

Contents

Chapter 1	Theoretical Organometallic Chemistry	1
	<i>By Stuart A. Macgregor</i>	
1	Introduction	1
2	s-Block Metals	1
	2.1 Structural and Spectroscopic Studies	1
	2.2 Mechanistic Studies	3
3	p-Block Metals	5
	3.1 Structural and Spectroscopic Studies	5
	3.2 Mechanistic Studies	8
4	d- and f-Block Metals	9
	4.1 Structural and Spectroscopic Studies	9
	4.2 Mechanistic Studies	22
	References	29
Chapter 2	Group 1: The Alkali and Coinage Metals	42
	<i>By David J. Linton and Andrew E.H. Wheatley</i>	
1	Alkali Metals	42
	1.1 Introduction	42
	1.2 Alkyl Derivatives	42
	1.3 Alkenyl, Allyl, Vinyl, Alkynyl and Related Derivatives	48
	1.4 Aryl Derivatives	51
	1.5 Cyclopentadienyl and Related Derivatives	54
2	Copper, Silver and Gold	55
	2.1 Introduction	55
	2.2 Copper Compounds	55
	2.3 Silver Compounds	58
	2.4 Gold Compounds	59
	References	61

Chapter 3	Group 2 (Be–Ba) and Group 12 (Zn–Hg)	69
	<i>By Richard A. Layfield and Dominic S. Wright</i>	
1	Scope and Organisation of the Review	69
2	Group 2	69
3	Group 12	75
	References	82
Chapter 4	Scandium, Yttrium and the Lanthanides	85
	<i>By John G. Brennan and Andrea Sella</i>	
1	Introduction	85
2	New Compounds – Structure and Reactivity	85
2.1	Cp Compounds	85
2.2	Substituted Cp Ancillaries	87
2.3	Cp* Chemistry	89
2.4	Donor Cp Chemistry	91
2.5	Indene Chemistry	92
2.6	Linked Cp Chemistry	92
2.7	Naphthalide Complexes	94
2.8	COT Chemistry	94
2.9	Miscellaneous Ancillary Ligands	95
3	Polymerization Catalysis	101
4	Applications to Organic Synthesis	104
5	Theoretical and Spectroscopic Studies	106
5.1	Computational Studies	106
5.2	Spectroscopic Studies	108
5.3	Gas Phase Chemistry	108
	References	109
Chapter 5	Carboranes, Including Their Metal Complexes	115
	<i>By Andrew S. Weller</i>	
1	Introduction	115
2	Theoretical Chemistry	116
3	Carboranes	116
3.1	{CB ₉ } and {CB ₁₁ }	116
3.2	{C ₂ B ₂ } and {C ₂ B ₆ } and {C ₂ B ₈ }	117
3.3	{C ₃ B ₈ } and {C ₄ B ₈ }	117
3.4	{C ₆ B ₆ } and {C ₅ B ₇ }	117
3.5	{C ₂ B ₉ }	117
3.6	{C ₂ B ₁₀ }	118

4	Metallacarbaboranes	119
4.1	{MC ₂ B ₄ }	119
4.2	{MC ₃ B ₈ }	120
4.3	{MC ₂ B ₉ }	120
4.4	{ <i>exo</i> -MC ₂ B ₉ }	121
4.5	{MCB ₁₀ }	121
4.6	{MC ₂ B ₁₀ }	122
4.7	{ <i>exo</i> -MC ₂ B ₁₀ }	122
5	Complexes with Sn and Si	123
	References	124
Chapter 6	Group 13: Boron, Aluminium, Gallium, Indium and Thallium	127
	<i>By Matthew J. Almond</i>	
1	Boron	127
1.1	General	127
1.2	Compounds Incorporating the B(C ₆ F ₅) ₃ Moiety	127
1.3	Compounds Containing Nitrogen or Phosphorus Atoms	129
1.4	Compounds Containing Oxygen Atoms	130
1.5	Compounds Containing Metal Atoms	131
2	Aluminium	134
2.1	General	134
2.2	Compounds Containing Group 15 Atoms	135
2.3	Compounds Containing Group 16 Atoms	140
2.4	Compounds Containing Another Metal Atom	142
3	Gallium	143
3.1	General	143
3.2	Compounds Containing Group 15 or 16 Atoms	144
3.3	Compounds Containing Another Metal Atom	146
4	Indium	147
	References	149
Chapter 7	Group 15: Phosphorus, Arsenic, Antimony and Bismuth	153
	<i>By Cameron Jones</i>	
1	Phosphorus	153
2	Arsenic, Antimony and Bismuth	160
	References	165

Chapter 8	Organic Aspects of Organometallic Chemistry	170
	<i>By Christopher G. Frost and Michael C. Willis</i>	
1	Introduction	170
2	Coupling Reactions	170
	2.1 Cross-coupling Reactions	170
	2.2 Allylic Substitution	175
3	Carbonylation Reactions	178
	3.1 Pauson-Khand and Related Reactions	179
4	Organometallic Methods of C–C Bond Formation	180
	4.1 Metathesis Reactions	180
	4.2 Diazo-carbenoid Chemistry	185
	4.3 1,2- and 1,4-Addition Reactions	187
	4.4 C–H and C–C Bond Activation	190
	4.5 Multi-component Cyclisations	191
5	Oxidative and Reductive Processes	192
	5.1 Oxidation Reactions	192
	5.2 Reduction Reactions	194
6	Lewis Acid Mediated Processes	196
7	Emerging Areas	200
	7.1 High-throughput Catalyst Identification	200
	7.2 Non-traditional Solvents in Organometallic Transformations	200
	References	203
Chapter 9	Metal Carbonyls	207
	<i>By John A. Timney</i>	
1	Introduction	207
2	Reviews	208
3	Theoretical, Spectroscopic and General Studies	208
	3.1 Theoretical Studies	208
	3.2 Spectroscopic Studies	209
	3.3 General Studies	211
4	Chemistry of the Metal Carbonyls	212
	4.1 Titanium, Zirconium and Hafnium	212
	4.2 Vanadium, Niobium and Tantalum	212
	4.3 Chromium, Molybdenum and Tungsten	212
	4.4 Manganese, Technetium and Rhenium	214

<i>Contents</i>		xi
4.5	Iron, Ruthenium and Osmium	216
4.6	Cobalt, Rhodium and Iridium	218
4.7	Nickel, Palladium and Platinum	219
4.8	Copper, Silver and Gold	220
4.9	Carbonyl Complexes Containing Two or More Different Metal Atoms	220
	References	221
Chapter 10	Complexes Containing Metal–Carbon σ-Bonds of the Groups Titanium to Manganese, Including Carbenes and Carbynes <i>By Patrick C. McGowan, Elizabeth M. Page, Michael K. Whittlesey and Jason M. Lynam</i>	
	Part I: Group 4, <i>By Patrick C. McGowan</i>	227
	References	253
	Part II: Group 5, <i>By Elizabeth M. Page</i>	256
1	Reviews	256
2	Alkyl Complexes	256
3	Alkylidene Complexes	257
4	Alkyne Complexes	260
5	Butadiene and Similar Complexes	263
6	Imido Complexes	264
7	Other Complexes	266
	References	268
	Part III: Group 6, <i>By Michael K. Whittlesey</i>	269
	References	275
	Part IV: Group 7, <i>By Jason M. Lynam</i>	278
	References	287
Chapter 11	Organo-Transition Metal Cluster Compounds <i>By Mark G. Humphrey and Marie P. Cifuentes</i>	289
1	Introduction	289

2	General Reviews	289
3	Spectroscopic Studies	289
3.1	IR	289
3.2	NMR	290
3.3	MS	290
3.4	Theory	290
4	Structural Studies	291
5	Large Clusters	291
6	Group 4	295
7	Group 5	295
8	Group 6	295
8.1	Chromium	295
8.2	Molybdenum and Tungsten	295
9	Group 7	296
9.1	Manganese	296
9.2	Rhenium	296
10	Group 8	297
10.1	General	297
10.2	Iron	298
10.3	Ruthenium	300
10.4	Osmium	310
10.5	Mixed-metal Clusters Containing Only Group 8 Metals	315
11	Group 9	316
11.1	Cobalt	316
11.2	Rhodium and Iridium	318
11.3	Mixed-metal Clusters Containing Only Group 9 Metals	318
12	Group 10	319
12.1	Nickel	319
12.2	Palladium	319
12.3	Platinum	320
13	Group 11	320
13.1	Copper	320
13.2	Silver	321
13.3	Gold	322
13.4	Mixed-metal Clusters Containing Only Group 11 Metals	323
14	Group 12	323
15	Mixed-metal Clusters	323

<i>Contents</i>		xiii
	15.1 Group 4	324
	15.2 Group 5	324
	15.3 Group 6	324
	15.4 Group 7	328
	15.5 Group 8	329
	15.6 Group 9	335
	15.7 Group 10	336
	15.8 Compounds Containing Three Different Metals	336
	References	338
Chapter 12	Complexes Containing Metal–Carbon σ-Bonds of the Groups Iron, Cobalts and Nickel, Including Carbenes and Carbynes	350
	<i>By Michael K. Whittlesey</i>	
	1 Reviews and Articles of General Interest	350
	2 Metal–Carbon σ -Bonds Involving Group 8, 9 and 10 Metals	350
	2.1 The Iron Triad	350
	2.2 The Cobalt Triad	359
	2.3 The Nickel Triad	365
	3 Carbene and Carbyne Complexes of Groups 8, 9 and 10	371
	References	375
Chapter 13	Hydrocarbon Transition Metal π-Complexes other than η-C₅H₅ and η-Arene Complexes	384
	<i>By Kevin R. Flower</i>	
	1 Introduction	384
	2 Reviews	384
	3 Complexes Containing Allyls or Monoalkenes	385
	3.1 Cr, Mo, W	385
	3.2 Fe, Ru, OS	387
	3.3 Co, Rh, Ir	390
	3.4 Ni, Pd, Pt	392
	3.5 Other Metals	396
	4 Complexes Containing Unconjugated Alkenes	399
	5 Complexes Containing Cyclic Conjugated Alkenes	403
	5.1 Cr, Mo, W	404
	5.2 Fe, Ru, Os	405
	5.3 Other Metals	406

6	Complexes Containing Acyclic Alkenes	408
7	Complexes Containing Alkynes	411
8	Polymetallic Complexes	413
8.1	Bimetallic Complexes	413
8.2	Multimetallic Complexes	419
8.3	Ferrocenyl Containing Complexes	423
	References	424
Chapter 14	Transition Metal Complexes of Cyclopentadienyl Ligands <i>By Ian R. Butler</i>	442
1	General Introduction	442
2	Main Group, Lanthanides and Actinides	443
3	Titanium, Zirconium and Hafnium	445
4	Vanadium, Niobium and Tantalum	449
5	Chromium, Molybdenum and Tungsten	450
6	Manganese and Rhenium	452
7	Iron, Ruthenium and Osmium	453
7.1	Ferrocenylphosphine Ligand Chemistry	457
7.2	Ferrocenophanes	458
7.3	Materials	458
8	Cobalt, Rhodium and Iridium	465
9	Nickel, Palladium and Platinum	467
	References	468
	Author Index	479