

Contents

Preface to the Third Edition	<i>V</i>
Preface to the First Edition	<i>VII</i>
Introduction	
1	Milestones in Organometallic Chemistry 3
2	Organoelement Compounds: Classification and Electronegativity Considerations 11
3	Energy, Polarity, and Reactivity of the M–C Bond 15
3.1	Stability of Main-Group Organometallic Compounds 15
3.2	Lability of Main-Group Organometallic Compounds 17
	Excursion 1: Where does our knowledge of M–C bond energies come from? 19
Main-Group Organometallics	
4	Overview of Preparation Methods 27
5	Organometallic Chemistry of Alkali Metals (Group 1) 33
5.1	Organolithium Compounds 33
	Excursion 2: ^6Li and ^7Li NMR Spectroscopy of Organolithium Compounds 39
5.2	Organometallic Compounds of the Heavier Alkali Metals 50
	Excursion 3: EPR Spectroscopy of Organoalkali-Metal Compounds 55
6	Organometallic Compounds of Groups 2 and 12 59
6.1	Organometallic Compounds of the Alkaline-Earth Metals (Group 2) 59
6.1.1	Organoberyllium Compounds 59
6.1.2	Organomagnesium Compounds 62
6.1.3	Organocalcium, -strontium, and -barium Compounds 70

6.2	Organometallic Compounds of Zn, Cd, Hg (Group 12)	73
6.2.1	Organozinc Compounds	73
6.2.2	Organocadmium Compounds	77
6.2.3	Organomercury Compounds	78
	Excursion 4: Organomercury Compounds in vivo	82
7	Organometallic Compounds of the Boron Group (Group 13)	87
7.1	Organoboron Compounds	87
7.1.1	Organoboranes	87
7.1.2	Organoboron–Transition–Metal Compounds	93
7.1.3	Boron Heterocycles	94
7.1.4	Polyhedral Boranes, Carbaboranes, and Heterocarbaboranes	99
	Excursion 5: ^{11}B NMR Spectroscopy of Organoboron Compounds	108
7.2	Organoaluminum Compounds	110
7.2.1	Organoaluminum ^{III} Compounds	111
7.2.2	Subvalent Organoaluminum Compounds	123
7.3	Gallium, Indium, and Thallium Organyls	126
7.3.1	Ga ^{III} , In ^{III} , and Tl ^{III} Organyls and their Lewis Base Adducts	126
7.3.2	Ga ^{II,I} , In ^{II,I} , and Tl ^{II,I} Organyls	129
7.3.3	Thallium in Organic Synthesis	136
8	Organoelement Compounds of the Carbon Group (Group 14)	139
8.1	Organosilicon Compounds	142
8.1.1	Silicon Organyls of Coordination Number 4	142
8.1.2	Organosilicon Compounds with Coordination Numbers 3, 2, and 1 and Their Subsequent Products	153
8.2	Organogermanium Compounds	171
8.2.1	Germanium Organyls of Coordination Number 4	171
8.2.2	Organogermanium Compounds with Coordination Numbers 3, 2, and 1 and Their Subsequent Products	175
8.3	Organotin Compounds	179
	Excursion 6: ^{119}Sn Mössbauer and ^{119}Sn NMR Spectroscopy	179
8.3.1	Organotin Compounds with Coordination Numbers 6, 5, and 4 and Their Subsequent Products	182
8.3.2	Organotin Compounds with Coordination Numbers 3, 2, and 1 and Their Subsequent Products	191
8.4	Organolead Compounds	198
8.4.1	Pb ^{IV} Organyls	199
8.4.2	Pb ^{III} , Pb ^{II} , and Pb ^I Organyls	203
9	Organoelement Compounds of the Nitrogen Group (Group 15)	211
9.1	E ^V Organyls (E = As, Sb, Bi)	212
9.1.1	Pentaorganoelement Compounds R ₅ E	212
9.1.2	Organoelement Derivatives R _n EX _{5-n}	215
9.2	E ^{III} Organyls (E = As, Sb, Bi)	217

9.2.1	Trisorganoelement Compounds R_3E	218
9.2.2	Organoelement Derivatives R_nEX_{3-n}	221
9.3	Chains and Rings Containing E–E Single Bonds	224
9.4	E (P, As, Sb, Bi) as Partners in Multiple Bonds	229
9.4.1	$E=C(p_\pi-p_\pi)$ Bonds	229
9.4.2	$E\equiv C(p_\pi-p_\pi)$ Bonds	232
9.4.3	$E=E(p_\pi-p_\pi)$ Bonds	235
9.4.3	$E\equiv E((p_\pi-p_\pi))$ Bonds	237
10	Organoelement Compounds of Selenium and Tellurium (Group 16)	239
11	Organometallic Compounds of Copper, Silver, and Gold (Group 11)	249
11.1	Copper and Silver Organyls	249
11.2	Gold Organyls	262
Organometallic Compounds of the Transition Metals		
12	Introduction	275
12.1	The 18 Valence Electron (18 VE) Rule	276
	Excursion 7: Can the VSEPR concept be applied to transition-metal complexes?	282
12.2	Organometallic Catalysis: Some Fundamental Principles	284
13	σ-Donor Ligands	291
13.1	Preparation of Transition-Metal–Alkyl and –Aryl Compounds	292
13.2	Selected Properties of Transition-Metal σ -Organyls	295
13.2.1	Thermodynamic Stability versus Kinetic Lability	295
13.2.2	Interactions of C–H σ Bonds with Transition Metals	299
13.2.3	Interaction of C–C σ Bonds with Transition Metals	308
13.2.4	Transition-Metal Perfluorocarbon σ Complexes	312
13.3	Transition-Metal Organyls In Vivo	315
14	σ-Donor/π-Acceptor Ligands	329
14.1	Transition-Metal–Alkenyl, –Aryl, and –Alkynyl Complexes	329
14.2	Transition-Metal Carbene Complexes	333
14.3	Transition-Metal–Carbyne Complexes	350
14.4	Metal Carbonyls	356
14.4.1	Preparation, Structure, and Properties	357
14.4.2	Variants of CO Bridging	360
14.4.3	Bonding Properties and Experimental Evidence	363
14.4.4	Principal Reaction Types	372
14.4.5	Carbonyl Metalates and Carbonyl Metal Hydrides	375
14.4.6	Carbonyl Metal Halides	378

14.5	Thio-, Seleno-, and Tellurocarbonyl Metal Complexes	379
14.6	Isocyanide Complexes (Metal Isonitriles)	381
	Excursion 8: Photochemistry of Organometallic Compounds	383
15	σ, π-Donor/π-Acceptor Ligands	395
15.1	Olefin Complexes	395
15.1.1	Homoalkene Complexes	395
15.1.2	Heteroalkene Complexes	413
15.1.3	Homo- and Heteroallene Complexes	415
15.2	Alkyne Complexes	424
15.2.1	Homoalkyne Complexes	425
15.2.2	Heteroalkyne Complexes	435
15.3	Allyl and Enyl Complexes	436
15.3.1	Allyl Complexes	436
15.3.2	Dienyl and Trienyl Complexes	445
	Excursion 9: NMR Spectroscopy of Organometallic Compounds	451
15.4	Complexes of the Cyclic π -Perimeters C_nH_n	478
15.4.1	$C_3R_3^+$ as a Ligand	479
15.4.2	C_4H_4 as a Ligand	480
15.4.3	$C_5H_5^-$ as a Ligand	484
15.4.3.1	Binary Cyclopentadienyl–Metal Complexes	486
15.4.3.2	Cyclopentadienyl Metal Carbonyls	507
15.4.3.3	Cyclopentadienyl Metal Nitrosyls	511
15.4.3.4	Cyclopentadienyl Metal Hydrides	512
15.4.3.5	Cyclopentadienyl Metal Halides and Their Products	514
15.4.3.6	Special Applications of Metallocene Derivatives	518
15.4.4	C_6H_6 as a Ligand	528
15.4.4.1	Bis(arene)metal Complexes	528
15.4.4.2	Arene Metal Carbonyls	539
15.4.4.3	Other Complexes of the Type $(\eta^6\text{-Arene})ML_n$	543
15.4.4.4	Benzene Cyclopentadienyl Complexes	544
	Excursion 10: Organometallic Chemistry of Fullerenes	546
15.4.5	C_7H_7 as a Ligand	549
15.4.6	C_8H_8 as a Ligand	555
15.5	Metal– π -Complexes of Heterocycles	560
15.5.1	S, Se, and Te Heterocycles	561
15.5.2	N Heterocycles	561
15.5.3	P and As Heterocycles	564
15.5.4	B Heterocycles	570
15.5.5	Metallaheterocycles	576
16	Metal–Metal Bonds and Transition-Metal-Atom Clusters	579
16.1	Formation of and Criteria for Metal–Metal Bonds	579
16.2	Dinuclear Clusters	584
16.3	Trinuclear Clusters	587

- 16.4 Tetranuclear Clusters 588
Excursion 11: Structure and Bonding in Clusters – The Isolobal Analogy 590
- 16.5 Approaches to Systematic Cluster Synthesis 595
- 16.6 Pentanuclear and Higher Clusters 599
- 17 Organometallic Chemistry of the Lanthanoids and Actinoids 609**
- 17.1 Comparative Considerations 610
- 17.2 Tour of the Ligands 614
- 18 Organometallic Catalysis in Synthesis and Production 635**
- 18.1 Olefin Isomerization 635
- 18.2 C–C Coupling Reactions 637
- 18.2.1 Allylic Alkylation 638
Excursion 12: Asymmetric Allylic Alkylation 640
- 18.2.2 The Heck Reaction 642
- 18.2.3 The Suzuki Reaction 645
- 18.2.4 The Stille Reaction 649
- 18.2.5 The Sonogashira Reaction 651
- 18.2.6 Hydrocyanation 652
- 18.3 C–Heteroatom Coupling 654
- 18.3.1 Amination of Arenes 654
- 18.3.2 Hydroamination 657
- 18.3.3 Hydroboration 658
- 18.3.4 Hydrosilation 659
- 18.4 Olefin Oxidation 660
- 18.5 Water-Gas-Shift and Fischer–Tropsch Reactions 665
- 18.6 Carbonylation of Alcohols 669
- 18.7 Hydrogenation of Alkenes 670
- 18.8 Hydroformylation 676
- 18.9 Reppe Syntheses 679
- 18.10 Alkene and Alkyne Metathesis 682
- 18.10.1 Alkene Metathesis 682
- 18.10.2 Alkyne Metathesis 688
- 18.10.3 Alkene–Alkyne Metathesis 689
- 18.11 Oligomerization and Polymerization of Alkenes and Alkynes 691
- 18.11.1 Oligomerizations 692
- 18.11.2 Olefin Polymerization 695
- 18.11.2.1 Polyethylene 697
- 18.11.2.2 Polypropylene 699
- 18.11.2.3 Homo- and Copolymerization; Functionalized Olefins, Cycloolefins, and Diolefins 706
- 18.11.2.4 Non-Group 4 Catalysts 709
- 18.11.2.4.1 Lanthanoidocene Catalysts 709
- 18.11.2.4.2 The Iron Age of Olefin Polymerization 710

Appendix	717	
A-1	Redox Reagents in Organometallic Chemistry	717
A-2	Nomenclature of Organometallic Compounds	721
A-3	Abbreviations and Symbols	726
A-4	Literature	732
Author Index	761	
Subject Index	783	