

Contents

Preface *xiii*

1	Introduction to Cobalt Chemistry and Catalysis	1
	<i>Marko Hapke and Gerhard Hilt</i>	
1.1	Introduction	1
1.2	Organometallic Cobalt Chemistry, Reactions, and Connections to Catalysis	4
1.2.1	Cobalt Compounds and Complexes of Oxidation States +3 to –1	4
1.2.1.1	Co(III) Compounds	5
1.2.1.2	Co(II) Compounds	5
1.2.1.3	Co(I) Compounds	7
1.2.1.4	Co(0) Compounds	8
1.2.1.5	Co(–I) Compounds	9
1.2.2	Bioorganometallic Cobalt Compounds	10
1.3	Applications in Organic Synthesis and Catalytic Transformations	12
1.4	Conclusion and Outlook	19
	Abbreviations	20
	References	20
 2	 Homogeneous Cobalt-Catalysed Hydrogenation Reactions	 25
	<i>Kathrin Junge and Matthias Beller</i>	
2.1	Introduction	25
2.2	Hydrogenation of C—C Multiple Bonds (Alkenes, Alkynes)	25
2.3	Hydrogenation of Carbonyl Compounds (Ketones, Aldehydes, Carboxylic Acid Derivatives, CO ₂)	34
2.3.1	Ketones and Aldehydes	34
2.3.2	Carboxylic Acid Derivatives (Acids, Esters, Imides)	39
2.3.3	Hydrogenation of Carbon Dioxide	47
2.4	Hydrogenation of C—X Multiple Bonds (Imines, Nitriles)	52

2.4.1	Nitrile Hydrogenation	52
2.4.2	Imine Hydrogenation	55
2.4.3	Hydrogenation of <i>N</i> -Heterocycles	56
2.5	Summary and Conclusions	58
2.6	Selected Experimental Procedures	59
2.6.1	Synthesis of Cobalt Complex [(PNHPC ^{Cr})Co(CH ₂ SiMe ₃)]BAR ^F ₄ (8a)	59
	Abbreviations	60
	References	61
3	Synthesis of C—C Bonds by Cobalt-Catalysed Hydrofunctionalisations	67
	<i>Daniel K. Kim and Vy M. Dong</i>	
3.1	Introduction	67
3.2	Cobalt-Catalysed C—C Bond Formations via Hydrofunctionalisation	67
3.2.1	Hydroformylation	67
3.2.2	Hydroacylation	68
3.2.3	Hydrovinylation	74
3.2.4	Hydroalkylation	78
3.2.5	Hydrocyanation	80
3.2.6	Hydrocarboxylation	81
3.3	Summary and Conclusions	83
	Abbreviations	84
	References	85
4	Cobalt-Catalysed C—H Functionalisation	89
	<i>Naohiko Yoshikai</i>	
4.1	Introduction	89
4.2	Low-valent Cobalt Catalysis	91
4.2.1	C—H Functionalisation with <i>In Situ</i> -Reduced Cobalt Catalysts	91
4.2.1.1	Hydroarylation of Alkynes and Alkenes	91
4.2.1.2	C—H Functionalisation with Electrophiles	98
4.2.1.3	C—H Functionalisation with Organometallic Reagents	103
4.2.1.4	C—H Functionalisation via 1,4-Cobalt Migration	103
4.2.1.5	Hydroacylation	103
4.2.2	C—H Functionalisation with Pincer-Type Ligands and Related Well-Defined Cobalt Catalysts	105
4.3	High-valent Cobalt Catalysis	106
4.3.1	Chelation-Assisted C—H Functionalisation with Cp*Co ^{III} Catalysts	106
4.3.1.1	C—H Addition to Polar C=X Bonds	108
4.3.1.2	Reaction with Alkynes, Alkenes, and Allenes	111
4.3.1.3	Reaction with Formal Nitrene or Carbene Precursors	121
4.3.1.4	Reaction with E—X-type Electrophiles	126
4.3.1.5	Miscellaneous	128

4.3.2	Bidentate Chelation-Assisted C–H Functionalisation with Co ^{III} Catalysts	130
4.3.2.1	Reaction with Alkynes, Alkenes, and Allenes	131
4.3.2.2	Dehydrogenative Cross-coupling Reactions	139
4.3.2.3	Carbonylation and Related Transformations	143
4.3.2.4	Miscellaneous Transformations	144
4.3.3	Miscellaneous	146
4.4	Summary and Outlook	146
	Abbreviations	150
	References	151
5	Low-valent Cobalt Complexes in C–X Coupling and Related Reactions	163
	<i>Céline Dorval and Corinne Gosmini</i>	
5.1	Introduction	163
5.2	Cobalt-Catalysed Coupling Reactions with Stoichiometric Organometallic Reagents	163
5.2.1	Cobalt-Catalysed Coupling Reactions with <i>Grignard</i> Reagents	163
5.2.1.1	C _{sp²–C_{sp² Bond Formation}}	164
5.2.1.2	C _{sp²–C_{sp³ Bond Formation}}	168
5.2.1.3	C _{sp} –C _{sp² Bond Formation}	173
5.2.1.4	C _{sp} –C _{sp³ Bond Formation}	173
5.2.1.5	C _{sp³–C_{sp³ Bond Formation}}	175
5.2.2	Cobalt-Catalysed Coupling Reactions with Organozinc Reagents	179
5.2.2.1	C _{sp} –C _{sp²/C_{sp}–C_{sp³ Bond Formation}}	179
5.2.2.2	C _{sp²–C_{sp² Bond Formation}}	181
5.2.2.3	C _{sp²–C_{sp³ Bond Formation}}	183
5.2.2.4	C _{sp²–CN Bond Formation}	186
5.2.2.5	C _{sp²–CO Bond Formation}	186
5.2.3	Carbon–Heteroatom Bond Formation	187
5.2.3.1	C–N Bond Formation	187
5.2.3.2	C–B Bond Formation	188
5.2.4	Cobalt-Catalysed Coupling Reactions with Organoboron Reagents	188
5.3	Cobalt-Catalysed Coupling Reactions with Organomanganese Reagents	192
5.4	Cobalt-Catalysed Coupling Reactions with Copper Reagents	192
5.5	Cobalt-Catalysed Reductive Cross-coupling Reactions	193
5.5.1	C _{sp²–C_{sp² Bond Formation}}	193
5.5.2	C _{sp²–C_{sp³ Bond Formation}}	196
5.5.3	Couplings with Benzylic Compounds	196
5.5.4	Couplings with Allylic Acetates	197
5.5.5	C _{sp³–C_{sp³ Carbon Bond Forming Reactions}}	197
5.6	Overview and Perspectives	199
5.7	Abbreviations	200
	References	201

6	Ionic and Radical Reactions of π-Bonded Cobalt Complexes	207
	<i>Gagik G. Melikyan and Elen Artashyan</i>	
6.1	Introduction	207
6.2	Cobalt-Alkyne Complexes: Electrophilic Reactions	209
6.2.1	Intramolecular <i>Diels–Alder</i> Reactions	210
6.2.2	Assembling Tricyclic Ring Systems	211
6.2.3	Assembling Bicyclic Ring Systems: Decalines	212
6.2.4	Assembling Heterocyclic Ring Systems: Benzopyrans	212
6.2.5	Synthesis of Enediyne	213
6.2.6	Assembling Strained Ring Systems	213
6.2.7	Assembling Natural Carbon Skeletons	215
6.3	Cobalt-Alkyne Complexes: Radical Reactions	217
6.4	Cobalt-1,3-enyne Complexes: Electrophilic Reactions	226
6.5	Cobalt-1,3-enyne Complexes: Radical Reactions	228
6.6	Prospects	228
	Abbreviations	230
	References	230
7	Cobalt-Catalysed Cycloaddition Reactions	235
	<i>Gerhard Hilt</i>	
7.1	Introduction	235
7.2	Four-Membered Carbocyclic Ring Formation Reactions	235
7.2.1	[2+2] Cycloaddition of Two Alkenes	235
7.2.2	[2+2] Cycloaddition of an Alkene and an Alkyne	237
7.2.3	[2+2] Cycloaddition of Two Alkynes	238
7.3	Six-Membered Ring Formation Reactions	240
7.3.1	Cobalt-Catalysed <i>Diels–Alder</i> Reactions	240
7.3.2	Cobalt-Catalysed [2+2+2] Cycloaddition Reactions Other than Cyclotrimerisation of Alkynes	248
7.3.3	Cobalt-Catalysed Benzannulation Reactions	249
7.4	Synthesis of Larger Carbocyclic Ring Systems	250
7.4.1	[3+2+2] and [5+2] Cycloaddition Reaction	250
7.4.2	[6+2] Cycloaddition Reaction	251
7.5	Conclusions	253
	Abbreviations	255
	References	255
8	Recent Advances in the Pauson–Khand Reaction	259
	<i>David M. Lindsay and William J. Kerr</i>	
8.1	Introduction	259
8.2	Advances in the <i>Pauson–Khand</i> Reaction	259
8.2.1	New Methods to Promote the <i>Pauson–Khand</i> Reaction	259
8.2.1.1	Flow Chemistry Applications of the <i>Pauson–Khand</i> Reaction	260
8.2.1.2	New Promoters	261
8.2.2	Novel Substrates	264
8.2.2.1	Maleimides as Alkene Partners	264

8.2.2.2	Novel Enyne Substrates	265
8.2.2.3	Strained Reaction Partners	268
8.3	Asymmetric <i>Pauson–Khand</i> Reaction	269
8.4	Mechanistic and Theoretical Studies	273
8.5	Total Synthesis	276
8.5.1	Synthesis of (+)-Ingenol	276
8.5.2	Towards Retigeranic Acid A	277
8.5.3	The Total Synthesis of Astellatol	278
8.5.4	The Total Synthesis of 2- <i>epi</i> - α -Cedrene-3-one	279
8.6	Summary and Conclusions	280
8.7	Practical Procedures for Stoichiometric and Substoichiometric <i>Pauson–Khand</i> Reactions	281
	Abbreviations	282
	References	283
9	Cobalt-Catalysed [2+2+2] Cycloadditions	287
	<i>Tim Gläsel and Marko Hapke</i>	
9.1	Introduction	287
9.2	Reaction Mechanisms of Cobalt-Catalysed Cyclotrimerisations	288
9.3	Cobalt-Based Catalysts and Catalytic Systems	292
9.4	CpCo-Based Cyclisations	296
9.4.1	Carbocyclic Compounds	296
9.4.2	Heterocyclic Compounds	298
9.5	Non-CpCo-Based Cobalt-Catalysed Cyclisations	302
9.5.1	Co ₂ (CO) ₈ -Mediated Cyclisations of Carbocyclic Compounds	302
9.5.2	In Situ-Generated Catalysts and Precatalysts in Carbocyclisations of Alkynes	304
9.5.3	In Situ-Generated Catalysts in the Cyclisation of Alkynes to Heterocyclic Compounds	309
9.6	Cobalt-Mediated Asymmetric [2+2+2] Cycloadditions	313
9.7	Cobalt-Mediated Cyclisations in Natural Product Synthesis	317
9.8	Novel Developments of Cobalt-Mediated Cycloaddition Catalysis	322
9.9	Summary and Outlook	326
9.10	Selected Experimental Procedures	327
9.10.1	Synthesis of [CpCo(CO)(<i>trans</i> -MeO ₂ CCH=CHCO ₂ Me)] (PCAT5)	327
9.10.2	Synthesis of [CpCo(CO){P(OEt) ₃ }] and [CpCo(<i>trans</i> -MeO ₂ CCH=CHCO ₂ Me){P(OEt) ₃ }] (PCAT8)	327
	Abbreviations	328
	References	330
10	Enantioselective Cobalt-Catalysed Transformations	337
	<i>H. Pellissier</i>	
10.1	Introduction	337
10.2	Synthesis of Chiral Acyclic Compounds Through Enantioselective Cobalt-Catalysed Reactions	338

10.2.1	<i>Michael</i> and (Nitro)-Aldol Reactions	338
10.2.1.1	<i>Michael</i> Reactions	338
10.2.1.2	(Nitro)-Aldol Reactions	342
10.2.2	Reduction Reactions	346
10.2.2.1	Reductions of Carbonyl Compounds and Derivatives	346
10.2.2.2	Reductions of Alkenes	349
10.2.3	Ring-Opening Reactions	353
10.2.3.1	Hydrolytic Ring-Openings of Epoxides	353
10.2.3.2	Ring-Openings of Epoxides by Nucleophiles Other than Water	356
10.2.4	Hydrovinylation and Hydroboration Reactions	358
10.2.4.1	Hydrovinylations	358
10.2.4.2	Hydroborations	361
10.2.5	Cross-coupling Reactions	363
10.2.6	Miscellaneous Reactions	366
10.3	Enantioselective Cobalt-Catalysed Cyclisation Reactions	370
10.3.1	[2+1] Cycloadditions	370
10.3.2	Miscellaneous Cycloadditions	379
10.3.2.1	(Hetero)- <i>Diels–Alder</i> Cycloadditions	379
10.3.2.2	1,3-Dipolar Cycloadditions	380
10.3.2.3	Other Cycloadditions	383
10.3.3	Cyclisations Through Domino Reactions	386
10.3.4	Miscellaneous Cyclisations	390
10.4	Conclusions	395
	Abbreviations	396
	References	397
11	Cobalt Radical Chemistry in Synthesis and Biomimetic Reactions (Including Vitamin B₁₂)	417
	<i>Michał Ociepa and Dorota Gryko</i>	
11.1	Introduction	417
11.2	Cobalt-Mediated Reactions of Carbon-Centred Radicals	417
11.2.1	Homocoupling Reactions	418
11.2.2	Cross-coupling Reactions	420
11.2.3	Additions to Alkenes and Alkynes	423
11.2.4	Cyclisation Reactions	425
11.2.5	Dehalogenation	429
11.2.6	Oxidation	431
11.2.7	Acylation	433
11.2.8	Applications of Cobalt Complexes in Photoredox Catalysis	435
11.2.9	Miscellaneous Reactions	438
11.3	Cobalt-Mediated Reactions of Heteroatom-Centred Radicals	440
11.3.1	Nitrogen-Centred Radicals	440
11.3.2	Other Types of Radicals	441
11.4	Overview and Conclusion	442
11.5	Experimental Section	443
11.5.1	Synthesis of Chloro(pyridine)cobaloxime Co(dmgH) ₂ Cl(py) (116)	443

- 11.5.2 Synthesis of Aqua(cyano)heptamethyl Cobyrrinate
(**56b**) – Hydrophobic Vitamin B12 Model 444
- 11.5.3 General Procedure for Synthesis of Co(II)(salen) and Co(III)(salen)
Complexes 445
Abbreviations 445
References 446

Index 453