–513
role in oxidation of cyclohexanone, 100–102
uncontracted triple- ζ Slater-type orbitals, basis set for shells, 76
Cobalt–carbon bond, cleavage, 491
Cobalt catalysis, reductive carbonylation of methanol, 323
Cobalt-catalyzed hydroformylation
mechanism, 75, 76f
olefins, reaction mechanism, 13–15
product formation, 86
Cobalt(II) porphyrin, reactions with CO, 252–253
Colloids
active catalyst precursors, 543
intermediacy in hydrosilation, 541–549
Competitive reactions
different substrates, 59
epoxidation
olefin pairs, 157–161
picnic-basket porphyrins, 158f
reactivity pattern, 161
results, 160t
¹H NMR spectra of hydrogenation, 59f
polarization decay, 60
trapping, transient CO species, 116f
Conjugate addition–cyclization reactions, 485–486t
Construction material, high-pressure IR cells, 21
Coordination compound, intermediate within the catalytic cycle, 8
Coordination geometries, M–M bonded dimer systems, 353–355
Coordination strength, σ donation and π back donation, 395
Coordinatively unsaturated species, temperature dependence, 406
Cooxidant, coupling reactions of ligands, 572
Copper
catalyst behavior on repeated use, 484
catalytic activity, 483–484
Grignard reaction, 486
tandem conjugate addition–cyclization, 486
Coupling constant, spin density, 254
Covalent bonding, carbonyl carbon rehybridization, 253
Cross-dimerization, cyclohexane and trioxane, 202
Crystal(s)
CIR reactors, 3
fragility, 5–6
polishing, 6
Crystallization, CIR reactor analyses, 12–13
Cubane reaction, oxidative addition at a tertiary C–H bond, 217
Cyclizations, transition metal catalysts, 463–478
Cyclohexane
carbonyl decay kinetics, 115f
reactivities of rhodium(I) phosphine intermediates, 108–109
wavelength of irradiation, 189
Cyclohexanone
kinetic model, 101–102
O₂ oxidation, 99–103
oscillations in the absence of Br[–] ion, 102
redox potential
dissolved O₂ concentrations, 99–100
visible absorbance, 100f
ring-opening reactions, 101f
stages in oxidation reaction, 100
Cycloisomerizations
acetylenes, 470–472
p-allylpalladium intermediates, 476–477
diynes, mechanistic rationale, 471f
special class of macrocyclizations, 466–467
vinyl epoxides, 473
Cyclooctane, dehydrogenation, 190
Cyclopentanones
asymmetric hydrogenation, 138–140
carbon–hydrogen insertion reactions, 445–448
synthesis, 484–487
Cyclopropanation studies, 482–484
Cyclopropane, yield from olefins and ethyl diazoacetate, 484t
Cylindrical internal-reflectance reactors (CIR)
advantages and disadvantages, 5–6
cross-sectional diagram, 5f
experimental procedure, 6–7
photograph, 4f
reaction-monitoring techniques, 3–18
Cytochrome P-450
catalytic cycle, 154–155
metalloporphyrin models, 156f
- D**
- d-electron vacancies, platinum colloids, 545
DANTE pulse sequence, magnetization transfer technique, 42
Decomposition, prolonged
hydroformylation, 372–373
Dehydroamino acids, hydrogenation, 144
Dehydrodimer, saturated functionalized substrates, 205
Dehydrogenation
alkanes, 190–194
driving force, 190
rate-determining step, 191
Density functional method, application to organometallic substances, 77

- Deoxygenation
allyloxy groups, 519–521
phenols
benzyne intermediate, 522–525
by CO, 515–528
experimental section, 516–519
metallolactone intermediate, 525–526
Deuterium exchange, catalysis by bases, 338
Deuterium isotope effect, water–gas shift
reaction, 340, 345
Deuterium oxide, inverse kinetic isotope
effect in reaction of deuterated formate,
342
Dialkyl fumarate, reaction with $\text{CoH}(\text{CO})_4$,
301–303
Diaryl esters, 525–526
Diastereofacial selectivities, hydroborations,
173
Diastereoselectivity
carbon–hydrogen insertion reactions, 446
catalytic conditions, 136
frontier orbitals, 169
substrate-controlled, 167–175
Diazo compounds
catalytic intramolecular carbon–hydrogen
insertion reactions, 443–463
reactions with rhodium acetate, 444–445
Diazoesters, synthesis of lactones, 455
Diethyl ether, carbonylation and
homologation reactions, 319–321
Diethyl fumarate, effect of initial $\text{Co}_2(\text{CO})_8$
concentration, 203*f,t*
Diethylene glycol, reactions with
morpholine and dimethylamine, 440*t*
Dihydride, stability, 87
Dihydrogen
characterization of complexes, 24
heterolytic cleavage, 337–338
proposed intermediate ion, 338–339
rhodium complexes, 25–28
Dihydrogen evolution
acetic acid, 345*f*
effect of sodium formate concentration,
341*f*
formic acid, 343*f*
triethylene glycol solutions, 344*f*
water–gas shift reaction, 340–343
Dihydrosilanes, reaction with manganese
acyl compounds, 503
Dimer(s), triphenylphosphine–
carbonylrhodium, 404
Dimer catalysts, advantages and problems,
350
Dimerization
activation energy, 255
mercury photosensitization, 197
reversibility, 255
Dimetal ketone, steric requirements of
tetramesitylporphyrin, 254
Dimethyl carbonate, formation, 512
Di- μ -methylenedirrhodium complexes,
organic chemistry of dinuclear
complexes, 565
Diols, chelating ligands, 439
Diphosphine ligands, hydroformylation of
methanol to acetaldehyde, 326
Dipolar relaxation
para-enriched H_2 , 72
PHIP decay, 52
polarization and signal enhancement,
67–72
Disproportionation
alkane dimerization, 203–204
dimerizations of light alcohols, 204
selectivity for alkanes, 206
Dissociation
CO ligand from $\text{HCo}(\text{CO})_4$, 77–78
enthalpy profile, 256*f*
expected C–C bond energy, 255
Donor–acceptor characteristics, phosphine
ligand, 409
Dynamic nuclear polarization, transition
metal hydrides, 47–48
- E**
- Early metal catalysts, heteroatom
substituents of functionalized olefins,
599
Electrochemical synthesis
cobalt species, 273
platinum species, 262–266
Electrochemistry, selective catalysts, 273
Electrode potential, production of different
oxidation states, 261
Electron-donor properties, rhodium
hydroformylation catalysts, 398–399
Electronic and steric control, catalytic
intramolecular carbon–hydrogen
insertion reactions, 443–463
Electronic effects, rhodium
hydroformylation catalysts, 395–418
Electronic structure, resonance hybrid, 255
Electrophilic addition, rate-limiting step in
carbenoid reactions, 444
Electroreduction, organometallic complex,
262
eLTTP, *See* Ethyl-substituted linear
tetratertiary phosphine
Enamides, asymmetric hydrogenation,
129–130
Enantiomeric excesses, hydroformylation of
styrene, 267
Enantioselective processes
catalysis, transition metal compounds,
143–152
conjugate addition, palladium-catalyzed
allylation-type reactions, 529–530
definition, 164

- Enantioselective processes—*Continued*
 hydroborations, feasibility, 165–167*t*
 hydrogenation
 formic acid, 145–147
 prochiral substrates, 131
 optical induction, 146
Enantioselectivity
 chloride anion, 268
 EPHOS ligand, 272
Endoergonic reactions, photosensitization, 198
Energy barrier, C–H oxidative addition, 213
Enzyme, substrate specificity, 153
Equilibrium
 cis and *trans* complexes, 43
 Cp_2TiMeCl and AlCl_3 , 585
Ethanol
 carbonylation–homologation, 310–321
 direct conversion to ethylene glycol, 221–232
 oxidation, 223–224, 226–228
 oxidation mechanisms
 nature of active Pt complex, 228–230
 selectivity in C–H attack, 230
 reaction sequence and rate of oxidation, 229*f*
Ethyl-substituted linear tetratertiary phosphine (eLTTP)
 bimetallic complexes, 353–355
 bimetallic hydroformylation chemistry, 355–364
 diastereomer structure, 353*f*
 future research, 363–364
Ethylene, catalyst system for polymerization, 587
Ethylene glycol
 affinity for Ru(II) center, 440
 selectivity control in amination, 433–442
Ethylene polymerization
 chromium catalysts, 595–598
 rate, 595–597
 Ziegler mechanism, 576–577
Exchange broadening of resonances, magnetization-transfer techniques, 37
Exciplex
 formation between Hg^* and substrate, 201
 mercury photosensitization, 198
Excitation sequence, frequency domain profile, 42
- F**
- Fischer–Tropsch products, labeled vinyl, 571–572
Fischer–Tropsch reactions
 model, 567–570
 new mechanism, 565
 over rhodium, products, 571*t*
 procedures to test mechanism, 570
- Flash kinetic studies, liquefied noble gases, 217–218
Flash photolysis
 picosecond laser excitation, 109
 reactive organometallic intermediates, 105–119
 short wavelength, 109–110
Flow cells, advantages and disadvantages, 23–24
Fluorinated hydrodimers, functionalization, 205
Formic acid
 enantioselective hydrogenation, 145–147
 rate of dihydrogen evolution, 345
Four-centered transition state, cleavage of dihydrogen, 338
Fragmentation
 carbonyltriruthenium clusters, 109–110
 dimer and cluster systems, 350
Free-radical mechanism, manganese acyl-catalyzed hydrosilation, 501
Frontier orbitals, diastereoselectivities, 169
Frozen-core approximation method, electrons in lower energy shells, 76
Functional groups
 C–H oxidative addition, 216
 H atom reaction, 205
 made from alkenes by H atom chemistry, 206*f*
Functionalization reactions
 homogeneous catalysis, 181–196
 incompatibility with thermodynamics or catalyst stability, 221–222
Functionalized organic molecules, conversion of alkane oxidative addition products, 215
Functionalized product, mercury photosensitization, 201–203
- G**
- Geometry, steric hindrance, 362
Geraniol, asymmetric hydrogenation, 132*t*
Glass NMR tubes, limited pressure range, 34
Glutamic acid, synthesis, 245*f*
Glycol(s), ligands, 439–441
Glycol aminations, control of selectivity, 434
Grignard reagent, copper-catalyzed reaction, 486
- H**
- Half neutralization potential, determination, 398
Haloalkanes, chemical shift, 588
Halocarbonylruthenium derivatives, reactivity on MgO surface, 317
Hemiamidals, formation, 283

- Heteroatom-substituted species
effectiveness as substrate, 201
mercury photosensitization, 200–201
- Heterobimetallic homogeneous catalysts,
effects on rate and selectivity of
hydroformylation, 356
- Heterobimetallic species, catalytic activity,
364
- Heterogeneous activation, suppression of
oxidation, 226
- Heterogeneous catalyzed reactions,
monitoring techniques, 7
- High-pressure cylindrical internal-
reflectance reactors, reaction-
monitoring techniques, 3–18
- High-pressure-high-temperature reactions,
in situ measurement, 19–20
- High-pressure IR cells, types, 22–23
- High-pressure IR spectroscopy (HPIR)
cell designs, 21–24
homogeneously catalyzed reactions, 20
speed and high sensitivity, 20–24
- High-pressure NMR spectroscopy
CO dissociation from $\text{HCo}(\text{CO})_4$, 39
techniques, 34–36
- High-velocity catalysis, palladium, 529–540
- Homobimetallic cooperativity
catalytic process, 349
hydroformylation catalyst system, 364
rate enhancement, 358
- Homogeneous catalysis
bimetallic hydroformylation, 349–366
functionalization of hydrocarbons, 181–196
in situ spectroscopic studies, 19–31
nuclear magnetic resonance spectroscopy,
33–46
observation of reactive intermediates,
105–106
organometallic intermediates, 105–119
synthesis of fine chemicals, 479
- Homogeneous catalysts, electrochemical vs.
chemical synthesis, 261–275
- Homogeneous metal-catalyzed reactions,
monitoring techniques, 7–8
- Homolysis of bonded dimers, reorganization
energies, 257t
- Homolytic dissociation energies, bond
energy, 258
- HPIR. *See* High-pressure IR spectroscopy
- Hydride
conversion to acyl complexes, 334
ion stabilization, 339, 346
1,2 shift reaction, 83
- Hydride bridge, ruthenium compound
crystal structure, 426
- Hydride ligand, dynamic site exchange, 427f
- Hydride resonance, catalytic hydrogenation
conditions, 61
- Hydridoalkyl complexes, alkene synthesis,
190
- Hydridosiloxanes
catalytic redistribution by transition
metals, 558
cocatalyst, 562
- Hydroboration
absolute and relative stereochemistry, 163
allylic amine derivatives, 175t
catalyzed and uncatalyzed, 163–177
chiral allylic alcohol derivatives, 167–175
enantioselectivity, 164–167t
phenyl-substituted allylic alcohols, 174t
prochiral alkenes, 264f
- Hydrocarbon(s)
functionalization by homogeneous
catalysis, 181–196
hydroxylation by platinum salts, 221–232
- Hydrocarbon autooxidation, oscillatory
behavior, 95
- Hydrocarbon glasses, photolysis product,
112
- Hydrocarbon transformation, solvent
stability, 191
- Hydrocarbonylation
N-allylacetamide, 278t
amide-directed, 283–289
N-benzoyl-2-hydroxy-4-methylpyrrolidine,
282f
1-butanol, 312t
chelation control, 277–296
ethanol
different promoter systems, 318f, 319f
oxides as promoters, 316t
products formed, 313f
soluble or insoluble aluminum
promoters, 311t
methyl acetate in acetic acid solution,
320t
N-(2-methyl-2-propenyl)benzamide, 281t
reaction products, 314
- Hydrocyanation studies, 480–482
- Hydrodeoxygenation of phenols, catalytic
methods, 516
- Hyrodimerization products, 205
- Hydroformylation
activity and selectivity of eLTTP, 363
1-alkenes catalyzed by rhodium
complexes, 279
asymmetric, styrene with rhodium
catalysts, 168t, 269t, 270t
1-butene
activity and selectivity of
triethylphosphite–rhodium catalyst,
415t
products and byproducts, 410f
rhodium–phosphine catalysts, 405f
triethylphosphine ligand concentration,
411t
catalyzed by trinuclear ruthenium cluster
anion, 422f
decomposition studies, 372–373

Hydroformylation—Continued

electron-rich phosphine–rhodium catalyst systems, 362*f*

Heck–Breslow mechanism, 355*f*

1-heptene, 369*t*

1-hexene on rhodium catalysts, 267*t*

isolation of intermediates, 370–372

linear internal and branched terminal olefins, 396–397

mechanism, 400–403

olefins catalyzed by anionic ruthenium clusters, influence of organophosphines, 419–429

platinum phosphinito complexes, 367–376

proposed mechanism, 287*f*

rhodium-based catalysts, 356

silicon version, 289

solvent concentration, 265*t*

tricarbonylhydridocobalt-based, 75–93

vs. hydrocarbonylation, 428*t*

Hydroformylation and amidocarbonylation

cocatalyst effect, 242*t*

diolefins, 240

functionalized olefins, 240, 242

product selectivity, 241*t*

reaction scope, 243*t*

simple olefins, 240

Hydroformylation catalysis

electronic and steric effects on precursors, 402–403

1-hexene, 356*t*

homogeneous bimetallic, 349–366

producing aldehydes or acetals, 262

Rh₂(eLTTP)-type bimetallic complexes, 356

Hydroformylation cocatalysts,

organophosphines, 421–429

Hydroformylation cycle, alternative

mechanism, 88–89

Hydroformylation rates, temperature dependence, 406**Hydrogen, rate of formation of acetic anhydride,** 381–384**Hydrogen activation, soluble metal oxide complexes,** 337–348**Hydrogen atoms**

compounds made from saturated substrates, 207*f*

reactions, 204–205

Hydrogen gas, quenching of Hg*, 204**Hydrogenation**

acrylic acid derivatives, 131

asymmetric hydrogenation catalyst, 62

dehydroamino acids, 144

mechanism for catalyst systems, 63–64

organic substrates, 339

oxidative addition reactions,

parahydrogen-induced polarization

and polarization transfer, 47–74

pairwise hydrogen transfer, 61

Hydrogenation—Continued

parahydrogen-induced polarization, 62

phenylacetylene, 64

platinum phosphinito complexes, 367–376

rates with varying catalysts, 374*t*

ruthenium complexes, 60–64

stereoselective, 123–142

styrene-d₈, 57*f*, 70

Hydrogenolysis

catalytic reactions with rhodium, 334

M–C bond, 86

possible mechanisms, 334–335

Hydrosilanes

influence of structure, 290

reactions with 1-hexyne, 291*t*

Hydrosilation

active catalyst precursors, 543

catalyst activity, 497–499

catalyzed by colloids, 541–549

changing the acyl ligand, 493

¹H NMR spectra, 498*f*, 500*f*

intramolecular noncatalyzed, 504*f*

iron acyl compounds

drawbacks as synthetic procedure, 494

mechanism, 494–495*f*

isolable α-siloxyalkyl derivatives, 492

manganese acyls, 496–505

organotransition metal acyl complexes, 491–506

Hydrosilylation

1-hexyne with triethylsilane, 289

ketones, 144–145

Hyperconjugation

σ-bond

bond shortening, 581

crystalline state, 587

developing positive charge, 588

Ti–C bond, shortening, 575

Hyperfine coupling constant, spin density, 252–253**I****Ibuprofen,** 480–481**In situ catalyst, optically active,** 143**In situ methods of measurement,**

advantages, 19–20

In situ spectroscopic studies, homogeneous catalysis, 19–31**Indenyl systems, oxidative**

addition–migratory insertion processes, 215

INEPT pulse sequence, generation of spectra, 68**Inhibition of fragmentation, dimer and cluster systems,** 350**Initial gas uptake rate**

iodide concentration, 332*f*

rhodium concentration, 331*f*

- Insertion reactions
 conformational influence on regioselectivities, 458
 relative reactivities, 457
- Intermediary position, 419–420
- Intermolecular condensation, regioselectivity, 471
- Intermolecular hydride transfer, cobalt-catalyzed hydroformylation, 355–356
- Intermolecular hydroacylation, sapphire NMR tube, 39
- Internal alkenes, conversion to linear products, 367
- Intramolecular amidocarbonylation
 3-butenamide, 286*t*
 new annulation method in organic synthesis, 283
 4-pentenamide, 288*t*
 rhodium catalysts, 285
- Intramolecular carbon–hydrogen insertion reactions, regio- and stereocontrol, 443–461
- Intramolecular hydride transfer
 closed-mode conformation, 360
 rate enhancement, 358
 single-atom bridge in eLTTP, 361
- Inverse deuterium kinetic isotope effect, water–gas shift, 345
- Inversion transfer
 exchange broadening of resonances, 37
 magnetization transfer technique, 41–42
 quantitative analysis, 43
- Iodide
 concentration, reaction rate variation, 331
 improvements in cobalt-based catalysts, 324
- Iodine, carbonylation reaction rate, 391, 392*f*
- Iodine-promoted rhodium catalyst system, development, 378–393
- Iodocarbonyl complexes of rhodium, water–gas shift reaction, 384
- Iodocarbonylruthenium catalysts, oxides as heterogeneous promoters, 309–321
- Iridium
 photochemical phosphine complexes, 197
 selectivity of triphenylphosphine complexes, 434
- Iridium–phosphine complexes, PHIP and polarization transfer, 64–70
- Iridium(II) porphyrin, reactions with CO, 258
- Iron
 electrochemical oxidation process, 268–269
 regioselectivity, 265
- Iron acyls, catalyzed hydrosilylation, 492–496
- Irradiation, C–H bonds, 212
- Isomerization activity, platinum phosphinito catalysts, 370
- Isonitriles, C–H oxidative addition, 189
- Isoselectivity
 1-alkenes, 279
 amide-directed chelation control, 279
- Isotopic labeling, ¹³C in Fischer–Tropsch reaction, 571–572
- Isotopic tracer studies, reductive carbonylation products, 332
- K**
- Karstedt catalyst
 formation of colloidal platinum, 547
 near-edge spectra, 545*f*
 platinum colloids, 542–543
 structure, 543*f*
- Ketones
 asymmetric hydrogenation, 133–138
 hydrosilylation, 144–145
- Kinetic studies, selectivity-determining step, 330
- Krypton, inert solvent for irradiation of rhodium dicarbonyl complex, 218
- L**
- Labeling studies, iodide involvement in reductive carbonylation, 331–332
- Lactams
 carbon–hydrogen insertion reactions, 448–455
 catalytic transformations of diazoamides, 453
 synthesis, 449
- Lactones
 carbon–hydrogen insertion reactions, 455–458
 strategy for macrolactonization, 465
- Lanthanum oxide, catalytic activity, 317–319
- Lead(II) oxide, water–gas shift, 347
- Ligand(s)
 effect on reaction rate, 242*t*
 rapid ring rotation, 40
- Ligand environment, reductive carbonylation, 324
- Ligand exchange, saturation-transfer experiments, 40
- Linear aldehydes, selectivity of rhodium hydroformylation catalysts, 396–397
- Linear isomer, formation, 371
- Linear tetratertiary phosphine (LTTP)
 chiral tetratertiary phosphine at the two internal phosphorus atoms, 352
 synthetic route, 352
- Liquid-phase hydrocarbonylation reactions, oxides as heterogeneous promoters, 309–321

- Lithium
 carbonylation reaction spectra, 389
 methyl acetate and acetyl iodide
 activation, 389–390
 tandem conjugate addition–cyclization, 486
- Lithium effect
 carbonylation catalytic cycle, 391–393
 potential mechanism, 391
- Lithium iodide
 complex role as promoter, 384–385
 rate-determining factors, 385
 rate of carbonylation, 386*f*
- M**
- M–M bonds, value as reaction sites, 350
- Macrocycle, C–C bond formation, 473
- Macrocycle applications, natural products, 472–476
- Macrocyclization
 acetylenes, 470–472
 allylic alkylation, 464–469
- Macrolide syntheses, exaltolide, 464
- Magnesium oxide, promoters, 314–317
- Magnetization transfer
 advantages and disadvantages, 41
 DANTE pulse sequence, 42
 examples, 43–45
 exchange broadening of resonances, 37
 inversion transfer, 41–42
 slow exchange in discrete equilibria, 41–45
 temperature range, 41
- Manganese acyl catalysts
 activity, 499*t*, 501*t*
 hydrosilation, 491
- Manganese acyl-catalyzed hydrosilation, 496–505
- Manganese picnic-basket porphyrin catalysts, 153–162
- Mechanistic studies, model substrate, 224
- Mercury photosensitization
 alkane dimerization, 203–204
 C–H bond functionalization, 197–210
 dimerization, 197
 formation of H atoms, 204
 functionalized product, 201–203
 heteroatom-substituted species, 200–201
 mechanism, 198–199
 quenching by H₂ gas, 204
 reaction rate, 206
 vapor-phase selectivity, 199–200
- Meso* and *racemic* diastereomers, eLTP, 353
- Metal carbenes
 C–H insertion, 451
 comparative stability, 453
- Metal carbonyl stretching frequencies, rhodium and cobalt complexes, 27–28
- Metal catalyst, role in oxidative addition, 64–67
- Metal clusters, intermediary position, 419–420*f*
- Metal formyl complexes, decarbonylation reaction, 83
- Metal hydride bond, olefin insertion, 400
- Metal oxide complexes, hydrogen activation, 337–348
- Metal oxide systems, water–gas shift, 347
- Metal phosphine catalysts, selectivity, 203
- Metallolactone(s)
 formation of phenol groups, 526–527
 formation pathways, 515
- Metallolactone complex
 deoxygenation of phenols, 525–526
 source of benzyne, 523–524
 structure, 523*f*
- Metalloradicals
 activation, structural and spin density changes, 252
 activation of CO, 249–259
 definition, 250
- Metathesis catalysts, chromium(III) alkylidenes, 599
- Methanol
 Co₂(CO)₈ solutions, reactions, 511*f*
 reduction by tetracarbonylcobalt anion assisted by carbon dioxide and cobalt cation, 507–513
 rhodium-catalyzed reductive carbonylation, 323–336
- Methyl acetate
 activation, 390
 homologation to ethyl acetate, 321
 rhodium-catalyzed carbonylation, 377–394
- Methyl acrylate, catalytic tail-to-tail dimerization, 485
- Methyl iodide, rate dependence at two Li levels, 388*f*
- Methyl migration, 83, 113
- Methylenes, coupling with vinyls in dirhodium complexes, 573
- Methyltitanocene chloride, structure, 580–583
- Methyltitanocenium cation
 experimental details of formation, 579–580
 soluble Ziegler catalyst system, 579
- Migratory insertion
 activation barrier, 83
 alkyl into Co–CO bond, 81–85
 functionalized molecules, 215
 solvent effects, 113
 transient complexes, 333–334
- Mixed-metal catalyst
 Co–Rh, 279, 289–294
 synergistic effects, 279–280, 290

Model systems

- bimetallic ligand systems, 360–361
- catalytic reactions, 565–574
- monometallic ligand analogs, 357–360

Monohydrosilanes, reactions with

- manganese benzoyl, 503–505

Multimetallic systems, advantages, 349–350

Multiplet polarizations

- ^1H NMR spectrum, 54, 55f
- PHIP due to hydrides, 65
- reversibility of H_2 oxidative addition, 65

N

Naproxen, 480–481

Near-edge region, platinum colloids, 544–546f

Nerol, asymmetric hydrogenation, 132t

Net polarization

- correlation diagram, 56f
- ^1H NMR spectrum, 54, 55f
- signal enhancements relative to multiplet polarization, 58
- spin-lattice relaxation time, 58

Neutralization, protonic species, 315–317

Nickel

- catalytic tetraphenylborate chemistry, 536–537
- degradation in HCN, 481

Nickel-catalyzed hydrocyanation

- ethylene, magnetization transfer, 45
- synthesis of fine chemicals, 479–480

Niobium pentoxide, Brønsted acidity strength, 319

Nitrogen heterocycles, syntheses through amide-directed hydrocarbonylations, 278–289

Noble gas, liquefied solvents, 216–220

Nonaxial symmetry, Rh(II) porphyrin, 254

Norbornadiene

- homo-Diels–Alder reactions, 147–150
- reaction with 1-hexyne, 148–149
- reaction with phenylacetylene, 148

Norbornene, ring-opening metathesis polymerization, 591

Nuclear magnetic resonance spectroscopy

- ^{13}C technique to trace exchange of free CO, 37
- high-pressure techniques, 34–36
- homogeneous catalysis, 20, 33–46
- quantitative data, 21
- structural information, 20–21

Nuclear Overhauser effect, enhanced NMR signals, 69–70

Nucleophiles, macrolide construction, 468

Nucleophilic dihydrogen activation

- processes, synthesis gas
- transformations, 339

Nucleophilic oxygen centers

- dihydrogen, 348
- metal oxide systems, 338

O

O–H bond activation, generation of intermediates, 507–508

 ^{18}O labeling, benzaldehyde oxidation, 97 O_2 oxidation

- benzaldehyde, 96–99
- cyclohexanone, 99–103
- oscillations and chaos, 95–104
- toluene, 103
- p-xylene, 103

OFCIR, *See* Optical-fiber coupled reactors

Olefin(s)

- complexation, 77
- ethyl complex, 79
- organophosphines, influence on hydroformylation, 419–429
- shape selectivity, 153–162

Olefin hydroformylation

- reaction, 262
- regio- and enantioselectivity, 261–275
- supposed intermediates, 297

Olefin hydrogenation, ruthenium catalyst, 60

Olefin insertion

- Co–H bond, 79–81
- energy profile, 80f
- magnetization transfer, 43
- metal hydride bond, 400
- relative orientation of ethylene and hydride, 79

Olefin polymerization

- comparison to metathesis catalysts, 599
- homogeneous chromium catalysts, 591–602

Oligomerization

- mild cooxidizing site, 572
- rate of hydrocyanation, 481

Oligonuclear species with intermetallic

- bonds, intermediary position, 419–420f

Optical-fiber coupled reactors

- construction, 6
- reaction-monitoring techniques, 3–18
- spectra of cobalt-catalyzed hydroformylation, 16f

Optical induction

- chemical yield, 148
- reaction with acetylenes, 147

Optical isomers, chirality, 123

Optical yields, catalyst systems, 165

Optically active compounds, preparation, 143

Organoaluminum Lewis acids, active sites in soluble Ziegler polymerization catalysts, 575–590

Organoiron ligand reactions, 494

- Organometallic analog of formyl radical coupling, 255
- Organometallic intermediates
homogeneous catalysis, 105–119
spectral properties, 108
- Organometallic reactions on clusters,
Fischer–Tropsch polymerization, 567
- Organophosphines
catalytic activity and selectivity, 421
hydroformylation cocatalysts, 421–429
hydroformylation of olefins, 419–429
- Organotin coupling reactions
palladium-catalyzed reactions, 536*t*
soluble chloride anion source, 537
tetraphenylborate chemistry, 537
- Organotransition metal complexes
C–H activation, 211–220
catalyzed and noncatalyzed hydrosilation, 491–506
- Orthometallation, aryloxy-carbonyls, 521
- Oscillating behavior, absence of Br[−], 102
- Oscillatory dynamics, O₂ oxidations, 95–104
- Oxidation
competition with H–D exchange, 224
ethanol, 223–224, 226–228
p-toluenesulfonic acid, 223–226
- Oxidative addition
activation energy, 88
catalytic activity, 186
characteristics, 212–213
energy profile, 89*f*
functionalized molecules, 215
intermolecular oxidative addition, 212
isomeric methyl complexes, 333
liquid xenon as inert solvent, 217
methane, methanol, and ethanol, 217
para-enriched hydrogen, 72
photochemical and thermal reaction mechanisms, 214–215
rate of direct conversion, 218–220
role of the metal catalyst, 64–67
unanswered questions, 214–215
- Oxidative addition–reductive elimination
equilibrate ortho- and parahydrogen, 65–66
equilibrium rate, 66
- Oxidative decomposition, mechanism, 566
- Oxides
hydrogenating activity, 321
liquid-phase hydrocarbonylation reactions, 309–321
- Oxo products, platinum phosphinito catalysts, 370
- Oxo reaction, *See* Hydroformylation
- P**
- ³¹P NMR studies
ligand exchange, 407*f*
trialkylphosphine complexes of rhodium, 406–408
- Palladium
access to macrocycles, 472
catalysis of neat methyl acrylate, 485–486
catalyst for ring formation, 463–478
catalyst precursor, 532–533
charge neutralization to facilitate ring formation, 464
cycloisomerization followed by reductive desulfonylation, 475
cycloisomerization of acetylenes, 471–472
high-velocity catalysis, 529–540
polyene macrolides, 475
transmetalation, 534
- Palladium-catalyzed reactions
carbonylation of aryl halides
difference spectrum, 11*f*
reaction mechanism, 9–10
steady-state in situ spectrum, 10*f*
conjugate addition reactions, overall chemistry, 531*t*
cyclizations, extension, 466
determination, 532–533
- Parahydrogen-induced polarization (PHIP)
ethane resonances, 53*f*
experimental observations, 50–54
homogeneous hydrogenation chemistry, 47–74
multiplet and net effect, 72
observation, 48–49
polarized resonances in hydride spectra, 65
reaction mechanism, 54
spin system due to H–D coupling, 52
Weitekamp proposal, 50
- Paramagnetic chromium alkyls, synthesis, characterization, and reactions with olefins, 591–602
- Partitioning of products, oxidation of ethanol, 228
- Pentacarbonyliron, water–gas shift catalyst, 340
- Pentacoordinate complexes, stability, 409
- Perfluorinated ion-exchange polymer
catalytic activity, 483–484
structure, 483
synthesis of fine chemicals, 479–480
- Periodic potentials, O₂ oxidation of toluene, 103
- PFIEP, *See* Perfluorinated ion-exchange polymer
- Phenol(s)
catalytic deoxygenation by CO, 515–528
regioselectivity of cyclization, 468
- Phenol deoxygenation
benzyne intermediate, 522–525
metallolactone intermediate, 525–526
- L-Phenylalanine, synthesis, 236–239*f*
- PHIP, *See* Parahydrogen-induced polarization
- Phosphido species, decomposition of triarylphosphine, 372–373

Phosphine(s)

- catalytic activity and selectivity for hydroformylation of olefins, 419–429
- selectivity control, 434–437

Phosphine complexes

- phosphine–rhodium complexes, selectivity for linear aldehydes, 396–397
- photocatalysts for benzene carbonylation, 107

Phosphine dissociation, equilibrium constant, 106

Phosphine ligands

- carbonylation of benzene, 186*t*
- catalyst stability, 357, 364
- catalytic effect, 186
- dehydrogenation of cyclooctane, 190*t*
- donor–acceptor characteristics, 409
- rac*- and *meso*-M₂(LTP) binuclear systems, 354
- selectivity, 357, 362, 438–439

Phosphine-modified rhodium-catalyzed hydroformylation of olefins

- reaction mechanism, 11–13
- steady-state in situ spectrum, 12*f*, 13*f*

Phosphinite group, equatorial position in pentacoordinate complex, 272

Phosphinous carboxylic acid anhydrides, formation, 373

Phosphorus, correlation of ligand bonding with catalyst activity and selectivity, 409*t*

Phosphorus ligands, rhodium complex hydroformylation catalysts, 399

Phosphorus–proton coupling, resonances, 67, 68*f*

Photochemical reactions, colored impurities, 202

Photoreactivity

- carbonylmetal clusters, 109
- reactive organometallic intermediates, 105–119

Photoreduction, aldehydes, 193

Photosensitization, catalytic mechanism, 198

 π back-donation, CO–Rh bond strength, 402

Picnic-basket porphyrins

- conformation, 155
- shape selectivity, 153–162
- substrate selectivity, 155
- system, 157*f*

Platinum

- catalytic hydroformylation, 367–376
- conversion of internal alkenes, 367–368
- crystallites, 546–548*f*
- deposition during reaction, 224–226
- effect of Cl[–] on oxidation reaction, 230
- electrochemical reduction of organometallic complexes, 261
- hydroformylation into linear aldehydes, 274
- orthometallation of aryloxy carbonyls, 521
- oxidation mechanism, 228–230

Platinum—*Continued*

- procedures for analysis of colloids, 542–543
- replacement with a cheaper oxidant, 230
- Platinum alkoxides, metathesis and catalytic reactions, 375
- Platinum colloids from catalyzed reactions, 545–546
- Platinum electrode
 - dissolved O₂ concentration
 - benzaldehyde, 98*f*
 - cyclohexanone, 99*f*
 - oxidation of *p*-xylene, 102*f*
- Platinum phosphinito complexes
 - hydroformylation and hydrogenation, 367–376
 - platinum–tin systems, comparison, 370
- Platinum salts, hydroxylation of hydrocarbons, 221–232
- Platinum–tin system, SnCl₂ cocatalyst, 262–266
- Polar aprotic solvents, accelerating effect on polymerization, 577
- Polarity of solvent, chemical shifts, 581
- Polarization
 - ¹³C NMR spectrum of hydrogenation product, 70–72
 - energy-level diagrams, 68, 69*f*
 - influence of magnetic field, 56
 - magnitude of enhancement, 66–67
- Polarization transfer
 - α -¹³C-ethylbenzene-d₈, 71
 - para-enriched H₂, 72
 - polarization and signal enhancement, 67–72
 - signal enhancement, 47
- Polyethylene
 - characterization, 598*t*
 - properties, 587
- Polymerization, ethylene with
 - trimethylsilylmethyltitanocene chloride and an aluminum chloride cocatalyst, 587
- Polymerization catalysis, chromium catalysts, 595–598
- Polymethylsilsequioxanes
 - catalytic synthesis, 553–563
 - ceramic compositions, 562*t*
 - chemical evolution during heating, 557*f*
 - dilution with toluene, 556
 - properties of thin films, 556
 - structure and applications, 554
- Polysilazane oligomers, thermogravimetric analysis, 561*f*
- Polysilazane polymerizations, 560–562
- (Porphyrin)/M(II) complexes, reactions with CO, 252–258
- Potassium, catalytic activity, 483–484
- Preceramic polymers, polysilazane oligomers, 560
- Pressure probe, studies of homogeneous catalysts, 34

Pressure stabilization, reactive species, 36–40
Process chemistry, new science and new applications, 479–489
Product distribution, function of ruthenium concentration, 327f
Product flash-off
 continuous hydroformylation processes, 414–417
 continuous hydroformylation unit, 416f
Promoters
 carbonylruthenium iodide systems, 310
 comparison of rates, 385t
 magnesium oxide, 314–317
 selectivities, change with time, 319
 soluble and insoluble aluminum compounds, 310–314
Propene- d_3 , proposed mechanism for formation, 566f
cis-2-Propenyl-1,3-dioxolanone reaction, stereospecificity, 539
Propylene carbonate, selectivities during styrene hydroformylation, 265
Propylene hydride
 ^1H NMR assignments, 44f
 magnetization transfer, 43–44
Proton source, water–gas shift, 344–345
Proton transfer, CH_3OH to $\text{Co}(\text{CO})_4^-$, 509
Protonation, intermediate monohydride species, 62
Puckering, chelate ring, 148–150
Pyrrole ^1H line broadening, temperature dependence, 255–256f

Q

Quaternization, resistance of diphosphine complexes, 329

R

Racemization, chloride anion, 268
Radical(s), reaction of alkanes with Hg^* , 208
Radical mechanism, carbonyl exchange, 38
Radicallike pathway in benzene, metalloformyl complex, 253
Rate constants, carbonyl exchange, 37–39
Reaction conditions, dependence on structures, 131
Reaction mechanism
 cobalt-catalyzed hydroformylation of olefins, 13–15
 palladium-catalyzed carbonylation of aryl halides, 9–10
 phosphine-modified rhodium-catalyzed hydroformylation of olefins, 11–13
 studies using CIR–FTIR reactors, 7
Reaction-monitoring techniques, OFCIR reactors, 16–17
Reaction order, method of initial rates, 330–332
Reaction parameters, variation, 8

Reaction rates, effect of ligand, 11
Reactive intermediates
 identification and characterization, 24–28
 oxidative addition, 213
Reactive species, pressure stabilization, 36–40
Reactivity patterns, metalloradicals with small molecules, 250
Reactor geometry, mercury photosensitization, 199–200
Reductive carbonylation
 ligand environment, 324
 methanol
 experimental procedure, 325–326
 rhodium-catalyzed reductive carbonylation, 323–336
 product distribution, 326t
Reductive elimination
 acetyl iodide, 324
 hydrogenolysis of Rh–carbon and formation of Rh(I)–hydride, 334
Regiocontrol
 bridging ligands of dirhodium(II) nucleus, 458
 electron-withdrawing groups, 447
Regioselectivity
 amide-directed chelation control, 279
 carbon–hydrogen insertion reactions, 446
 carbonylation of C–H bond, 187
 cycloisomerization, 467–468
 dehydrogenative silylation and vinylation of toluene, 194
 effective control, 456
 effects of phosphine ligands, 285
 functionalized reactions, 222–223
 1-heptanal with Pt–Sn system, 263
 1-hexene with platinum, 261
 ligand effect on linear aldehyde, 264t
 nature of solvent and ligand, 265
 reaction temperature, 468
 silylformylation and hydrosilylation, 290–291
 wavelength of irradiation, 187
Rehybridization
 carbonyl carbon, 254
 formyl radical, 257
Relative reactivities, insertion reactions, 457
Remote sensing, optical-fiber coupled high-pressure reactors, 3
Reorganization energy, rehybridization of carbonyl unit, 257
Reversibility, oxidative addition, 213
Reversible reduction wave, chromium catalyst, 599
Rhodium
 asymmetric hydroformylation, 274
 carbonylation of benzene, 185–189
 catalyst behavior on repeated use, 484
 catalyst combinations in synthesis gas chemistry, 28–29

Rhodium—Continued

- catalyst for carbenoid reactions, 443–444
- catalytic activity, 483–484
- coupling of surface methylenes with surface vinyls, 573
- electrochemical reduction of organometallic complexes, 261
- eLTTP complex, rotational and conformational flexibility, 358
- formation of higher hydrocarbons, 571
- functionalization of C–H bonds in carbenoid reactions, 443–461
- hydroformylation catalysts, 277–296
- hydrosilation of iron acyls, 492–496
- lithium effect on reaction rate, 389
- olefin hydroformylation, 266–272
- organic chemistry of di- μ -methylenedirhodium complexes, 565–567
- overall reaction selectivity, 327
- performance as a catalyst, 324
- potential role of dianions, 391
- rate dependence at two Li levels, 387f
- reductive carbonylation of methanol, 334
- sterically hindered geometry, 362
- water–gas shift reaction, 384
- Rhodium catalysts, formation from bulky or nonbulky phosphine ligands, 403f
- Rhodium-catalyzed reactions
 - carbonylation
 - experimental procedures, 378–379
 - methyl acetate, 377–394
 - selectivity, 379
 - thermodynamic parameters, 379
 - hydroformylation reaction, mechanism, 400–403
 - oxo study, CIR in situ analyses, 11–13
 - reductive carbonylation of methanol, 323–336
- Rhodium complex hydroformylation catalysts
 - generic formula, 400f
 - phosphorus ligands, 399
- Rhodium concentration, reaction rate variation, 331
- Rhodium-containing species, reactions with carbon monoxide and dihydrogen, 25–28
- Rhodium hydroformylation
 - 1-butene
 - phosphite ester ligands, 414–415t
 - triethylphosphine ligand, 413t
 - ligand effects, 399–400
 - mechanism, 400–403
 - spectra, 271f
- Rhodium hydroformylation catalysts
 - alkyldiphenylphosphine–rhodium complexes, 398
 - electron-donor properties, 398–399
 - electronic effects on synthesis, structure, reactivity, and selectivity, 395–418

Rhodium hydroformylation catalysts—*Continued*

- selectivity for linear aldehydes, 396–397
- stereochemical effects, 397–398
- Rhodium(I) phosphine intermediates
 - flash photolysis studies, 106–109
 - reaction dynamics, 107f
- Rhodium(II) porphyrin, reactions with CO, 253–258
- Rhodium(II) porphyrin derivatives, carbon monoxide activation, 249
- Ring construction, carbon–carbon bond formation, 463–478
- Ring-opening metathesis polymerization, 591, 599–601
- Ring oxidation, 226
- Ring slippage, sapphire NMR tube, 40
- Rotational flexibility
 - eLTTP complex, 358
 - single-atom bridge in eLTTP, 361
- Ruthenium
 - addition to rhodium catalyst, 323
 - anionic clusters, 419–429
 - catalyst combinations in synthesis gas chemistry, 28–29
 - cycloisomerization followed by reductive desulfonylation, 475
 - homogeneous catalysts, 72
 - homologation of methanol to ethanol, 327
 - hydrogenation catalysts, 60–64
 - selectivity of triphenylphosphine complexes, 434
- Ruthenium-catalyzed reactions
 - ethylene glycol and secondary amines, 437f
 - ethylene glycol with morpholine, effect of temperature on selectivity, 438t
 - morpholine with ethylene glycol, effect of phosphines, 435t
- Ruthenium cluster anion, molecular structure, isolation, and characterization, 425–429
- Ruthenium complexes, catalysis and selectivity, 436t
- Ruthenium-containing species, reaction with dihydrogen, 24–28

S**Safety**

- organic–O₂ oxidations, 95
- sapphire NMR tubes, 36
- Sapphire NMR tubes
 - catalytic reactions under moderate pressure, 33–40
 - development, 35–36
 - intermolecular hydroacylation, 39
 - operation, 36
 - ring slippage, 40
 - safety, 36
- Sarcosinate specialty surfactants, 238–239f

- Selective insertion, 1-alkynes to Rh–Si bond, 294
- Selective inversion, exchange broadening of resonances, 37
- Selectivity
- attack at the methyl position, 226
 - bimetallic hydroformylation, 361–362
 - bridging ligands of dirhodium(II) nucleus, 458
 - C–H attack, 230
 - C–H oxidative addition, 187
 - catalyst systems, 203
 - diphosphine ligand, 327, 328*t*
 - fragment geometry, 116–117
 - functionalized reactions, 222–223
 - high-temperature reactions, 438
 - hydrocarbonylation of ethanol, 312*t*
 - hydrogenation and homologation products, 311
 - insertion into C–H bond close to carbenoid center, 450
 - iridium and rhodium C–H oxidative addition, 212
 - mixed-ligand systems, 438
 - reaction products, 214
 - reactions of diethylene glycol, 438–439
 - reductive carbonylation products, 332
 - rhodium cocatalyst, 240, 241*f*
- Selectivity control, amination of ethylene glycol, 433–442
- Selectivity ratio, nature of phosphine ligand, 434
- Sequential double carbonylation, proposed mechanism, 280*f*
- Shape selectivity
- olefin epoxidation, metallo picnic-basket porphyrins, 153–162
 - oxygenation catalysts, 155
- Shunt pathway, oxygen-transfer agents, 155
- Signal enhancements, calculation, 58
- Silicon crystal, corrosive acidic conditions, 6
- Siloxyalkyl compounds, generation, 492
- Silsesquioxanes
- characterization of methoxy derivative, 559–560
 - structure and properties, 553–556, 558
- Silyl ester derivative, 535, 536*f*
- Silylformylation
- active catalyst species, 291–293
 - 1-alkyne, 289–294
 - catalytic cycles, 293
 - description, 289
 - mechanism, 291, 295*f*
 - mixed-metal version, 290
- Sodium formate, water–gas shift reaction, 340–345
- Sodium tetraphenylborate reactions, typical procedure, 532
- Solid-state inorganic metal oxide formation, monitoring techniques, 7
- Solvent polarity, chemical shifts, 581
- Spacer groups, metal centers, 360
- Spectroscopic data, correlation with catalytic performance, 29
- Spectroscopic studies
- electroreduced rhodium complexes, 268–272
 - Pt(DIOP)Cl₂ electroreduced solution, 265–266
- Spin density, hyperfine coupling constant, 252–253
- Spirocyclization of alkyl isocyanates in tetrahydrofuran, 420*f*
- Stabilizing electronic effect, Me₃Si group, 578
- Stereochemical effects, rhodium hydroformylation catalysts, 397–398
- Stereochemical relay, macrolide product synthesis, 472–473
- Stereocomplementary behavior, hydroborations, 174
- Stereocontrol, catalyzed and uncatalyzed hydroborations, 163–177
- Stereoselectivity
- asymmetric hydrogenation, 123–142
 - cuprate additions, 176
 - hydrogenation, binap–Ru catalysts, 134
 - orientations of adjacent chiral center, 169, 171*f*
 - palladium-catalyzed allyl acetate reactions, 530
 - preferential orientation in hydroborations, 172*f*
 - reactive conformer, 171
 - silylformylation and hydrosilylation, 290–291
- Stereospecificity, *cis*-2-propenyl-1,3-dioxolanone reaction, 539
- Steric destabilization, caused by phosphines, 437
- Steric effects
- catalyzed hydroborations, 171
 - rhodium hydroformylation catalysts, 395–396
- Steric hindrance, structure identification, 576–577
- Stirring, importance in cell design, 23
- Stretching frequencies, carbonyl, 27–28
- Styrene hydrocyanation, 481–482
- Styrene hydroformylation, 263*t*
- Substrate(s), relative reactivities, 207–208
- Substrate specificity, enzyme, 153
- Supported catalysts, yields, 483–484
- Surface vinyl, metal surfaces, 567
- Syn* selectivities, hydroborations, 175
- Syngas, *See* Synthesis gas
- Synthesis gas
- amidocarbonylation, 235–247
 - composite homogeneous catalysts, 28
 - extreme reaction conditions, 28–29

Synthesis gas—*Continued*

- reactions with a catalyst, 30f
- synthesis of fuel alcohols, 324
- transformations with metal oxide catalysts, 339

Synthetic catalysts, asymmetric hydrogenation, 124

T

- Temperature, effect on catalyzed yields, 484
- Temperature dependence, carbonylation, 381
- Template, polyphosphine ligand, 351
- Terminal acetylenes, couplings, 470–472
- Terminal alkenes, isomerization, 190

Tetracarbonylalkylcobalts

- experimental details, 298–301
- intermediate complex formation, 298
- preparation from tetracarbonylhydridocobalt and dimethyl fumarate or aldehydes, 297–306

Tetracarbonylcobalt anion

- disproportionation, 508–509
- generation, 508
- reduction of methanol, 507–513

Tetrahydrofuran

- competitive trapping, 112
- rate-limiting dissociation, 110

Tetraphenylborate chemistry

- nickel chemistry as model, 537
- organotin coupling reactions, 537
- reaction speed, 538–539
- solvent, effect on reaction speed, 539
- stereospecificity, 539
- synthesis of allylpalladium complexes, 537–538
- transmetallation step, 539

Tetravinylsilane, Fischer–Tropsch products, 571–572

Thermal decomposition,

- carbonyl(methoxycarbonyl)cobalts, 510

Tin anode, generation of Pt–Sn couple, 263

Titanium

- catalyst for silsesquioxanes, 559–562
- chemical shift, 587
- σ -bond metathesis, 559
- Ziegler polymerization catalysts, 575–590

Titanium–alloy valve

- hydrogen embrittlement, 39
- sapphire NMR tube, 35

Titanium–chlorine bond

- polarization, 588
- stretching and rupture, 588, 589

Titanium oxide, catalytic activity, 317–319

Titanocene dichloride–methylaluminum dichloride system, interconversions, 585–587

Titanocene halides, active sites in soluble

- Ziegler polymerization catalysts, 575–590

Titanocenium ion, active catalyst center, 577

Titanocenium ion pair, generation, 589

Toluene

- aperiodic temporal oscillations, 103
- O₂ oxidation, 103

p-Toluenesulfonic acid, oxidation, 223–226

Transfer hydrogenation

- t*-butylethylene with alkanes, 183
- chelate phosphines, 146
- formic acid, 145

Transient yields, photolysis, 116

Transition metal(s), catalysts for deoxygenation of phenols by CO, 520–521

Transition metal catalysts, cyclizations, 463–478

Transition metal clusters, new generation of catalysts, 419

Transition metal complexes

- catalysis of carbonylations, 277–296
- enantioselective catalysis, 143–152

Transmetallation, palladium(0) species, 534

Transmission cells, monitoring of homogeneous metal-catalyzed reactions, 4–5

Trapping radicals, Hg* attack, 208

Trialkylphosphine ligands, value in high-temperature rhodium hydroformylation, 417

Tricarbonylhydridocobalt

- formation, 77
- hydroformylation process, 75–93
- molecular conformation, 77–78

Trichlorostannate, platinum hydride activity as hydroformylation catalyst, 367

Tricyclic nucleus, transannular cyclization, 475

Triethylphosphine ligand concentration, rhodium hydroformylation rate and selectivity, 410–412

Triethylphosphine–rhodium catalyst system comparison with triphenylphosphine system, 412–414

- hydroformylation of 1-butene, 410

Trimethylphosphine complex

- activation of hydrocarbon C–H bonds, 107–108

- dehydrogenation of organic substrates, 107

Trimethylphosphine intermediates, lifetimes, 109

Trimethylsilylmethyl ligands, 598

Trimethylsilylmethyltitanocene chloride

- bond angles and distances, 582f
- interaction with aluminum chlorides, 584–585

- solvent dependence of chemical shifts, 583t

- space-filling molecular model, 583f
- structure, 580–583

Trinuclear ruthenium cluster anions

- catalysts, 420
- chemo- and regioselectivity, 421t

- Triphenylphosphine
 ¹H NMR spectra, 423f
 trinuclear ruthenium cluster anions,
 reaction system, 424f
- U
- Unstable molecules, identification and
 characterization, 24–28
- V
- van der Waals energy map, SYBYL
 molecular-modeling program, 359f
- Vapor-phase selectivity, mercury
 photosensitization, 199–200
- Vapor-pressure biasing, skewed product mix,
 202
- Vapor-selectivity effect, photochemical setup,
 199–200
- Vibrational spectroscopy, homogeneously
 catalyzed reactions, 20
- Vinyl
 complexes from iron acetyl compounds,
 493–494
 Fischer–Tropsch products, 571–572
 metal surfaces, 567
- W
- Water–gas shift
 activation barrier for catalysis, 339
 catalysis, 337–348
 cation reactivity, 340
 equilibrium, 339
 intermediate substances, 346
 involvement of proton source, 344–345
 iodocarbonyl complexes of rhodium, 384
- Water–gas shift—*Continued*
 iron oxide, 340
 kinetic order in sodium formate, 342f
 metal centers, 347
 pentacarbonyliron, 340
- Wavelength of irradiation
 cyclohexane, 189
 methyl selectivity of alkanes, 189
 regioselectivity, 187
- Weitekamp proposal, parahydrogen-induced
 polarization, 50
- White line, d-electron vacancies in platinum
 colloids, 544–545
- Wilkinson's compound, hydrosilation of
 organoiron acetyl complexes, 491
- Window materials, high-pressure IR cells, 22
- X
- Xenon, inert solvent, 217
- p*-Xylene
 electrochemical oscillations, 103
 O₂ oxidation, 103
- Z
- Zeolite(s), catalysts in the petroleum industry,
 154
- Zeolite formation, monitoring techniques, 7
- Zeolite synthesis, corrosive acidic conditions,
 6
- Ziegler–Natta catalysis, molecular basis,
 575–576
- Ziegler polymerization catalysts, active sites,
 575–590
- Ziegler polymerization of ethylene,
 titanocenium cations, 589