

Contents

Foreword *xv*

Preface *xvii*

Part I Theoretical View of Organometallic Catalysis 1

1	Introduction of Computational Organometallic Chemistry	3
1.1	Overview of Organometallic Chemistry	3
1.1.1	General View of Organometallic Chemistry	3
1.1.2	A Brief History of Organometallic Chemistry	6
1.2	Using Computational Tool to Study the Organometallic Chemistry Mechanism	8
1.2.1	Mechanism of Transition Metal Catalysis	8
1.2.2	Mechanistic Study of Transition Metal Catalysis by Theoretical Methods	10
	References	13
2	Computational Methods in Organometallic Chemistry	19
2.1	Introduction of Computational Methods	19
2.1.1	The History of Quantum Chemistry Computational Methods	19
2.1.2	Post-HF Methods	21
2.2	Density Functional Theory (DFT) Methods	23
2.2.1	Overview of Density Functional Theory Methods	23
2.2.2	Jacob's Ladder of Density Functionals	25
2.2.3	The Second Rung in "Jacob's Ladder" of Density Functionals	25
2.2.4	The Third Rung in "Jacob's Ladder" of Density Functionals	26
2.2.5	The Fourth Rung in "Jacob's Ladder" of Density Functionals	26
2.2.6	The Fifth Rung in "Jacob's Ladder" of Density Functionals	26
2.2.7	Correction of Dispersion Interaction in Organic Systems	27
2.3	Basis Set and Its Application in Mechanism Studies	29
2.3.1	General View of Basis Set	29
2.3.2	Pople's Basis Sets	30
2.3.3	Polarization Functions	31

2.3.4	Diffuse Functions	31
2.3.5	Correlation-Consistent Basis Sets	31
2.3.6	Pseudo Potential Basis Sets	32
2.4	Solvent Effect	33
2.5	How to Choose a Method in Computational Organometallic Chemistry	34
2.5.1	Why DFT Method Is Chosen	34
2.5.2	How to Choose a Density Functional	34
2.5.3	How to Choose a Basis Set	36
2.6	Revealing a Mechanism for An Organometallic Reaction by Theoretical Calculations	37
2.7	Overview of Popular Computational Programs	37
2.8	The Limitation of Current Computational Methods	40
2.8.1	The Accuracy of DFT Methods	40
2.8.2	Exact Solvation Effect	41
2.8.3	Evaluation of Entropy Effect	41
2.8.4	The Computation of Excited State and High Spin State	41
2.8.5	Speculation on the Reaction Mechanism	41
	References	42
3	Elementary Reactions in Organometallic Chemistry	51
3.1	General View of Elementary Reactions in Organometallic Chemistry	51
3.2	Coordination and Dissociation	52
3.2.1	Coordination Bond and Coordination	52
3.2.2	Dissociation	55
3.2.3	Ligand Exchange	57
3.3	Oxidative Addition	59
3.3.1	Concerted Oxidative Addition	60
3.3.2	Substitution-type Oxidative Addition	62
3.3.3	Radical-type Addition	67
3.3.4	Oxidative Cyclization	68
3.4	Reductive Elimination	70
3.4.1	Concerted Reductive Elimination	71
3.4.2	Substitution-type Reductive Elimination	73
3.4.3	Radical-Substitution-type Reductive Elimination	74
3.4.4	Bimetallic Reductive Elimination	75
3.4.5	Eliminative Reduction	78
3.5	Insertion	78
3.5.1	1,2-Insertion	79
3.5.2	1,1-Insertion	80
3.5.3	Conjugative Insertion	83
3.5.4	Outer-Sphere Insertion	84
3.6	Elimination	86
3.6.1	β -Elimination	86
3.6.2	α -Elimination	90

3.7	Transmetallation	92
3.7.1	Concerted Ring-Type Transmetallation	92
3.7.2	Transmetallation Through Electrophilic Substitution	98
3.7.3	Stepwise Transmetallation	99
3.8	Metathesis	100
3.8.1	σ -Bond Metathesis	100
3.8.2	Olefin Metathesis	102
3.8.3	Alkyne Metathesis	106
	References	106

Part II On the Mechanism of Transition-metal-assisted Reactions 125

4	Theoretical Study of Ni-Catalysis	127
4.1	Ni-Mediated C—H Bond Activation	128
4.1.1	Ni-Mediated Arene C—H Activation	128
4.1.2	Ni-Mediated Aldehyde C—H Activation	132
4.2	Ni-Mediated C—Halogen Bond Cleavage	133
4.2.1	Concerted Oxidative Addition of C—Halogen Bond	133
4.2.2	Radical-Type Substitution of C—Halogen Bond	135
4.2.3	C—Halogen Bond Cleavage by β -Halide Elimination	137
4.2.4	Nucleophilic Substitution of C—Halogen Bond	139
4.3	Ni-Mediated C—O Bond Activation	140
4.3.1	Ether C—O Bond Activation	140
4.3.2	Ester C—O Bond Activation	142
4.4	Ni-Mediated C—N Bond Cleavage	148
4.5	Ni-Mediated C—C Bond Cleavage	151
4.5.1	C—C Single Bond Activation	151
4.5.2	C=C Double Bond Activation	152
4.6	Ni-Mediated Unsaturated Bond Activation	153
4.6.1	Oxidative Cyclization with Unsaturated Bonds	153
4.6.2	Electrophilic Addition of Unsaturated Bonds	156
4.6.3	Unsaturated Compounds Insertion	157
4.6.4	Nucleophilic Addition of Unsaturated Bonds	159
4.7	Ni-Mediated Cyclization	160
4.7.1	Ni-Mediated Cycloadditions	161
4.7.2	Ni-Mediated Ring Substitutions	163
4.7.3	Ni-Mediated Ring Extensions	166
	References	168
5	Theoretical Study of Pd-Catalysis	181
5.1	Pd-Catalyzed Cross-coupling Reactions	182
5.1.1	Suzuki–Miyaura Coupling	183
5.1.2	Negishi Coupling	186

5.1.3	Stille Coupling	189
5.1.4	Hiyama Coupling	190
5.1.5	Heck–Mizoroki Reaction	192
5.2	Pd-Mediated C—Hetero Bond Formation	196
5.2.1	C—B Bond Formation	196
5.2.2	C—S Bond Formation	197
5.2.3	C—I Bond Formation	200
5.2.4	C—Si Bond Formation	201
5.3	Pd-Mediated C—H Activation Reactions	204
5.3.1	Chelation-Free C(sp ³)—H Activation	206
5.3.2	Chelation-Free C(sp ²)—H Activation	208
5.3.3	Coordinative Chelation-Assisted <i>ortho</i> -C(aryl)—H Activation	210
5.3.4	Covalent Chelation-Assisted <i>ortho</i> -C(aryl)—H Activation	212
5.3.5	Chelation-Assisted <i>meta</i> -C(aryl)—H Activation	214
5.3.6	Coordinative Chelation-Assisted C(sp ³)—H Activation	216
5.3.7	Covalent Chelation-Assisted C(sp ³)—H Activation	216
5.3.8	C—H Bond Activation Through Electrophilic Deprotonation	219
5.3.9	C—H Bond Activation Through σ -Complex-Assisted Metathesis	221
5.3.10	C—H Bond Activation Through Oxidative Addition	223
5.4	Pd-Mediated Activation of Unsaturated Molecules	224
5.4.1	Alkene Activation	225
5.4.2	Alkyne Activation	225
5.4.3	Enyne Activation	226
5.4.4	Imine Activation	229
5.4.5	CO Activation	229
5.4.6	Isocyanide Activation	231
5.4.7	Carbene Activation	231
5.5	Allylic Pd Complex	234
5.5.1	Formation from Allylic Oxidative Addition	235
5.5.2	Formation from Allylic Nucleophilic Substitution	236
5.5.3	Formation from the Nucleophilic Attack onto Allene	237
5.5.4	Formation from Allylic C—H Activation	237
5.5.5	Formation from Allene Insertion	238
	References	239
6	Theoretical Study of Pt-Catalysis	257
6.1	Mechanism of Pt-Catalyzed C—H Activation	258
6.1.1	Oxidative Addition of C—H Bond	259
6.1.2	Electrophilic Dehydrogenation	259
6.1.3	Carbene Insertion into C—H Bonds	261
6.2	Mechanism of Pt-Catalyzed Alkyne Activation	264
6.2.1	Nucleophilic Additions	264
6.2.2	Cyclopropanation	266
6.2.3	Oxidative Cycloaddition	268
6.3	Mechanism of Pt-Catalyzed Alkene Activation	270

- 6.3.1 Hydroamination of Alkenes 270
- 6.3.2 Hydroformylation of Alkenes 272
- 6.3.3 Isomerization of Cyclopropenes 273
- References 274

7 Theoretical Study of Co-Catalysis 289

- 7.1 Co-Mediated C—H Bond Activation 289
 - 7.1.1 Hydroarylation of Alkenes 291
 - 7.1.2 Hydroarylation of Allenes 293
 - 7.1.3 Hydroarylation of Alkynes 294
 - 7.1.4 Hydroarylation of Nitrenoid 296
 - 7.1.5 Oxidative C—H Alkoxylation 297
- 7.2 Co-Mediated Cycloadditions 297
 - 7.2.1 Co-Mediated Pauson–Khand Reaction 298
 - 7.2.2 Co-Catalyzed [4+2] Cyclizations 299
 - 7.2.3 Co-Catalyzed [2+2+2] Cyclizations 299
 - 7.2.4 Co-Catalyzed [2+2] Cyclizations 300
- 7.3 Co-Catalyzed Hydrogenation 301
 - 7.3.1 Hydrogenation of Carbon Dioxide 301
 - 7.3.2 Hydrogenation of Alkenes 304
 - 7.3.3 Hydrogenation of Alkynes 306
- 7.4 Co-Catalyzed Hydroformylation 307
 - 7.4.1 Direct Hydroformylation by H₂ and CO 308
 - 7.4.2 Transfer Hydroformylation 309
- 7.5 Co-Mediated Carbene Activation 310
 - 7.5.1 Arylation of Carbene 310
 - 7.5.2 Carboxylation of Carbene 312
- 7.6 Co-Mediated Nitrene Activation 313
 - 7.6.1 Aziridination of Olefins 314
 - 7.6.2 Amination of Isonitriles 314
 - 7.6.3 Amination of C—H Bonds 315
- References 317

8 Theoretical Study of Rh-Catalysis 329

- 8.1 Rh-Mediated C—H Activation Reactions 330
 - 8.1.1 Rh-Catalyzed Arylation of C—H Bond 330
 - 8.1.2 Rh-Catalyzed Alkylation of C—H Bond 332
 - 8.1.3 Rh-Catalyzed Alkenylation of C—H Bond 335
 - 8.1.4 Rh-Catalyzed Amination of C—H Bond 338
 - 8.1.5 Rh-Catalyzed Halogenation of C—H Bond 340
- 8.2 Rh-Catalyzed C—C Bond Activations and Transformations 341
 - 8.2.1 Strain-driven Oxidative Addition 341
 - 8.2.2 The Carbon—Cyano Bond Activation 342
 - 8.2.3 β -Carbon Elimination 343
- 8.3 Rh-Mediated C—Hetero Bond Activations 343

8.3.1	C—N Bond Activation	344
8.3.2	C—O Bond Activation	345
8.4	Rh-Catalyzed Alkene Functionalizations	345
8.4.1	Hydrogenation of Alkene	346
8.4.2	Diboration of Alkene	347
8.5	Rh-Catalyzed Alkyne Functionalizations	349
8.5.1	Hydroacylation of Alkynes	349
8.5.2	Hydroamination of Alkynes	349
8.5.3	Hydrothiolation of Alkynes	351
8.5.4	Hydroacetoxylation of Alkynes	351
8.6	Rh-Catalyzed Addition Reactions of Carbonyl Compounds	352
8.6.1	Hydrogenation of Ketones	352
8.6.2	Hydrogenation of Carbon Dioxide	353
8.6.3	Hydroacylation of Ketones	353
8.7	Rh-Catalyzed Carbene Transformations	354
8.7.1	Carbene Insertion into C—H Bonds	354
8.7.2	Arylation of Carbenes	357
8.7.3	Cyclopropanation of Carbenes	358
8.7.4	Cyclopropenation of Carbenes	359
8.8	Rh-Catalyzed Nitrene Transformations	359
8.8.1	Nitrene Insertion into C—H Bonds	360
8.8.2	Aziridination of Nitrenes	361
8.9	Rh-Catalyzed Cycloadditions	362
8.9.1	(3+2) Cycloadditions	365
8.9.2	Pauson–Khand-type (2+2+1) Cycloadditions	367
8.9.3	(5+2) Cycloadditions	367
8.9.4	(5+2+1) Cycloadditions	369
	References	369
9	Theoretical Study of Ir-Catalysis	387
9.1	Ir-Catalyzed Hydrogenations	387
9.1.1	Hydrogenation of Alkenes	388
9.1.2	Hydrogenation of Carbonyl Compounds	391
9.1.3	Hydrogenation of Imines	393
9.1.4	Hydrogenation of Quinolines	396
9.2	Ir-Catalyzed Hydrofunctionalizations	397
9.2.1	Ir-Catalyzed Hydroaminations	397
9.2.2	Ir-Catalyzed Hydroarylations	397
9.2.3	Ir-Catalyzed Hydrosilylations	399
9.3	Ir-Catalyzed Borylations	401
9.3.1	Borylation of Alkanes	402
9.3.2	Borylation of Arenes	403
9.4	Ir-Catalyzed Aminations	405
9.4.1	Amination of Alcohols	405
9.4.2	Amination of Arenes	407

9.5	Ir-Catalyzed C—C Bond Coupling Reactions	407
	References	409
10	Theoretical Study of Fe-Catalysis	419
10.1	Fe-Mediated Oxidations	420
10.1.1	Alkane Oxidations	420
10.1.2	Arene Oxidations	422
10.1.3	Alkene Oxidations	423
10.1.4	Oxidative Catechol Ring Cleavage	425
10.2	Fe-Mediated Hydrogenations	426
10.2.1	Hydrogenation of Alkenes	427
10.2.2	Hydrogenation of Carbonyls	429
10.2.3	Hydrogenation of Imines	430
10.2.4	Hydrogenation of Carbon Dioxide	430
10.3	Fe-Mediated Hydrofunctionalizations	431
10.3.1	Hydrosilylation of Ketones	431
10.3.2	Hydroamination of Allenes	432
10.4	Fe-Mediated Dehydrogenations	434
10.4.1	Dehydrogenation of Alcohols	434
10.4.2	Dehydrogenation of Formaldehyde	435
10.4.3	Dehydrogenation of Formic Acid	435
10.4.4	Dehydrogenation of Ammonia-Borane	437
10.5	Fe-Catalyzed Coupling Reactions	438
10.5.1	C—C Cross-Couplings with Aryl Halide	438
10.5.2	C—N Cross-Couplings with Aryl Halide	438
10.5.3	C—C Cross-Couplings with Alkyl Halide	441
10.5.4	Iron-Mediated Oxidative Coupling	441
	References	441
11	Theoretical Study of Ru-Catalysis	451
11.1	Ru-Mediated C—H Bond Activation	452
11.1.1	Mechanism of the Ru-Mediated C—H Bond Cleavage	452
11.1.2	Ru-Catalyzed C—H Bond Arylation	456
11.1.3	Ru-Catalyzed <i>ortho</i> -Alkylation of Arenes	460
11.1.4	Ru-Catalyzed <i>ortho</i> -Alkenylation of Arenes	461
11.2	Ru-Catalyzed Hydrogenations	464
11.2.1	Hydrogenation of Alkenes	464
11.2.2	Hydrogenation of Carbonyls	465
11.2.3	Hydrogenation of Esters	466
11.2.4	Hydrodefluorination of Fluoroarenes	467
11.3	Ru-Catalyzed Hydrofunctionalizations	468
11.3.1	Hydroacylations	469
11.3.2	Hydrocarboxylations	470
11.3.3	Hydroborations	471
11.4	Ru-Mediated Dehydrogenations	472

11.4.1	Dehydrogenation of Alcohols	473
11.4.2	Dehydrogenation of Formaldehyde	473
11.4.3	Dehydrogenation of Formic Acid	474
11.5	Ru-Catalyzed Cycloadditions	475
11.5.1	Ru-Mediated (2+2+2) Cycloadditions	475
11.5.2	Ru-Mediated Pauson–Khand Type (2+2+1) Cycloadditions	478
11.5.3	Ru-Mediated Click Reactions	478
11.6	Ru-Mediated Metathesis	480
11.6.1	Ru-Mediated Intermolecular Olefin Metathesis	482
11.6.2	Ru-Mediated Intramolecular Diene Metathesis	484
11.6.3	Ru-Mediated Alkyne Metathesis	484
	References	485
12	Theoretical Study of Mn-Catalysis	499
12.1	Mn-Mediated Oxidation of Alkanes	500
12.1.1	C—H Hydroxylations	500
12.1.2	C—H Halogenations	501
12.1.3	C—H Azidations	501
12.1.4	C—H Isocyanations	501
12.2	Mn-Mediated C—H Activations	502
12.2.1	Electrophilic Deprotonation	503
12.2.2	σ -Complex-Assisted Metathesis	504
12.2.3	Concerted Metalation–Deprotonation	505
12.3	Mn-Mediated Hydrogenations	507
12.3.1	Hydrogenation of Carbon Dioxide	507
12.3.2	Hydrogenation of Carbonates	508
12.4	Mn-Mediated Dehydrogenations	510
12.4.1	Dehydrogenation of Alcohols	510
12.4.2	Dehydrogenative Couplings	511
	References	512
13	Theoretical Study of Cu-Catalysis	517
13.1	Cu-Mediated Ullmann Condensations	518
13.1.1	C—N Bond Couplings	520
13.1.2	C—O Bond Couplings	522
13.1.3	C—F Bond Couplings	522
13.2	Cu-Mediated Trifluoromethylations	524
13.2.1	Trifluoromethylations Through Cross-Coupling	524
13.2.2	Trifluoromethylations Through Oxidative Coupling	524
13.2.3	Radical-Type Trifluoromethylations	525
13.3	Cu-Mediated C—H Activations	527
13.3.1	C—H Arylations	527
13.3.2	C—H Aminations	529
13.3.3	C—H Hydroxylation	531
13.3.4	C—H Etherifications	532

13.4	Cu-Mediated Alkyne Activations	533
13.4.1	Azide–Alkyne Cycloadditions	533
13.4.2	Nucleophilic Attack onto Alkynes	535
13.4.3	Alkynyl Cu Transformations	536
13.5	Cu-Mediated Carbene Transformations	539
13.5.1	[2+1] Cycloadditions with Alkenes	539
13.5.2	Carbene Insertions	541
13.5.3	Rearrangement of Carbenes	542
13.6	Cu-Mediated Nitrene Transformations	542
13.6.1	[2+1] Cycloadditions with Alkenes	543
13.6.2	Amination of Nitrenes	543
13.6.3	Nitrene Insertions	544
13.7	Cu-Catalyzed Hydrofunctionalizations	545
13.7.1	Hydroborylations	547
13.7.2	Hydrosilylation	547
13.7.3	Hydrocarboxylations	548
13.8	Cu-Catalyzed Borylations	549
13.8.1	Borylation of Alkenes	551
13.8.2	Borylation of Alkynes	552
13.8.3	Borylation of Carbonyls	553
	References	554
14	Theoretical Study of Ag-Catalysis	567
14.1	Ag-Mediated Carbene Complex Transformations	568
14.1.1	Silver–Carbene Formation	568
14.1.2	Carbene Insertion into C—Cl Bond	572
14.1.3	Carbene Insertion into O—H Bond	573
14.1.4	Nucleophilic Attack by Carbonyl Groups	573
14.1.5	Carbene Insertion into C—H Bond	574
14.2	Ag-Mediated Nitrene Transformations	576
14.2.1	Silver–Nitrene Complex Formation	577
14.2.2	Nucleophilic Attack by Unsaturated Bonds	580
14.2.3	Nucleophilic Attack by Amines	582
14.3	Ag-Mediated Silylene Transformations	583
14.4	Ag-Mediated Alkyne Activations	585
14.4.1	π -Activation of Alkynes	586
14.4.2	C—H Activation of Alkynes	587
	References	588
15	Theoretical Study of Au-Catalysis	597
15.1	Au-Mediated Alkyne Activations	598
15.1.1	Isomerization of Alkynes	599
15.1.2	Nucleophilic Attack by Oxygen-Involved Nucleophiles	599
15.1.3	Nucleophilic Attack by Nitrogen-Involved Nucleophiles	602
15.1.4	Nucleophilic Attack by Arenes	606

15.2	Au-mediated Alkene Activations	607
15.2.1	Nucleophilic Addition of Alkenes	607
15.2.2	Allylic Substitutions	608
15.3	Au-mediated Allene Activations	609
15.3.1	Hydroamination of Allenes	610
15.3.2	Hydroalkoxylation of Allenes	610
15.3.3	Cycloisomerization of Allenyl Ketones	613
15.4	Au-mediated Enyne Transformations	613
15.4.1	1,5-Enyne Cycloisomerizations	614
15.4.2	1,6-Enyne Cycloisomerizations	615
15.4.3	Allenyne Cycloisomerizations	617
15.4.4	Conjugative Enyne Cycloisomerizations	617
	References	618

Index	629
--------------	-----