

**Volume 1:  
Compounds with Transition Metal–Carbon  $\pi$ -Bonds  
and Compounds of groups 10–8 (Ni, Pd, Pt, Co, Rh,  
Ir, Fe, Ru, Os)**

|              |   |     |
|--------------|---|-----|
|              | <b>Preface</b> .....  | V   |
|              | <b>Table of Contents</b> .....                                | IX  |
|              | <b>Introduction</b>   |     |
|              | M. Lautens .....  | 1   |
| <b>1.1</b>   | <b>Product Class 1: Organometallic Complexes of Nickel</b>    |     |
|              | J. Montgomery .....   | 11  |
| <b>1.2</b>   | <b>Product Class 2: Organometallic Complexes of Palladium</b> |     |
| <b>1.2.1</b> | <b>Product Subclass 1: Palladium–Diene Complexes</b>          |     |
|              | J. M. Takacs, X. Jiang, and S. Vayalakkada .....              | 63  |
| <b>1.2.2</b> | <b>Product Subclass 2: Palladium–Allyl Complexes</b>          |     |
|              | R. W. Friesen .....   | 113 |
| <b>1.2.3</b> | <b>Product Subclass 3: Palladium–Alkyne Complexes</b>         |     |
|              | J. M. Takacs, S. Vayalakkada, and X. Jiang .....              | 265 |
| <b>1.2.4</b> | <b>Product Subclass 4: Palladium–Alkene Complexes</b>         |     |
|              | J. M. Takacs and S. Vayalakkada .....                         | 319 |
| <b>1.3</b>   | <b>Product Class 3: Organometallic Complexes of Platinum</b>  |     |
|              | A. Ogawa and T. Hirao .....                                   | 389 |
| <b>1.4</b>   | <b>Product Class 4: Organometallic Complexes of Cobalt</b>    |     |
|              | M. Malacria, C. Aubert, and J.-L. Renaud .....                | 439 |
| <b>1.5</b>   | <b>Product Class 5: Organometallic Complexes of Rhodium</b>   |     |
|              | I. Ojima, A. T. Vu, and D. Bonafoux .....                     | 531 |
| <b>1.6</b>   | <b>Product Class 6: Organometallic Complexes of Iridium</b>   |     |
|              | J. M. O'Connor .....  | 617 |

|              |   |      |
|--------------|---|------|
| <b>1.7</b>   | <b>Product Class 7: Organometallic Complexes of Iron</b>      |      |
| <b>1.7.1</b> | <b>Product Subclass 1: Iron–Arene Complexes</b>               |      |
|              | G. R. Stephenson .....  | 749  |
| <b>1.7.2</b> | <b>Product Subclass 2: Iron–Dienyl Complexes</b>              |      |
|              | G. R. Stephenson .....  | 755  |
| <b>1.7.3</b> | <b>Product Subclass 3: Iron–Diene Complexes</b>               |      |
|              | G. R. Stephenson .....  | 778  |
| <b>1.7.4</b> | <b>Product Subclass 4: Iron–Allyl Complexes</b>               |      |
|              | G. R. Stephenson .....  | 826  |
| <b>1.7.5</b> | <b>Product Subclass 5: Iron–Alkene Complexes</b>              |      |
|              | G. R. Stephenson .....  | 839  |
| <b>1.7.6</b> | <b>Product Subclass 6: Iron–Carbene Complexes</b>             |      |
|              | G. R. Stephenson .....  | 846  |
| <b>1.7.7</b> | <b>Product Subclass 7: Iron–Alkyl Complexes</b>               |      |
|              | G. R. Stephenson .....  | 853  |
| <b>1.7.8</b> | <b>Product Subclass 8: Ferrocenes</b>                         |      |
|              | M. Perseghini and A. Togni .....                              | 889  |
| <b>1.8</b>   | <b>Product Class 8: Organometallic Complexes of Ruthenium</b> |      |
|              | N. Chatani .....  | 931  |
| <b>1.9</b>   | <b>Product Class 9: Organometallic Complexes of Osmium</b>    |      |
|              | J. Gonzalez and W. D. Harman .....                            | 981  |
|              | <b>Keyword Index</b> .....                                    | 1017 |
|              | <b>Author Index</b> .....                                     | 1055 |
|              | <b>Abbreviations</b> .....                                    | 1107 |

## Table of Contents

|                  |   |    |
|------------------|---|----|
|                  | <b>Introduction</b>   |    |
|                  | M. Lautens  |    |
|                  | <b>Introduction</b> .....   | 1  |
| <b>1.1</b>       | <b>Product Class 1: Organometallic Complexes of Nickel</b>  |    |
|                  | J. Montgomery   |    |
| <b>1.1</b>       | <b>Product Class 1: Organometallic Complexes of Nickel</b> .....  | 11 |
| <b>1.1.1</b>     | <b>Product Subclass 1: Nickel Complexes of 1,3-Dienes</b> .....   | 12 |
|                  | Synthesis of Product Subclass 1 .....   | 12 |
| <b>1.1.1.1</b>   | Method 1: Ligand Exchange with Bis( $\eta^4$ -cycloocta-1,5-diene)nickel(0) ...                                       | 12 |
|                  | Applications of Product Subclass 1 in Organic Synthesis .....   | 13 |
| <b>1.1.1.2</b>   | Method 2: Diene–Diene Cycloadditions .....  | 13 |
| <b>1.1.1.3</b>   | Method 3: Diene–Alkyne Cycloadditions .....   | 14 |
| <b>1.1.1.4</b>   | Method 4: Diene–Aldehyde Reductive Cyclizations .....   | 15 |
| <b>1.1.1.4.1</b> | Variation 1: Triethylsilane-Mediated Reactions .....  | 15 |
| <b>1.1.1.4.2</b> | Variation 2: Triethylborane-Mediated Reactions .....  | 16 |
| <b>1.1.1.5</b>   | Method 5: 1,4-Dialkylation of Dienes .....  | 16 |
| <b>1.1.1.6</b>   | Method 6: Hydrocyanation of Dienes .....  | 17 |
| <b>1.1.2</b>     | <b>Product Subclass 2: Nickel–Allyl Complexes</b> .....   | 17 |
|                  | Synthesis of Product Subclass 2 .....   | 17 |
| <b>1.1.2.1</b>   | Method 1: Oxidative Addition of Nickel(0) with Allylic Electrophiles .....  | 17 |
| <b>1.1.2.2</b>   | Method 2: Addition of Allylmagnesium Halides to Nickel(II) Salts .....  | 18 |
| <b>1.1.2.3</b>   | Method 3: Oxidative Addition of Nickel(0) with Enones in<br>the Presence of Lewis Acids .....                         | 19 |
| <b>1.1.2.4</b>   | Method 4: Oxidative Cyclization of Nickel(0) Complexes of<br>Conjugated Dienes .....                                  | 20 |
|                  | Applications of Product Subclass 2 in Organic Synthesis .....   | 21 |
| <b>1.1.2.5</b>   | Method 5: Coupling of Allyl Halide Derived Nickel–Allyl Complexes<br>with Alkyl Halides and Other Electrophiles ..... | 21 |
| <b>1.1.2.6</b>   | Method 6: Coupling of Enal-Derived Nickel–Allyl Complexes<br>with Alkyl Halides and Other Electrophiles .....         | 22 |
| <b>1.1.2.7</b>   | Method 7: Coupling of Nickel–Allyl Complexes with<br>Main Group Organometallics .....                                 | 24 |
| <b>1.1.2.7.1</b> | Variation 1: Allylic Ether Derived $\pi$ -Allyl Complexes .....   | 24 |
| <b>1.1.2.7.2</b> | Variation 2: Enal-Derived $\pi$ -Allyl Complexes .....  | 26 |
| <b>1.1.2.7.3</b> | Variation 3: Allylic Alcohol Derived $\pi$ -Allyl Complexes .....   | 26 |

|           |              |   |    |
|-----------|--------------|---|----|
| 1.1.2.8   | Method 8:    | Addition of Stabilized Nucleophiles to Nickel–Allyl Complexes | 27 |
| 1.1.2.9   | Method 9:    | Alkyne Insertions with Nickel–Allyl Complexes                 | 27 |
| 1.1.2.10  | Method 10:   | Alkene Insertions with Nickel–Allyl Complexes                 | 29 |
| 1.1.3     |              | <b>Product Subclass 3: Nickel–Alkyne Complexes</b>            | 29 |
|           |              | Synthesis of Product Subclass 3                               | 30 |
| 1.1.3.1   | Method 1:    | Ligand Exchange with Nickel–Alkene Complexes                  | 30 |
|           |              | Applications of Product Subclass 3 in Organic Synthesis       | 31 |
| 1.1.3.2   | Method 2:    | Coupling of Alkynes with Carbon Dioxide                       | 31 |
| 1.1.3.3   | Method 3:    | Coupling of Alkynes with Isocyanides                          | 32 |
| 1.1.3.4   | Method 4:    | Coupling of Alkynes with Aldehydes                            | 32 |
| 1.1.3.5   | Method 5:    | Coupling of Two Alkynes                                       | 35 |
| 1.1.3.6   | Method 6:    | Coupling of Alkynes with Alkenes                              | 36 |
| 1.1.3.7   | Method 7:    | [2+2+2] Cycloadditions  | 38 |
| 1.1.3.8   | Method 8:    | Alkyne Carbonylation  | 40 |
| 1.1.3.9   | Method 9:    | Alkyne Hydrocyanation   | 40 |
| 1.1.3.10  | Method 10:   | Alkyne Hydrosilylation  | 40 |
| 1.1.3.11  | Method 11:   | Alkyne Carbozincation   | 41 |
| 1.1.4     |              | <b>Product Subclass 4: Nickel–Alkene Complexes</b>            | 42 |
|           |              | Synthesis of Product Subclass 4                               | 42 |
| 1.1.4.1   | Method 1:    | Ligand Exchange with Nickel(0) Complexes                      | 42 |
|           |              | Applications of Product Subclass 4 in Organic Synthesis       | 43 |
| 1.1.4.2   | Method 2:    | Conjugate Addition to Electrophilic Double Bonds              | 43 |
| 1.1.4.2.1 | Variation 1: | Organoaluminums   | 43 |
| 1.1.4.2.2 | Variation 2: | Organozincs   | 44 |
| 1.1.4.2.3 | Variation 3: | Organozirconiums  | 46 |
| 1.1.4.2.4 | Variation 4: | Direct Conjugate Addition of Alkyl Halides                    | 47 |
| 1.1.4.3   | Method 3:    | Coupling of Two Alkenes                                       | 48 |
| 1.1.4.4   | Method 4:    | Alkene Carbonylation  | 51 |
| 1.1.4.5   | Method 5:    | Alkene Hydrocyanation   | 52 |
| 1.1.4.6   | Method 6:    | Alkene Hydrosilylation  | 53 |
| 1.1.4.7   | Method 7:    | Alkene Hydroalumination                                       | 53 |
| 1.1.4.8   | Method 8:    | Alkene Hydrozincation   | 55 |
| 1.1.4.9   | Method 9:    | Alkene Carbozincation   | 56 |
| 1.1.4.10  | Method 10:   | Homo-Diels–Alder Cycloadditions                               | 57 |
| 1.1.4.11  | Method 11:   | Alkene Polymerization   | 57 |

|                  |  |     |
|------------------|--|-----|
| <b>1.2</b>       | <b>Product Class 2: Organometallic Complexes of Palladium</b>  |     |
| <b>1.2.1</b>     | <b>Product Subclass 1: Palladium–Diene Complexes</b><br>J. M. Takacs, X. Jiang, and S. Vayalakkada   |     |
| <b>1.2.1</b>     | <b>Product Subclass 1: Palladium–Diene Complexes</b> .....   | 63  |
|                  | Synthesis of Product Subclass 1 .....  | 64  |
| <b>1.2.1.1</b>   | Method 1: Preparation and Characterization of<br>Palladium–Diene Complexes .....   | 64  |
|                  | Applications of Product Subclass 1 in Organic Synthesis .....  | 65  |
| <b>1.2.1.2</b>   | Method 2: 1,3-Dienes: The 1,4-Addition of Nucleophiles .....   | 65  |
| <b>1.2.1.2.1</b> | Variation 1: The Oxidative Addition of Carbon Nucleophiles .....   | 67  |
| <b>1.2.1.2.2</b> | Variation 2: The Reductive Addition of Carbon Nucleophiles .....   | 69  |
| <b>1.2.1.2.3</b> | Variation 3: The Oxidative Addition of Oxygen Nucleophiles .....   | 70  |
| <b>1.2.1.2.4</b> | Variation 4: The Reductive Addition of Oxygen Nucleophiles .....   | 77  |
| <b>1.2.1.2.5</b> | Variation 5: The Addition of Nitrogen Nucleophiles .....   | 78  |
| <b>1.2.1.2.6</b> | Variation 6: The Reductive Addition of Sulfur Nucleophiles .....   | 79  |
| <b>1.2.1.2.7</b> | Variation 7: The Oxidative Carbonylation of 1,3-Dienes .....   | 80  |
| <b>1.2.1.2.8</b> | Variation 8: The Reductive Carbonylation of 1,3-Dienes .....   | 81  |
| <b>1.2.1.3</b>   | Method 3: Allenes: The Addition of Nucleophiles .....  | 82  |
| <b>1.2.1.3.1</b> | Variation 1: The Addition of Carbon and Hydrogen Across the Allene .....   | 83  |
| <b>1.2.1.3.2</b> | Variation 2: The Addition of Carbon and Silicon Across the Allene .....  | 88  |
| <b>1.2.1.3.3</b> | Variation 3: The Addition of Heteroatoms (i.e., O, N, S, or Se)<br>and Hydrogen Across the Allene .....                                      | 89  |
| <b>1.2.1.3.4</b> | Variation 4: The Addition of the Oxygen, Nitrogen,<br>or Carbon and Carbon Moiety Across the Allene .....                                    | 93  |
| <b>1.2.1.3.5</b> | Variation 5: The Addition of the Oxygen or Nitrogen and Halogen Moiety<br>Across the Allene .....  | 104 |
| <b>1.2.1.3.6</b> | Variation 6: The Addition of the Oxygen, Nitrogen, or Carbon and<br>Carbon Moiety via the Insertion of Carbon Monoxide or<br>an Alkene ..... | 105 |
| <b>1.2.2</b>     | <b>Product Subclass 2: Palladium–Allyl Complexes</b><br>R. W. Friesen  |     |
| <b>1.2.2</b>     | <b>Product Subclass 2: Palladium–Allyl Complexes</b> .....   | 113 |
|                  | Synthesis of Product Subclass 2 .....  | 115 |
| <b>1.2.2.1</b>   | Method 1: Transmetalation with Allyl Organometallics .....   | 115 |
| <b>1.2.2.1.1</b> | Variation 1: From Allylsilanes .....   | 115 |
| <b>1.2.2.1.2</b> | Variation 2: From Allylstannanes .....   | 116 |
| <b>1.2.2.1.3</b> | Variation 3: From Allylmercurials .....  | 117 |
| <b>1.2.2.1.4</b> | Variation 4: From Allyl Grignard Reagents .....  | 118 |

|            |              |  |     |
|------------|--------------|--|-----|
| 1.2.2.2    | Method 2:    | From Allylic Hydrogen Abstraction of Alkenes   | 118 |
| 1.2.2.2.1  | Variation 1: | Palladation of Unsaturated Esters  | 118 |
| 1.2.2.2.2  | Variation 2: | Palladation of $\beta$ -Oxo Esters and Diketene  | 119 |
| 1.2.2.2.3  | Variation 3: | Palladation of Unsaturated Ketones   | 120 |
| 1.2.2.2.4  | Variation 4: | Palladation of Unactivated Alkenes   | 121 |
| 1.2.2.3    | Method 3:    | Bridge Splitting   | 128 |
| 1.2.2.4    | Method 4:    | Palladation of 1,2-Dienes (Allenenes)  | 129 |
| 1.2.2.4.1  | Variation 1: | From Reaction of Allenenes and Palladium Salts   | 129 |
| 1.2.2.4.2  | Variation 2: | Insertion of Allenenes into Allylpalladium Complexes   | 131 |
| 1.2.2.5    | Method 5:    | Palladation of 1,3- and 1,4-Dienes   | 132 |
| 1.2.2.5.1  | Variation 1: | Hydropalladation of 1,3-Dienes   | 132 |
| 1.2.2.5.2  | Variation 2: | Heteropalladation of 1,3-Dienes  | 133 |
| 1.2.2.5.3  | Variation 3: | Methoxypalladation of Cyclic 1,4-Dienes  | 138 |
| 1.2.2.5.4  | Variation 4: | Insertion of 1,3-Dienes into Allylpalladium Complexes  | 139 |
| 1.2.2.5.5  | Variation 5: | Palladation of Dienol Silyl Ethers   | 140 |
| 1.2.2.5.6  | Variation 6: | Reaction of Dienes and Organomercurials with Palladium Salts   | 141 |
| 1.2.2.6    | Method 6:    | From Reaction of Allyl and Benzyl Halides  | 142 |
| 1.2.2.6.1  | Variation 1: | From Reaction with Allyl Halides   | 142 |
| 1.2.2.6.2  | Variation 2: | From Reaction with Benzyl Halides  | 145 |
| 1.2.2.7    | Method 7:    | Insertion of Palladium(0) into Allyloxy Derivatives  | 146 |
| 1.2.2.8    | Method 8:    | Palladation of Cyclopropane Derivatives  | 147 |
| 1.2.2.8.1  | Variation 1: | From Vinylcyclopropanes  | 147 |
| 1.2.2.8.2  | Variation 2: | From Methylene-cyclopropanes   | 149 |
| 1.2.2.8.3  | Variation 3: | From Cyclopropenes   | 150 |
| 1.2.2.9    | Method 9:    | Palladative Coupling of Vinyl Organometallics with Alkenes   | 151 |
| 1.2.2.9.1  | Variation 1: | Vinylpalladation of Alkenes Using Vinylmercurials  | 151 |
| 1.2.2.9.2  | Variation 2: | Palladative Dimerization of Vinylsilanes   | 152 |
| 1.2.2.10   | Method 10:   | Ligand Metathesis  | 153 |
|            |              | Applications of Product Subclass 2 in Organic Synthesis  | 154 |
| 1.2.2.11   | Method 11:   | Allylsilanes from Reaction of Allylpalladium Complexes and Disilanes                                       | 157 |
| 1.2.2.12   | Method 12:   | Allylsilanes from Allylic Esters and Chlorides   | 158 |
| 1.2.2.12.1 | Variation 1: | Via Reaction with (Trialkylsilyl)aluminum Reagents   | 158 |
| 1.2.2.12.2 | Variation 2: | Via Palladium-Catalyzed Electroreductive Cleavage and Reaction with Trialkylchlorosilanes                  | 159 |
| 1.2.2.12.3 | Variation 3: | Via Reaction with Disilanes  | 159 |
| 1.2.2.13   | Method 13:   | Allylsilanes from Reduction of Allylic Carbonates  | 162 |
| 1.2.2.14   | Method 14:   | Allylsilanes from Hydrosilylation of 1,3-Dienes with Silanes   | 162 |
| 1.2.2.15   | Method 15:   | Allylstannanes from Allylic Acetates and Phosphates  | 163 |
| 1.2.2.15.1 | Variation 1: | Via Reaction with Trialkylstannylaluminates  | 163 |
| 1.2.2.15.2 | Variation 2: | Via Reaction with Trialkylchlorostannane and Samarium(II) Iodide   | 164 |
| 1.2.2.16   | Method 16:   | Allylmercurials from Reaction of Allylpalladium Complexes and Metallic Mercury                             | 165 |
| 1.2.2.17   | Method 17:   | $\alpha,\beta$ -Unsaturated Esters from Dehydrogenation of Saturated Esters via Their Ketene Silyl Acetals | 166 |

|            |              |   |     |
|------------|--------------|---|-----|
| 1.2.2.18   | Method 18:   | $\alpha,\beta$ -Unsaturated Nitriles from Decarboxylation of Allyl $\alpha$ -Cyanocarboxylates .....  | 167 |
| 1.2.2.19   | Method 19:   | $\beta,\gamma$ -Unsaturated Esters from Carbonylation of Allylpalladium Complexes .....   | 168 |
| 1.2.2.20   | Method 20:   | $\beta,\gamma$ -Unsaturated Esters from Carbonylation of Allylic Compounds .....  | 168 |
| 1.2.2.20.1 | Variation 1: | Via Allylic Carbonates .....  | 169 |
| 1.2.2.20.2 | Variation 2: | Via Allylic Esters .....  | 169 |
| 1.2.2.20.3 | Variation 3: | Via Allylic Phosphates .....  | 170 |
| 1.2.2.21   | Method 21:   | $\beta,\gamma$ -Unsaturated Nitriles from Cyanation of Allylic Carbonates and Acetates .....  | 171 |
| 1.2.2.22   | Method 22:   | $\gamma,\delta$ -Unsaturated Esters from Allylation of Ketene Silyl Acetals .....   | 172 |
| 1.2.2.23   | Method 23:   | Aldehydes and Ketones from Oxidation of Allyl Carbonates ..   | 173 |
| 1.2.2.24   | Method 24:   | $\alpha,\beta$ -Unsaturated Aldehydes and Ketones from Oxidation of Allylpalladium Complexes .....  | 173 |
| 1.2.2.25   | Method 25:   | $\alpha,\beta$ -Unsaturated Aldehydes and Ketones from Oxidation of Enol Derivatives .....  | 174 |
| 1.2.2.25.1 | Variation 1: | From Oxidation of Enol Carbonates .....   | 175 |
| 1.2.2.25.2 | Variation 2: | From Oxidation of Enol Acetates .....   | 176 |
| 1.2.2.25.3 | Variation 3: | From Oxidation of Silyl Enol Ethers .....   | 176 |
| 1.2.2.26   | Method 26:   | $\alpha,\beta$ -Unsaturated Ketones from Decarboxylation of Allyl $\beta$ -Oxocarboxylates .....  | 177 |
| 1.2.2.27   | Method 27:   | $\beta,\gamma$ -Unsaturated Ketones from Reaction of Allylpalladium Complexes with Acyliron or Acylnickel Carbanions .....                                  | 178 |
| 1.2.2.28   | Method 28:   | $\beta,\gamma$ -Unsaturated Aldehydes and Ketones from Carbonylation of Allyl Halides with Organostannanes .....  | 179 |
| 1.2.2.29   | Method 29:   | $\beta,\gamma$ -Unsaturated Ketones from Rearrangement of Cyclic Vinyl Epoxides .....   | 181 |
| 1.2.2.30   | Method 30:   | $\gamma,\delta$ -Unsaturated Ketones from Allylation of Enolates and Enolate Equivalents .....  | 181 |
| 1.2.2.31   | Method 31:   | $\gamma,\delta$ -Unsaturated Ketones from Decarboxylative Allylation of $\beta$ -Oxo Esters and Acids .....   | 184 |
| 1.2.2.31.1 | Variation 1: | Decarboxylative Allylation of Allyl $\beta$ -Oxocarboxylate Esters ..   | 184 |
| 1.2.2.31.2 | Variation 2: | Decarboxylative Alkylation of $\beta$ -Oxo Acids with Allylic Electrophiles .....   | 186 |
| 1.2.2.32   | Method 32:   | $\gamma,\delta$ -Unsaturated Aldehydes and Ketones from Rearrangement of Allyl Enol Carbonates .....  | 187 |
| 1.2.2.33   | Method 33:   | Allylic Esters from Allylic Acetoxylation of Alkenes .....  | 188 |
| 1.2.2.33.1 | Variation 1: | $\gamma$ -Acetoxy-( <i>E</i> )- $\alpha,\beta$ -Unsaturated Esters and Sulfones from Acetoxylation of $\beta,\gamma$ -Unsaturated Esters and Sulfones ..... | 188 |
| 1.2.2.33.2 | Variation 2: | Allylic Acetoxylation of Simple Alkenes .....   | 189 |
| 1.2.2.34   | Method 34:   | Allylic Esters from Allylpalladium Complexes .....  | 190 |
| 1.2.2.35   | Method 35:   | Allylic Esters from Reaction of Allyl Electrophiles with Carboxylate Anions .....   | 191 |

|            |              |  |     |
|------------|--------------|--|-----|
| 1.2.2.36   | Method 36:   | 4-Heterosubstituted 1-Acetoxyalk-2-enes from 1,3-Dienes  | 192 |
| 1.2.2.36.1 | Variation 1: | 1,4-Diacetoxyalk-2-enes from 1,4-Diacetoxylation of 1,3-Dienes   | 193 |
| 1.2.2.36.2 | Variation 2: | 1-Acetoxy-4-chloroalk-2-enes from 1,4-Acetoxychlorination of 1,3-Dienes  | 194 |
| 1.2.2.36.3 | Variation 3: | 1-Acetoxy-4-(trifluoroacetoxy)alk-2-enes from 1,4-Acetoxytrifluoroacetoxylation of 1,3-Dienes                            | 195 |
| 1.2.2.37   | Method 37:   | Allylic Acetates by Rearrangement  | 196 |
| 1.2.2.38   | Method 38:   | Allylic Ethers from Reaction of Allylic Electrophiles with Alcohols and Alkoxide Anions                                  | 197 |
| 1.2.2.39   | Method 39:   | Allylic Alcohols from Oxidation of Allylpalladium Complexes  | 198 |
| 1.2.2.40   | Method 40:   | Homoallylic Alcohols by Carbonyl Allylation with Allyl Organometallics Generated by Umpolung of Allylpalladium Complexes | 199 |
| 1.2.2.41   | Method 41:   | S-Allyl Phosphorothioates from Rearrangement of O-Allyl Phosphorothioates  | 201 |
| 1.2.2.42   | Method 42:   | Allylic Sulfones from Reaction of Allylic Electrophiles with Sulfinates  | 202 |
| 1.2.2.43   | Method 43:   | Allylic Sulfones from Hydrosulfination of Allenes and 1,3-Dienes   | 205 |
| 1.2.2.44   | Method 44:   | Allylic Sulfones from Rearrangement of O-Allyl Sulfinates  | 206 |
| 1.2.2.45   | Method 45:   | Allylic Sulfones from 1,3-Rearrangement of Allylic Sulfones  | 207 |
| 1.2.2.46   | Method 46:   | Unsaturated Sulfones from Protiodepalladation of [4-Sulfonyl-(1,2,3- $\eta$ )-alk-2-enyl]palladium Complexes             | 207 |
| 1.2.2.47   | Method 47:   | Allylic Sulfides from Reaction of Allylic Carbonates with Thiols   | 208 |
| 1.2.2.48   | Method 48:   | Allylic Amines from Amination of Allylpalladium Complexes  | 209 |
| 1.2.2.49   | Method 49:   | Allylic Amines from Amination of Allylic Electrophiles   | 210 |
| 1.2.2.49.1 | Variation 1: | Allylic Amination with Primary and Secondary Amines  | 211 |
| 1.2.2.49.2 | Variation 2: | Allylic Amination with Imides and Iminodicarbonates  | 213 |
| 1.2.2.49.3 | Variation 3: | Allylic Amination with Sulfonamides  | 215 |
| 1.2.2.49.4 | Variation 4: | Allylic Amination with Azide   | 216 |
| 1.2.2.50   | Method 50:   | Allylic Amines from Hydroamination of Allenes  | 217 |
| 1.2.2.51   | Method 51:   | 4-Vinyloxazolidin-2-ones from Vinyl Epoxides and But-2-ene-1,4-diols   | 219 |
| 1.2.2.51.1 | Variation 1: | From Vinyl Epoxides  | 219 |
| 1.2.2.51.2 | Variation 2: | From But-2-ene-1,4-diols   | 220 |
| 1.2.2.52   | Method 52:   | Homoallylic Amines by Imine Allylation with Allylstannanes   | 221 |
| 1.2.2.53   | Method 53:   | Allylic Phosphine Sulfides from Displacement of Allylic Carboxylates with Diphenylphosphorothioyllithium                 | 222 |
| 1.2.2.54   | Method 54:   | Allyl Arenes from Coupling of Allylic Electrophiles and Aryl Organometallics   | 222 |
| 1.2.2.54.1 | Variation 1: | From Tetrabutylammonium Difluorotriphenylsilicate  | 223 |
| 1.2.2.54.2 | Variation 2: | From Arylstannanes   | 223 |
| 1.2.2.54.3 | Variation 3: | From Sodium Tetraphenylborate  | 225 |
| 1.2.2.54.4 | Variation 4: | From Arylzincs   | 225 |
| 1.2.2.54.5 | Variation 5: | From Aryl Grignard Reagents  | 226 |
| 1.2.2.55   | Method 55:   | 1,3-Dienes from $\beta$ -Elimination of Allylic Alcohol Derivatives  | 227 |



|            |   |  |     |
|------------|---|--|-----|
| 1.2.2.56   | Method 56:  | 1,3-Dienes from Reductive Elimination of Dicarbonates of Ene-diols                               | 229 |
| 1.2.2.57   | Method 57:  | 1,3-Dienes from Decarboxylative Elimination of $\beta$ -Acetoxy Carboxylic Acids                 | 229 |
| 1.2.2.58   | Method 58:  | 1,4-Dienes from Coupling of Alkenylzirconiums and Allylpalladium Complexes                       | 230 |
| 1.2.2.59   | Method 59:  | 1,4-Dienes from Coupling of Vinyl Organometallics and Allyl Electrophiles                        | 231 |
| 1.2.2.59.1 | Variation 1:  | From Alkenylaluminum Reagents  | 231 |
| 1.2.2.59.2 | Variation 2:  | From Vinylstannanes  | 232 |
| 1.2.2.60   | Method 60:  | 1,5-Dienes from Coupling of Allylstannanes and Allyl Electrophiles                               | 234 |
| 1.2.2.61   | Method 61:  | 1,6-Dienes from Dimerization of Butadienes (Telomerization)                                      | 235 |
| 1.2.2.62   | Method 62:  | Methylenecyclopentenes via [3+2]-Cycloaddition Reactions of Trimethylenemethanes                 | 237 |
| 1.2.2.63   | Method 63:  | Vinylcyclopentanes via [3+2]-Cycloaddition Reactions of Vinylcyclopropanes                       | 240 |
| 1.2.2.64   | Method 64:  | Vinylcyclopentanes from Palladium-Catalyzed Intramolecular Ene Reactions                         | 241 |
| 1.2.2.65   | Method 65:  | Alkenes from Reduction of Allylic Heterosubstituents   | 243 |
| 1.2.2.66   | Method 66:  | 4-Substituted Alkenes from Alkylation of Stabilized Carbon Nucleophiles with Allyl Electrophiles | 245 |
| 1.2.3      | <b>Product Subclass 3: Palladium–Alkyne Complexes</b>   |  |     |
|            | J. M. Takacs, S. Vayalakkada, and X. Jiang              |  |     |
| 1.2.3      | <b>Product Subclass 3: Palladium–Alkyne Complexes</b>   |  | 265 |
|            | Synthesis of Product Subclass 3                         |  | 266 |
| 1.2.3.1    | Method 1:   | Preparation and Characterization of Palladium–Alkyne Complexes                                   | 266 |
|            | Applications of Product Subclass 3 in Organic Synthesis |  | 268 |
| 1.2.3.2    | Method 2:   | Addition of Oxygen Nucleophiles: Carboxylates  | 268 |
| 1.2.3.2.1  | Variation 1:  | Intramolecular Addition of Carboxylates Followed by Protonation                                  | 269 |
| 1.2.3.2.2  | Variation 2:  | Intramolecular Addition of Carboxylates Followed by Allylation                                   | 272 |
| 1.2.3.2.3  | Variation 3:  | Intramolecular Addition of Carboxylates Followed by Arylation or Vinylation                      | 274 |
| 1.2.3.3    | Method 3:   | Addition of Oxygen Nucleophiles: Hydroxy Moieties  | 276 |
| 1.2.3.3.1  | Variation 1:  | Intramolecular Addition of Alcohols Followed by Protonation                                      | 277 |
| 1.2.3.3.2  | Variation 2:  | Intramolecular Addition of Alcohols Followed by Carbon Monoxide Insertion                        | 280 |
| 1.2.3.3.3  | Variation 3:  | Intramolecular Addition of Alcohols Followed by Allylation                                       | 282 |

|           |   |   |     |
|-----------|---|---|-----|
| 1.2.3.3.4 | Variation 4:  | Intramolecular Addition of Alcohols Followed by<br>Vinylolation or Arylation .....  | 284 |
| 1.2.3.4   | Method 4:   | Addition of Nitrogen Nucleophiles .....   | 287 |
| 1.2.3.4.1 | Variation 1:  | Intramolecular Addition of Nitrogen Nucleophiles<br>Followed by Protonation .....   | 288 |
| 1.2.3.4.2 | Variation 2:  | Intramolecular Addition of Nitrogen Nucleophiles<br>Followed by Allylation .....  | 291 |
| 1.2.3.4.3 | Variation 3:  | Intramolecular Addition of Nitrogen Nucleophiles<br>Followed by Vinylolation or Arylation .....                           | 294 |
| 1.2.3.4.4 | Variation 4:  | Intramolecular Addition of Nitrogen Nucleophiles<br>Followed by Vinyl or Aryl Carbonylation .....                         | 297 |
| 1.2.3.5   | Method 5:   | Addition of Carbon Nucleophiles .....   | 298 |
| 1.2.3.5.1 | Variation 1:  | Intramolecular Addition of Malononitriles to Alkynes<br>under Neutral Conditions .....                                    | 299 |
| 1.2.3.5.2 | Variation 2:  | Tandem Michael Addition Followed by Intramolecular<br>Addition of Malonate Derivatives to Alkynes .....                   | 301 |
| 1.2.3.5.3 | Variation 3:  | Intramolecular Addition of Malonate Derivatives to Alkynes<br>under Strongly Basic Conditions: Four Modes of Reaction ... | 302 |
| 1.2.3.6   | Method 6:   | Addition of Sulfur Nucleophiles .....   | 303 |
| 1.2.3.6.1 | Variation 1:  | Addition of Arenethiols to Alkynes To Form Vinyl Sulfides ...   | 304 |
| 1.2.3.6.2 | Variation 2:  | Thiocarbonylation of Alkynes with Thiols and<br>Carbon Monoxide .....   | 306 |
| 1.2.3.6.3 | Variation 3:  | Addition of Diaryl Disulfides to Alkynes To Form<br>1,2-Disulfanylalkenes .....   | 308 |
| 1.2.3.6.4 | Variation 4:  | Thiocarbonylation of Acetylenes with Disulfides .....   | 309 |
| 1.2.3.6.5 | Variation 5:  | Palladium-Catalyzed Thioboration of Acetylenes<br>with 9-(Alkylsulfanyl)-9-borabicyclo[3.3.1]nonanes .....                | 311 |
| 1.2.3.7   | Method 7:   | Addition of Halides .....   | 312 |
| 1.2.3.7.1 | Variation 1:  | Palladium-Catalyzed Addition of Halides to Alkynes<br>Followed by Alkene Insertion and Protonolysis .....                 | 313 |
| 1.2.3.7.2 | Variation 2:  | Palladium-Catalyzed Addition of Halides to Alkynes<br>Followed by Alkene Insertion and $\beta$ -Elimination .....         | 314 |
| 1.2.3.7.3 | Variation 3:  | Palladium-Catalyzed Addition of Halides to Alkynes<br>Followed by Alkene Insertion and Oxidation .....                    | 315 |
| 1.2.4     | <b>Product Subclass 4: Palladium–Alkene Complexes</b>         |   |     |
|           | J. M. Takacs and S. Vayalakkada                               |   |     |
| 1.2.4     | <b>Product Subclass 4: Palladium–Alkene Complexes</b> .....   |   | 319 |
|           | Synthesis of Product Subclass 4 .....                         |   | 320 |
| 1.2.4.1   | Method 1:   | From a Palladium(II) Salt and an Alkene .....   | 320 |
| 1.2.4.2   | Method 2:   | From Palladium(0) and an Alkene .....   | 321 |
|           | Applications of Product Subclass 4 in Organic Synthesis ..... |   | 322 |
| 1.2.4.3   | Method 3:   | Palladium-Catalyzed Intermolecular Addition<br>of Oxygen Nucleophiles: Water and Alcohols .....                           | 322 |

|            |               |   |     |
|------------|---------------|---|-----|
| 1.2.4.3.1  | Variation 1:  | Addition of Water to Terminal Alkenes To Form Ketones;<br>the Wacker Oxidation  | 323 |
| 1.2.4.3.2  | Variation 2:  | The Wacker Oxidation Using a Fluorous Biphasic System   | 327 |
| 1.2.4.3.3  | Variation 3:  | The Wacker Oxidation in Solid-Phase Synthesis   | 329 |
| 1.2.4.3.4  | Variation 4:  | Addition of Water to Terminal Alkenes To Form Aldehydes   | 330 |
| 1.2.4.3.5  | Variation 5:  | Addition of Water to Allylic Carbonates<br>To Form $\alpha,\beta$ -Unsaturated Aldehydes                                  | 333 |
| 1.2.4.3.6  | Variation 6:  | Palladium-Catalyzed Oxidative Removal of<br>Allyl Protecting Groups   | 334 |
| 1.2.4.3.7  | Variation 7:  | Palladium-Catalyzed Oxidation of Internal Alkenes:<br>Allylic and Homoallylic Ethers                                      | 335 |
| 1.2.4.3.8  | Variation 8:  | Palladium-Catalyzed Oxidation of Internal Alkenes:<br>Unsaturated Carbonyl Compounds                                      | 337 |
| 1.2.4.3.9  | Variation 9:  | Intermolecular Addition of Alcohol To Form Acetals and Ketals   | 338 |
| 1.2.4.3.10 | Variation 10: | Intermolecular Addition of Alcohol To Form Acetals<br>from $\alpha,\beta$ -Unsaturated Carbonyl Compounds                 | 339 |
| 1.2.4.4    | Method 4:     | Palladium-Catalyzed Heterocyclization:<br>Intramolecular Addition of Oxygen Nucleophiles                                  | 340 |
| 1.2.4.4.1  | Variation 1:  | Intramolecular Addition of Alcohol Followed by<br>$\beta$ -Hydroxide Elimination  | 340 |
| 1.2.4.4.2  | Variation 2:  | Intramolecular Addition of Alcohol Followed by<br>$\beta$ -Hydrogen Elimination   | 342 |
| 1.2.4.4.3  | Variation 3:  | Intramolecular Addition of Alcohol Followed by<br>$\beta$ -Hydrogen Elimination: A Catalytic Asymmetric Variant           | 344 |
| 1.2.4.4.4  | Variation 4:  | Double Addition of Alcohol To Form Mixed Ketals   | 345 |
| 1.2.4.4.5  | Variation 5:  | Intramolecular Addition of Alcohol Followed by<br>Carbon Monoxide Insertion and Alcoholysis                               | 347 |
| 1.2.4.4.6  | Variation 6:  | Addition of Alcohol Followed by Alkene Insertion  | 350 |
| 1.2.4.4.7  | Variation 7:  | Intramolecular Addition of Carboxylate Followed by<br>$\beta$ -Hydride Elimination  | 352 |
| 1.2.4.4.8  | Variation 8:  | Intramolecular Addition of Carboxylate Followed by<br>Carbon Monoxide Trapping  | 354 |
| 1.2.4.5    | Method 5:     | Intermolecular Addition of Nitrogen Nucleophiles  | 355 |
| 1.2.4.5.1  | Variation 1:  | Intermolecular Addition of Amines Followed by<br>$\beta$ -Hydride Elimination   | 356 |
| 1.2.4.5.2  | Variation 2:  | Intermolecular Addition of Amides and Carbamates  | 356 |
| 1.2.4.6    | Method 6:     | Palladium-Catalyzed Heterocyclization:<br>Intramolecular Addition of Nitrogen Nucleophiles                                | 357 |
| 1.2.4.6.1  | Variation 1:  | Intramolecular Addition of Amine Followed by<br>$\beta$ -Hydride Elimination  | 358 |
| 1.2.4.6.2  | Variation 2:  | Intramolecular Addition of Amine Followed by $\beta$ -Elimination:<br>In Situ Reduction of Aromatic Nitro Compounds       | 359 |
| 1.2.4.6.3  | Variation 3:  | Intramolecular Addition of Amine Followed by<br>Carbon Monoxide Insertion   | 360 |
| 1.2.4.6.4  | Variation 4:  | Intramolecular Addition of <i>N</i> -Sulfonyl and <i>N</i> -Acyl Derivatives<br>Followed by $\beta$ -Hydrogen Elimination | 361 |

|              |  |  |     |
|--------------|--|--|-----|
| 1.2.4.6.5    | Variation 5:   | Intramolecular Addition of <i>N</i> -Acyl and <i>N</i> -Sulfonyl Derivatives Followed by Carbon Monoxide Insertion (Carbonylation) . . . . . | 363 |
| 1.2.4.6.6    | Variation 6:   | Intramolecular Addition of <i>N</i> -Acyl and <i>N</i> -Sulfonyl Derivatives Followed by Alkene Insertion . . . . .                          | 367 |
| 1.2.4.7      | Method 7:  | Palladium(II)-Catalyzed [3,3]-Sigmatropic Rearrangements . . . . .   | 367 |
| 1.2.4.7.1    | Variation 1:   | Palladium(II)-Catalyzed Cope Rearrangements . . . . .  | 368 |
| 1.2.4.7.2    | Variation 2:   | Oxy-Cope Rearrangement . . . . .   | 371 |
| 1.2.4.7.3    | Variation 3:   | Claisen and Thia-Claisen Rearrangements . . . . .  | 371 |
| 1.2.4.7.4    | Variation 4:   | Enolate Claisen Rearrangements . . . . .   | 374 |
| 1.2.4.7.5    | Variation 5:   | Allylic Imidate Rearrangements . . . . .   | 375 |
| 1.2.4.7.6    | Variation 6:   | Allylic Ester Rearrangement . . . . .  | 379 |
| <b>1.3</b>   | <b>Product Class 3: Organometallic Complexes of Platinum</b>             |  |     |
|              | A. Ogawa and T. Hirao  |  |     |
| <b>1.3</b>   | <b>Product Class 3: Organometallic Complexes of Platinum . . . . .</b>   |  |     |
| <b>1.3.1</b> | <b>Product Subclass 1: Platinum–Cyclopentadienyl Complexes . . . . .</b> |  |     |
|              | Synthesis of Product Subclass 1 . . . . .                                |  |     |
| 1.3.1.1      | Method 1:  | Cyclopentadienylplatinum(II) Complexes from Platinum Halide Complexes and Cyclopentadienyl Anions . . . . .                                  | 389 |
| 1.3.1.2      | Method 2:  | Cyclopentadienylplatinum(IV) Complexes from Platinum Halide Complexes and Cyclopentadienyl Anions . . . . .                                  | 391 |
| <b>1.3.2</b> | <b>Product Subclass 2: Platinum–Diene Complexes . . . . .</b>            |  |     |
|              | Synthesis of Product Subclass 2 . . . . .                                |  |     |
| 1.3.2.1      | Method 1:  | Platinum(0)–Allene Complexes . . . . .   | 394 |
| 1.3.2.2      | Method 2:  | Platinum(II)–Allene Complexes . . . . .  | 396 |
| 1.3.2.3      | Method 3:  | Platinum(0)–Conjugated Polyene Complexes . . . . .   | 397 |
| 1.3.2.4      | Method 4:  | Platinum(II)–Conjugated Polyene Complexes . . . . .  | 399 |
| 1.3.2.5      | Method 5:  | Platinum(0)–Nonconjugated Polyene Complexes . . . . .  | 400 |
| 1.3.2.6      | Method 6:  | Platinum(II)–Nonconjugated Polyene Complexes . . . . .   | 402 |
|              | Applications of Product Subclass 2 in Organic Synthesis . . . . .        |  |     |
| 1.3.2.7      | Method 7:  | Platinum(0)-Catalyzed Dimerization of Conjugated Dienes and Related Reactions . . . . .  | 404 |
| <b>1.3.3</b> | <b>Product Subclass 3: Platinum–Allyl Complexes . . . . .</b>            |  |     |
|              | Synthesis of Product Subclass 3 . . . . .                                |  |     |
| 1.3.3.1      | Method 1:  | Allylplatinum Complexes from Platinum(II) Complexes and Allylic Compounds . . . . .  | 405 |
| 1.3.3.2      | Method 2:  | Allylplatinum Complexes by Addition of Platinum(II) Hydrides to Unsaturated Bonds . . . . .  | 406 |
| 1.3.3.3      | Method 3:  | Allylplatinum Complexes from Allylic Platinum(II) Precursors . . . . .   | 407 |
| 1.3.3.4      | Method 4:  | Allylplatinum Complexes from Platinum(0) Precursors . . . . .  | 409 |

|                  |  |     |
|------------------|--|-----|
| <b>1.3.4</b>     | <b>Product Subclass 4: Platinum–Alkyne Complexes</b> .....   | 411 |
|                  | Synthesis of Product Subclass 4 .....  | 411 |
| <b>1.3.4.1</b>   | Method 1: Platinum(0)–Alkyne Complexes Starting from<br>Platinum(II) Complexes .....   | 411 |
| <b>1.3.4.2</b>   | Method 2: Platinum(0)–Alkyne Complexes by Ligand-Exchange Reactions<br>with Platinum(0)–Phosphine Complexes .....            | 413 |
| <b>1.3.4.3</b>   | Method 3: Platinum(0)–Alkyne Complexes by Ligand-Exchange Reactions<br>with Platinum(0)–Alkene Complexes .....               | 414 |
| <b>1.3.4.4</b>   | Method 4: Platinum(II)–Alkyne Complexes by Ligand-Exchange Reactions<br>with Platinum(II) Halide and Related Complexes ..... | 416 |
|                  | Applications of Product Subclass 4 in Organic Synthesis .....  | 417 |
| <b>1.3.4.5</b>   | Method 5: Catalytic Addition of Main Group Element–Hydrogen Bond<br>Compounds to Acetylenes .....                            | 417 |
| <b>1.3.4.5.1</b> | Variation 1: Hydrosilylation .....   | 417 |
| <b>1.3.4.5.2</b> | Variation 2: Addition of Other Main Group<br>Element–Hydrogen Bond Compounds .....   | 418 |
| <b>1.3.5</b>     | <b>Product Subclass 5: Platinum–Alkene Complexes</b> .....   | 420 |
|                  | Synthesis of Product Subclass 5 .....  | 420 |
| <b>1.3.5.1</b>   | Method 1: Platinum(0)–Monoalkene Polydentate Complexes .....   | 420 |
| <b>1.3.5.2</b>   | Method 2: Platinum(II)–Monoalkene Polydentate Complexes .....  | 421 |
| <b>1.3.5.3</b>   | Method 3: Platinum(0)–Monoalkene Monodentate Complexes<br>Starting from Platinum(II) Complexes .....                         | 423 |
| <b>1.3.5.4</b>   | Method 4: Platinum(0)–Monoalkene Monodentate Complexes<br>by Ligand-Exchange Reactions with Platinum(0) Complexes ..         | 425 |
| <b>1.3.5.5</b>   | Method 5: Platinum(II)–Monoalkene Monodentate Complexes<br>by Ligand-Exchange Reactions .....                                | 427 |
| <b>1.3.5.6</b>   | Method 6: Pentacoordinate Platinum(II)–Monoalkene<br>Monodentate Complexes .....   | 428 |
|                  | Applications of Product Subclass 5 in Organic Synthesis .....  | 430 |
| <b>1.3.5.7</b>   | Method 7: Catalytic Hydrogenation of Alkenes .....   | 430 |
| <b>1.3.5.8</b>   | Method 8: Catalytic Hydrosilylation of Alkenes and<br>Related Addition Reactions .....                                       | 431 |
| <b>1.4</b>       | <b>Product Class 4: Organometallic Complexes of Cobalt</b><br>M. Malacria, C. Aubert, and J.-L. Renaud                       |     |
| <b>1.4</b>       | <b>Product Class 4: Organometallic Complexes of Cobalt</b> .....   | 439 |
| <b>1.4.1</b>     | <b>Product Subclass 1: Cobalt–Dienyl Complexes</b> .....   | 439 |
|                  | Synthesis of Product Subclass 1 .....  | 440 |
| <b>1.4.1.1</b>   | Method 1: Bis(alkene)(cyclopentadienyl)cobalt(I) Complexes by<br>Ligand Exchange .....                                       | 440 |
| <b>1.4.1.1.1</b> | Variation 1: Via Displacement of Carbon Monoxide .....   | 440 |
| <b>1.4.1.1.2</b> | Variation 2: Via Ligand Substitution .....   | 441 |

|            |              |   |     |
|------------|--------------|---|-----|
| 1.4.1.2    | Method 2:    | Bis(alkene)( $\eta^5$ -cyclopentadienyl)cobalt(I) Complexes<br>by Reduction of Cobalt(II) Complexes   | 442 |
| 1.4.1.2.1  | Variation 1: | Via Elimination of Alkali Metal Cyclopentadienide   | 442 |
| 1.4.1.2.2  | Variation 2: | Via Reduction of (Pentaalkylcyclopentadienyl)cobalt(II)<br>Halide Dimers  | 443 |
| 1.4.1.3    | Method 3:    | Dicarbonyl( $\eta^5$ -cyclopentadienyl)cobalt(I) by<br>Oxidative Addition   | 444 |
| 1.4.1.4    | Method 4:    | Cyclopentadienyl(maleoyl)cobalt(III) and<br>Cyclopentadienyl(phthaloyl)cobalt(III) Complexes by<br>Insertion into Substituted Cyclobutenediones | 444 |
| 1.4.1.5    | Method 5:    | Cyclopentadienylbis(triarylphosphine)cobalt(I) Complexes<br>by Reduction of Cobalt(III) Complexes   | 445 |
|            |              | Applications of Product Subclass 1 in Organic Synthesis   | 446 |
| 1.4.1.6    | Method 6:    | Hydroacylation  | 446 |
| 1.4.1.7    | Method 7:    | Epoxide Opening   | 447 |
| 1.4.1.8    | Method 8:    | Inter- and Intramolecular [2 + 2 + 2] Cyclizations  | 448 |
| 1.4.1.8.1  | Variation 1: | Intermolecular [2 + 2 + 2] Cyclization of Diynes and Nitriles:<br>Synthesis of Pyridines  | 448 |
| 1.4.1.8.2  | Variation 2: | Inter- and Intramolecular [2 + 2 + 2] Cyclization of Triynes<br>in Aromatic and Aqueous Solvents  | 451 |
| 1.4.1.8.3  | Variation 3: | Inter- and Intramolecular [2 + 2 + 2] Cyclization of<br>Ene-diyne and Allenediyne   | 455 |
| 1.4.1.8.4  | Variation 4: | Inter- and Intramolecular [2 + 2 + 2] Cyclization of<br>Diynes with Heteroatom-Substituted Multiple Bonds                                       | 458 |
| 1.4.1.9    | Method 9:    | Inter- and Intramolecular [2 + 2] Cyclizations  | 461 |
| 1.4.1.10   | Method 10:   | Cobalt-Mediated Ene-Yne Cyclizations  | 462 |
| 1.4.1.10.1 | Variation 1: | Alder Ene-Type Cyclizations of Enynes and Allenynes   | 463 |
| 1.4.1.10.2 | Variation 2: | Ene-Type Reactions of $\beta$ -Oxo Ester $\epsilon$ -Ynes   | 464 |
| 1.4.1.11   | Method 11:   | Synthesis of Quinones   | 466 |
| 1.4.2      |              | <b>Product Subclass 2: Cobalt-Diene Complexes</b>   | 467 |
|            |              | Synthesis of Product Subclass 2   | 468 |
| 1.4.2.1    | Method 1:    | Tricarbonyl( $\eta^4$ -diene)cobalt(I) Tetrafluoroborate Complexes  | 468 |
|            |              | Applications of Product Subclass 2 in Organic Synthesis   | 468 |
| 1.4.2.2    | Method 2:    | 1,4-Difunctionalization of Dienes   | 468 |
| 1.4.2.2.1  | Variation 1: | Synthesis of Z-Disubstituted Alkenes  | 469 |
| 1.4.2.2.2  | Variation 2: | Synthesis of Heterocyclic Compounds   | 469 |
| 1.4.3      |              | <b>Product Subclass 3: Cobalt-Allyl Complexes</b>   | 472 |
|            |              | Synthesis of Product Subclass 3   | 472 |
| 1.4.3.1    | Method 1:    | Allylcobalt Complexes by Ligand Exchange  | 472 |
| 1.4.3.2    | Method 2:    | Allylcobalt Complexes by Elimination of Leaving Groups  | 473 |
| 1.4.3.3    | Method 3:    | Allylcobalt Complexes by Hydridocobaltation of 1,3-Dienes   | 475 |
| 1.4.3.4    | Method 4:    | Allylcobalt Complexes by Addition of Alkyl- and<br>Acylcobalt Complexes to Conjugated Dienes and<br>Various Unsaturated Compounds               | 476 |

|            |  |     |
|------------|--|-----|
|            | Applications of Product Subclass 3 in Organic Synthesis  | 478 |
| 1.4.3.5    | Method 5: Synthesis of Acyldienes  | 478 |
| 1.4.3.6    | Method 6: 1,4-Acylation/Alkylation of 1,3-Dienes and Allenes:<br>Synthesis of Substituted Enones | 479 |
| 1.4.3.7    | Method 7: Acylation–Cyclization of Allenes: Synthesis of Heterocycles                            | 481 |
| 1.4.3.8    | Method 8: Synthesis of Butenolides   | 482 |
| 1.4.4      | <b>Product Subclass 4: Miscellaneous Complexes</b>   | 483 |
|            | Synthesis of Product Subclass 4  | 483 |
| 1.4.4.1    | Method 1: Cobalt(III) Complexes  | 483 |
| 1.4.4.1.1  | Variation 1: From Cobalt(III) Complexes  | 484 |
| 1.4.4.1.2  | Variation 2: From Cobalt(II) Complexes   | 485 |
| 1.4.4.1.3  | Variation 3: From Cobalt(I) Complexes  | 486 |
| 1.4.4.2    | Method 2: ( $\mu$ -Alkyne)hexacarbonyldicobalt(0) Complexes by<br>Ligand Exchange                | 487 |
| 1.4.4.3    | Method 3: Chlorotris(triphenylphosphine)cobalt(I)  | 488 |
| 1.4.4.4    | Method 4: Tetrakis(trimethylphosphine)cobalt(0) by Reduction<br>of Cobalt(II) Chloride           | 489 |
| 1.4.4.5    | Method 5: Tetracarbonylhydridocobalt(I)  | 490 |
| 1.4.4.6    | Method 6: Tris(acetylacetonato)cobalt(III) as a Precatalyst                                      | 491 |
| 1.4.4.7    | Method 7: Cobalt(II) Complexes as Precatalysts   | 491 |
|            | Applications of Product Subclass 4 in Organic Synthesis  | 493 |
| 1.4.4.8    | Method 8: Reformatsky- and Aldol-Type Reactions  | 493 |
| 1.4.4.9    | Method 9: Silylcarbonylation   | 494 |
| 1.4.4.10   | Method 10: Hydroformylation  | 496 |
| 1.4.4.11   | Method 11: Synthesis of Epoxides   | 498 |
| 1.4.4.11.1 | Variation 1: Synthesis of Enantiomerically Pure Epoxides Using<br>Cobalt(III) Complexes          | 498 |
| 1.4.4.11.2 | Variation 2: Synthesis of Epoxides Using Cobalt(II) Complexes under<br>Neutral Conditions        | 499 |
| 1.4.4.12   | Method 12: Carbon–Heteroatom Bond Formation  | 500 |
| 1.4.4.12.1 | Variation 1: Cobalt(II)-Mediated Aerobic Oxygenation of Alkenes                                  | 500 |
| 1.4.4.12.2 | Variation 2: Cobalt(II) Chloride Catalyzed Carbon–Heteroatom<br>Bond Formation                   | 501 |
| 1.4.4.13   | Method 13: Synthesis of Carbonyl Compounds   | 502 |
| 1.4.4.13.1 | Variation 1: Syntheses Catalyzed by Cobalt(II) Complexes   | 502 |
| 1.4.4.13.2 | Variation 2: Syntheses Catalyzed by<br>Chlorotris(triphenylphosphine)cobalt(I)                   | 504 |
| 1.4.4.14   | Method 14: C–C Bond Formation by Addition  | 504 |
| 1.4.4.14.1 | Variation 1: Formation of C–C Bonds via Radical Addition Reactions                               | 505 |
| 1.4.4.14.2 | Variation 2: The Nicholas Reaction   | 508 |
| 1.4.4.14.3 | Variation 3: The Inter- and Intramolecular Pauson–Khand Reaction                                 | 512 |
| 1.4.4.15   | Method 15: C–C Bond Formation by Rearrangement   | 517 |
| 1.4.4.15.1 | Variation 1: Rearrangement of 1-(Alk-1-ynyl)cyclopropanols                                       | 518 |
| 1.4.4.15.2 | Variation 2: Diels–Alder Reaction with 2-Cobaloxime-Substituted<br>1,3-Dienes                    | 519 |

|                  |  |     |
|------------------|--|-----|
| 1.4.4.15.3       | Variation 3: Homo-Diels–Alder Reactions  | 520 |
| 1.4.4.15.4       | Variation 4: Additional Methods  | 521 |
| <b>1.5</b>       | <b>Product Class 5: Organometallic Complexes of Rhodium</b><br>I. Ojima, A. T. Vu, and D. Bonafoux |     |
| <b>1.5</b>       | <b>Product Class 5: Organometallic Complexes of Rhodium</b>  | 531 |
| <b>1.5.1</b>     | <b>Product Subclass 1: Rhodium–Arene Complexes</b>   | 532 |
|                  | Synthesis of Product Subclass 1  | 532 |
| <b>1.5.1.1</b>   | Method 1: Cationic Complexes by Ligand Substitution  | 532 |
| <b>1.5.1.1.1</b> | Variation 1: From Arenes and Cationic Rhodium–Diene Complexes                                      | 532 |
| <b>1.5.1.1.2</b> | Variation 2: From Arenes and Rhodium–Acetylacetonate Complexes                                     | 533 |
| <b>1.5.1.1.3</b> | Variation 3: From Arenes and Rhodium(III) Chloride   | 534 |
| <b>1.5.1.1.4</b> | Variation 4: From Arenes and Rhodium–Acetate Complexes   | 534 |
| <b>1.5.1.1.5</b> | Variation 5: Via Displacement of Weakly Bound Ligands  | 535 |
| <b>1.5.2</b>     | <b>Product Subclass 2: Rhodium–Cumulene Complexes</b>  | 536 |
|                  | Synthesis of Product Subclass 2  | 536 |
| <b>1.5.2.1</b>   | Method 1: Cumulatriene Complexes by Ligand Substitution  | 536 |
| <b>1.5.2.2</b>   | Method 2: Cumulapentaene Complex by Ligand Substitution  | 537 |
| <b>1.5.3</b>     | <b>Product Subclass 3: Rhodium–Dienyl Complexes</b>  | 537 |
|                  | Synthesis of Product Subclass 3  | 538 |
| <b>1.5.3.1</b>   | Method 1: Cyclopentadienylrhodium Complexes by Ligand Substitution                                 | 538 |
| <b>1.5.3.1.1</b> | Variation 1: From Cyclopentadienyl Anions and Rhodium Halides                                      | 538 |
| <b>1.5.3.1.2</b> | Variation 2: Cationic Bis(cyclopentadienyl) Complexes by<br>Ligand Substitution                    | 539 |
| <b>1.5.3.2</b>   | Method 2: From Pentamethylcyclopentadienyl Anions and<br>Rhodium Halides                           | 540 |
| <b>1.5.3.2.1</b> | Variation 1: Dimeric Pentamethylcyclopentadienyl Complexes   | 541 |
| <b>1.5.3.2.2</b> | Variation 2: Monomeric Pentamethylcyclopentadienyl Complexes                                       | 542 |
| <b>1.5.3.3</b>   | Method 3: Indenyl Complexes by Ligand Substitution   | 542 |
| <b>1.5.3.4</b>   | Method 4: Acyclic Pentadienyl Complexes by Dehydration   | 544 |
| <b>1.5.3.5</b>   | Method 5: $\eta^5$ -Cyclohexadienyl Complexes  | 544 |
| <b>1.5.3.5.1</b> | Variation 1: Via Ligand Substitution   | 545 |
| <b>1.5.3.5.2</b> | Variation 2: Cationic Complexes via Hydride Abstraction  | 546 |
| <b>1.5.3.5.3</b> | Variation 3: Via Nucleophilic Addition to an Arene Ligand  | 546 |
| <b>1.5.3.6</b>   | Method 6: Norbornadienyl Complexes by Dehydration  | 547 |
| <b>1.5.3.7</b>   | Method 7: $\eta^5$ -Cycloheptadienyl Complexes by Nucleophilic Addition                            | 548 |
| <b>1.5.3.8</b>   | Method 8: $\eta^5$ -Cyclooctadienyl Complexes  | 548 |
| <b>1.5.4</b>     | <b>Product Subclass 4: Rhodium–Diene Complexes</b>   | 549 |
|                  | Synthesis of Product Subclass 4  | 549 |
| <b>1.5.4.1</b>   | Method 1: Allene Complexes by Ligand Substitution  | 549 |
| <b>1.5.4.2</b>   | Method 2: Alka-1,3-diene Complexes   | 550 |
| <b>1.5.4.2.1</b> | Variation 1: Via Ligand Substitution   | 551 |



|           |              |   |     |
|-----------|--------------|---|-----|
| 1.5.4.2.2 | Variation 2: | Via Displacement of Weakly Bound Ligands  | 551 |
| 1.5.4.2.3 | Variation 3: | Cationic Complexes via Ligand Substitution  | 553 |
| 1.5.4.2.4 | Variation 4: | Cyclobutadiene Complexes via Alkyne Cyclodimerization   | 553 |
| 1.5.4.2.5 | Variation 5: | $\eta^4$ -Cyclopentadiene Complexes via Nucleophilic Addition to $\eta^5$ -Cyclopentadienyl Ligands | 555 |
| 1.5.4.2.6 | Variation 6: | $\eta^4$ -Cyclopentadienone Complexes   | 556 |
| 1.5.4.3   | Method 3:    | Cycloocta-1,5-diene Complexes   | 558 |
| 1.5.4.3.1 | Variation 1: | Via Ligand Substitution   | 558 |
| 1.5.4.3.2 | Variation 2: | Via Displacement of Weakly Bound Ligands  | 559 |
| 1.5.4.3.3 | Variation 3: | Homoleptic Cationic Cycloocta-1,5-diene Complexes via Anionic Ligand Abstraction                    | 560 |
| 1.5.4.3.4 | Variation 4: | Monomeric Cycloocta-1,5-diene Complexes   | 561 |
| 1.5.4.4   | Method 4:    | Norbornadiene Complexes   | 563 |
| 1.5.4.4.1 | Variation 1: | Via Ligand Substitution   | 563 |
| 1.5.4.4.2 | Variation 2: | Via Displacement of Weakly Bound Ligands  | 564 |
| 1.5.4.4.3 | Variation 3: | Homoleptic, Cationic Norbornadiene Complexes via Anionic Ligand Abstraction                         | 565 |
| 1.5.4.4.4 | Variation 4: | Monomeric Norbornadiene Complexes   | 566 |
| 1.5.4.5   | Method 5:    | Cycloocta-1,3,5,7-tetraene Complexes  | 567 |
| 1.5.4.6   | Method 6:    | Synthesis of Cationic Chiral Diene Complexes  | 569 |
|           |              | Applications of Product Subclass 4 in Organic Synthesis   | 571 |
| 1.5.4.7   | Method 7:    | Reactions Involving Allenes   | 571 |
| 1.5.4.7.1 | Variation 1: | Carbonylative [4 + 1] Cycloaddition of Vinylallene  | 571 |
| 1.5.4.7.2 | Variation 2: | [4 + 2] Diene–Allene Cycloaddition  | 573 |
| 1.5.4.7.3 | Variation 3: | [5 + 2] Vinylcyclopropane–Allene Cycloaddition  | 573 |
| 1.5.4.8   | Method 8:    | [4 + 2] Cycloaddition Involving 1,3-Dienes  | 574 |
| 1.5.5     |              | <b>Product Subclass 5: Rhodium–Allyl Complexes</b>  | 577 |
|           |              | Synthesis of Product Subclass 5   | 577 |
| 1.5.5.1   | Method 1:    | Monoallyl Complexes via Transmetalation   | 577 |
| 1.5.5.2   | Method 2:    | Allyl Complexes by Hydrometalation  | 579 |
| 1.5.5.3   | Method 3:    | Allyl Complexes by Allylation of Metal Salts  | 583 |
| 1.5.5.4   | Method 4:    | Allyl Complexes by Oxidative Addition   | 583 |
| 1.5.5.5   | Method 5:    | Bis(allyl) Complexes  | 585 |
| 1.5.5.6   | Method 6:    | Tris(allyl) Complexes   | 587 |
|           |              | Applications of Product Subclass 5 in Organic Synthesis   | 588 |
| 1.5.5.7   | Method 6:    | Metallo-Ene Cyclization   | 588 |
| 1.5.6     |              | <b>Product Subclass 6: Rhodium–Alkyne Complexes</b>   | 589 |
|           |              | Synthesis of Product Subclass 6   | 589 |
| 1.5.6.1   | Method 1:    | Via Simple Alkyne Addition  | 589 |
| 1.5.6.2   | Method 2:    | Via Displacement of Weakly Bound Ligands  | 590 |
| 1.5.6.3   | Method 3:    | Alkyne-Bridged Dimeric Complexes via Ligand Displacement  | 592 |
|           |              | Applications of Product Subclass 6 in Organic Synthesis   | 594 |
| 1.5.6.4   | Method 4:    | [2 + 2 + 2] Cycloaddition   | 594 |

|           |   |   |     |
|-----------|---|---|-----|
| 1.5.6.4.1 | Variation 1:  | [2+2+2] Cyclotrimerization  | 594 |
| 1.5.6.4.2 | Variation 2:  | Silylcarbocyclization of Triynes  | 596 |
| 1.5.6.5   | Method 5:   | Rhodium-Catalyzed Pauson–Khand Reaction   | 596 |
| 1.5.6.6   | Method 6:   | [5+2] Vinylcyclopropane–Alkyne Cycloaddition  | 597 |
| 1.5.6.6.1 | Variation 1:  | Intramolecular [5+2] Cycloaddition  | 598 |
| 1.5.6.6.2 | Variation 2:  | Intermolecular [5+2] Cycloaddition  | 599 |
| 1.5.6.7   | Method 7:   | Enyne Carbocyclization  | 600 |
| 1.5.6.8   | Method 8:   | Silylcarbocyclization   | 600 |
| 1.5.6.8.1 | Variation 1:  | Silylcarbocyclization of 1,6-Diynes   | 600 |
| 1.5.6.8.2 | Variation 2:  | Silylcarbocyclization of Enynes   | 601 |
| 1.5.7     | <b>Product Subclass 7: Rhodium–Alkene Complexes</b>         |   | 603 |
|           | Synthesis of Product Subclass 7                             |   | 604 |
| 1.5.7.1   | Method 1:   | Via Ligand Substitution   | 604 |
| 1.5.7.2   | Method 2:   | Monomeric Complexes via<br>Chlorine-Bridge Cleavage Reactions   | 605 |
| 1.5.7.3   | Method 3:   | Via Displacement of the Ethene Ligand   | 606 |
| 1.5.7.4   | Method 4:   | Via Displacement of Weakly Bound Ligands  | 607 |
|           | Applications of Product Subclass 7 in Organic Synthesis     |   | 608 |
| 1.5.7.5   | Method 5:   | [5+2] Vinylcyclopropane–Alkene Cycloaddition  | 608 |
| 1.5.7.6   | Method 6:   | Carbocyclization of 1,6-Dienes  | 609 |
| 1.5.7.7   | Method 7:   | Intramolecular Hydroacylation   | 610 |
| 1.6       | <b>Product Class 6: Organometallic Complexes of Iridium</b> |   |     |
|           | J. M. O'Connor  |   |     |
| 1.6       | <b>Product Class 6: Organometallic Complexes of Iridium</b> |   | 617 |
| 1.6.1     | <b>Product Subclass 1: Iridium–Arene Complexes</b>          |   | 617 |
|           | Synthesis of Product Subclass 1                             |   | 618 |
| 1.6.1.1   | Method 1:   | Preparation of Cationic Iridium(I)–Arene Complexes by<br>Ligand Substitution  | 618 |
| 1.6.1.2   | Method 2:   | Preparation of Cationic Iridium(I)–Arene Complexes by<br>Elimination  | 618 |
| 1.6.1.2.1 | Variation 1:  | From $[\text{Ir}_2(\mu\text{-Cl})_2(\eta^4\text{-cod})_2]$ or $[\text{Ir}_2(\mu\text{-Cl})_2(\eta^4\text{-Me}_3\text{TFB})_2]$ and<br>Silver(I) Tetrafluoroborate | 618 |
| 1.6.1.2.2 | Variation 2:  | From $[\text{Ir}(\text{acac})(\eta^4\text{-cod})]$ and<br>Triphenylcarbenium Tetrafluoroborate  | 620 |
| 1.6.1.2.3 | Variation 3:  | From $[\text{Ir}_2(\mu\text{-OMe})_2(\eta^4\text{-cod})_2]$ and Tetrafluoroboric Acid   | 620 |
| 1.6.1.2.4 | Variation 4:  | From $[\text{IrCl}(\eta^4\text{-TFB})_2]$ and Silver(I) Tetrafluoroborate   | 621 |
| 1.6.1.2.5 | Variation 5:  | From $[\text{Ir}_2(\mu\text{-Cl})_2\text{Cl}_2\text{H}_2(\eta^4\text{-cod})_2]$ and Silver(I) Tetrafluoroborate   | 622 |
| 1.6.1.2.6 | Variation 6:  | From $[\text{IrH}_2(\text{OCMe}_2)_2(\text{PPh}_3)_2]\text{SbF}_6$  | 623 |
| 1.6.1.3   | Method 3:   | Preparation of Cationic Iridium(I)–Arene Complexes by<br>Addition   | 623 |
| 1.6.1.4   | Method 4:   | Preparation of Dicationic Iridium(III)–Arene Complexes by<br>Elimination  | 624 |

|           |   |   |     |
|-----------|---|---|-----|
| 1.6.1.4.1 | Variation 1:  | From $[\text{Ir}_2(\text{Cp}^*)_2(\mu\text{-Cl})_2\text{Cl}_2]$ and Silver(I) Hexafluorophosphate or Tetrafluoroborate                              | 624 |
| 1.6.1.4.2 | Variation 2:  | From $[\text{Ir}_2(\text{Cp}^*)_2(\mu\text{-Cl})_2\text{Cl}_2]$ and Silver(I) Tetrafluoroborate Using an Acidic Workup                              | 626 |
| 1.6.1.4.3 | Variation 3:  | From $[\text{Ir}_2(\text{Cp}^*)_2(\mu\text{-Cl})_2\text{Cl}_2]$ and Trifluoroacetic Acid  | 627 |
|           |   | Applications of Product Subclass 1 in Organic Synthesis   | 628 |
| 1.6.1.5   | Method 5:   | Dehydration of Cyclohexene  | 628 |
| 1.6.2     | <b>Product Subclass 2: Iridium–Dienyl Complexes</b> |   | 628 |
|           |   | Synthesis of Product Subclass 2   | 630 |
| 1.6.2.1   | Method 1:   | Preparation of Neutral Iridium(I)–Dienyl Complexes by Ligand Substitution   | 630 |
| 1.6.2.1.1 | Variation 1:  | From $[\text{Ir}_2(\mu\text{-Cl})_2(\eta^4\text{-cod})_2]$  | 630 |
| 1.6.2.1.2 | Variation 2:  | From $[\text{Ir}_2(\mu\text{-Cl})_2(\eta^2\text{-coe})_4]$  | 632 |
| 1.6.2.1.3 | Variation 3:  | From $[\text{Ir}_2(\mu\text{-Cl})_2(\eta^2\text{-coe})_4]$ and Phosphines   | 632 |
| 1.6.2.1.4 | Variation 4:  | From $[\text{Ir}_2(\mu\text{-Cl})_2(\eta^2\text{-coe})_4]$ and Ethene   | 634 |
| 1.6.2.1.5 | Variation 5:  | From $[\text{Ir}_n\text{Cl}_n(\text{CO})_{3n}]$   | 635 |
| 1.6.2.1.6 | Variation 6:  | From $[\text{IrCl}_3 \cdot 3\text{H}_2\text{O}]$  | 635 |
| 1.6.2.2   | Method 2:   | Preparation of Cationic Iridium(III)–Dienyl Complexes by Elimination  | 636 |
| 1.6.2.2.1 | Variation 1:  | From $[\text{IrH}_2(\text{OCMe}_2)_2(\text{PPh}_3)_2]\text{X}$ (X = $\text{SbF}_6$ or $\text{BF}_4$ )   | 636 |
| 1.6.2.2.2 | Variation 2:  | From $[\text{Ir}_2(\text{Cp}^*)_2(\mu\text{-Cl})_2\text{Cl}_2]$   | 637 |
| 1.6.2.3   | Method 3:   | Preparation of Cationic Iridium(I)–Dienyl Complexes by Rearrangement  | 638 |
| 1.6.2.4   | Method 4:   | Preparation of Cationic Iridium(III)–Cyclohexadienyl and Iridium(III)–Cycloheptadienyl Complexes by Elimination                                     | 640 |
| 1.6.2.4.1 | Variation 1:  | From $[\text{IrH}_2(\text{OCMe}_2)_2(\text{PPh}_3)_2]\text{BF}_4$   | 640 |
| 1.6.2.4.2 | Variation 2:  | From $[\text{Ir}(\eta^4\text{-cod})(\text{L})_2]\text{SbF}_6$ (L = phosphine)   | 641 |
| 1.6.2.4.3 | Variation 3:  | Oxo- $\eta^5$ -cyclohexadienyl Complexes from $[\text{Ir}_2(\text{Cp}^*)_2(\mu\text{-Cl})_2\text{Cl}_2]$  | 641 |
| 1.6.2.4.4 | Variation 4:  | Imino- $\eta^5$ -cyclohexadienyl Complexes from $[\text{Ir}_2(\text{Cp}^*)_2(\mu\text{-Cl})_2\text{Cl}_2]$  | 642 |
| 1.6.2.5   | Method 5:   | Preparation of Cationic Iridium(III)–Cyclohexadienyl Complexes by Addition  | 644 |
| 1.6.2.6   | Method 6:   | Preparation of (Dienyl)iridium(III) Complexes with Retention of the Cyclopentadienyl Ligand   | 645 |
| 1.6.2.6.1 | Variation 1:  | Dienyl Hydrides from Borohydride and (Dienyl)iridium Halides  | 645 |
| 1.6.2.6.2 | Variation 2:  | Dienyl Hydrides from Reaction of Dienyl Halides and Zinc/Acetic Acid  | 646 |
| 1.6.2.6.3 | Variation 3:  | Conversion of $[\text{Ir}_2(\text{Cp}^*)_2(\mu\text{-Cl})\text{Cl}_2(\mu\text{-H})]$ into $[\text{Ir}_2(\text{Cp}^*)_2(\mu\text{-H})_3]\text{PF}_6$ | 647 |
| 1.6.2.6.4 | Variation 4:  | Conversion of $[\text{Ir}_2(\text{Cp}^*)_2(\mu\text{-H})_3]\text{PF}_6$ into $[\text{Ir}(\text{Cp}^*)\text{H}_4]$                                   | 648 |
| 1.6.2.6.5 | Variation 5:  | Dienyl Hydrides from Protonation at Iridium   | 649 |
| 1.6.2.6.6 | Variation 6:  | Dienyl Fluoride Complexes by Ligand Substitution  | 650 |
| 1.6.2.6.7 | Variation 7:  | Dienyl Alkoxide Complexes by Ligand Substitution  | 651 |
| 1.6.2.6.8 | Variation 8:  | Dienyl Acetate Complexes by Ligand Substitution   | 652 |
| 1.6.2.6.9 | Variation 9:  | Dienyl $\alpha$ -Amino Acidate Complexes by Ligand Substitution   | 652 |

|            |  |  |     |
|------------|--|--|-----|
| 1.6.2.6.10 | Variation 10:                                      | Dienyl Triflate (Coordinated) Complexes by Substitution  | 654 |
| 1.6.2.6.11 | Variation 11:                                      | Dienyl Hydroxo Complexes by Ligand Substitution  | 655 |
| 1.6.2.6.12 | Variation 12:                                      | A Dienyl $\mu$ -Oxo Complex by Ligand Substitution   | 656 |
| 1.6.2.6.13 | Variation 13:                                      | Dienyl Imido Complexes by Ligand Substitution  | 656 |
| 1.6.2.6.14 | Variation 14:                                      | A Mononuclear (Dienyl)iridium–Nitrosyl Complex by Ligand Substitution  | 657 |
| 1.6.2.6.15 | Variation 15:                                      | A Mononuclear (Dienyl)iridium–Aryldiazenido Complex by Ligand Substitution   | 658 |
| 1.6.2.6.16 | Variation 16:                                      | A Mononuclear (Dienyl)iridium–Amido Complex by Ligand Substitution   | 659 |
| 1.6.2.6.17 | Variation 17:                                      | (Dienyl)iridium–Amine Complexes by Ligand Addition   | 660 |
| 1.6.2.6.18 | Variation 18:                                      | Cationic (Dienyl)iridium–Amine Complexes by Ligand Addition  | 661 |
| 1.6.2.6.19 | Variation 19:                                      | Cationic (Dienyl)iridium–Acetonitrile Complexes  | 662 |
| 1.6.2.6.20 | Variation 20:                                      | (Dienyl)iridium–Alkyl Complexes by Substitution of Alkyl for Halide  | 663 |
| 1.6.2.6.21 | Variation 21:                                      | (Dienyl)iridium–Alkyl Complexes by Alkylation of a Dienyl Metalate Anion   | 664 |
| 1.6.2.6.22 | Variation 22:                                      | (Dienyl)iridium–Alkyl Complexes by Oxidative Addition of Alkanes to $[\text{Ir}(\text{Cp}^*)(\text{PMe}_3)]$                           | 665 |
| 1.6.2.6.23 | Variation 23:                                      | (Dienyl)iridium–Aryl Complexes by Oxidative Addition of Arenes   | 666 |
| 1.6.2.6.24 | Variation 24:                                      | (Dienyl)iridium–Alkyl Complexes by Oxidative Addition of Alkyl Halides   | 667 |
| 1.6.2.6.25 | Variation 25:                                      | (Dienyl)iridium–Carbon Monoxide Complexes by Substitution  | 667 |
| 1.6.2.6.26 | Variation 26:                                      | (Dienyl)iridium–Carbon Monoxide Complexes by Addition  | 668 |
| 1.6.2.6.27 | Variation 27:                                      | Dienyl Chloride Complexes by Oxidative Addition of Chlorine  | 669 |
| 1.6.2.6.28 | Variation 28:                                      | Dienyl Bis(Sulfido) Complexes by Substitution  | 669 |
| 1.6.2.6.29 | Variation 29:                                      | Dienyl Phosphine Complexes by Substitution   | 671 |
| 1.6.2.6.30 | Variation 30:                                      | $[\text{Ir}(\text{Cp}^*)\{\text{P}(\text{OMe})_3\}_3](\text{ClO}_4)_2$ from $[\text{Ir}_2(\text{Cp}^*)_2(\mu\text{-Cl})_2\text{Cl}_2]$ | 672 |
| 1.6.2.6.31 | Variation 31:                                      | Dienyl Silyl Complexes by Silylation of a Dienyl Metalate Anion  | 673 |
| 1.6.2.6.32 | Variation 32:                                      | Dienyl Bromo Complexes by Substitution   | 673 |
| 1.6.2.6.33 | Variation 33:                                      | Dienyl Bromo Complexes by Oxidative Addition of Bromine  | 674 |
| 1.6.2.6.34 | Variation 34:                                      | Dienyl Diselenolate Complexes by Oxidative Addition of Diselenides   | 674 |
| 1.6.2.6.35 | Variation 35:                                      | Dienyl Iodo Complexes by Oxidative Addition of Iodine  | 675 |
|            |  | Applications of Product Subclass 2 in Organic Synthesis  | 675 |
| 1.6.2.7    | Method 7:  | Conversion of Alkynes and Hexaborane(10) into Alkenylboranes   | 675 |
| 1.6.3      | <b>Product Subclass 3: Iridium–Diene Complexes</b> |  | 676 |
|            |  | Synthesis of Product Subclass 3  | 677 |
| 1.6.3.1    | Method 1:  | Iridium–Diene Complexes by Ligand Substitution   | 677 |
| 1.6.3.1.1  | Variation 1:                                       | Synthesis of $[\text{Ir}(\eta^4\text{-C}_6\text{H}_6)(\text{triphos})]\text{BPh}_4$  | 677 |
| 1.6.3.1.2  | Variation 2:                                       | From $[\text{Ir}_2(\mu\text{-Cl})_2(\eta^2\text{-coe})_4]$   | 678 |
| 1.6.3.2    | Method 2:  | Iridium–Diene Complexes by Ligand Elimination  | 678 |

|            |               |   |     |
|------------|---------------|---|-----|
| 1.6.3.2.1  | Variation 1:  | Synthesis of $[\text{Ir}_2(\mu\text{-Cl})_2(\eta^4\text{-cod})_2]$ .....  | 679 |
| 1.6.3.2.2  | Variation 2:  | Synthesis of $[\text{IrCl}(\eta^4\text{-TFB})_2]$ .....   | 680 |
| 1.6.3.2.3  | Variation 3:  | Synthesis of $[\text{Ir}(\eta^4\text{-cod})_2]\text{BF}_4$ .....  | 680 |
| 1.6.3.2.4  | Variation 4:  | Synthesis of $[\text{IrH}(\eta^4\text{-1,3-C}_6\text{H}_8)(\eta^4\text{-cod})]$ .....   | 681 |
| 1.6.3.3    | Method 3:     | Iridium–Diene Complexes by Addition Reactions .....   | 682 |
| 1.6.3.3.1  | Variation 1:  | Synthesis of $[\text{Ir}(\text{Cp}^*)(\eta^4\text{-1,3-C}_6\text{H}_8)]$ from<br>$[\text{Ir}(\text{Cp}^*)(\eta^6\text{-C}_6\text{H}_6)](\text{BF}_4)_2$ ..... | 682 |
| 1.6.3.3.2  | Variation 2:  | Synthesis of the $\eta^4$ -Cyclohexadienone Complex<br>$[\text{Ir}(\text{Cp}^*)\{\eta^4\text{-C}_6\text{H}_5(\text{O})\text{OMe}\}]$ .....                    | 683 |
| 1.6.3.4    | Method 4:     | Iridium–Diene Complexes by Rearrangement .....  | 684 |
| 1.6.3.5    | Method 5:     | Preparation of Iridium–Diene Complexes with Retention of<br>the Diene Ligand .....  | 685 |
| 1.6.3.5.1  | Variation 1:  | Synthesis of a (Diene)iridium Dihydride Complex:<br><i>cis,trans</i> - $[\text{IrH}_2(\eta^4\text{-cod})(\text{PMePh}_2)_2]\text{PF}_6$ .....                 | 685 |
| 1.6.3.5.2  | Variation 2:  | Synthesis of (Diene)iridium Hydride Complexes from<br>HX Addition to Iridium .....  | 686 |
| 1.6.3.5.3  | Variation 3:  | Synthesis of $[\text{IrH}(\eta^4\text{-cod})(\text{PPh}_3)_2]$ .....  | 686 |
| 1.6.3.5.4  | Variation 4:  | Synthesis of $[\text{Ir}_2(\mu\text{-OMe})_2(\eta^4\text{-cod})_2]$ .....   | 687 |
| 1.6.3.5.5  | Variation 5:  | Synthesis of $[\text{Ir}(\text{hfac})(\eta^4\text{-cod})]$ .....  | 688 |
| 1.6.3.5.6  | Variation 6:  | Synthesis of Iridium–Amine Complexes: $[\text{IrCl}(\text{bipy})(\eta^4\text{-TFB})]$ ..  | 688 |
| 1.6.3.5.7  | Variation 7:  | Synthesis of $[\text{Ir}(\text{Tp})(\eta^4\text{-cod})]$ .....  | 689 |
| 1.6.3.5.8  | Variation 8:  | Synthesis of $[\text{Ir}(\eta^4\text{-cod})(\text{py})_2]\text{PF}_6$ .....   | 690 |
| 1.6.3.5.9  | Variation 9:  | Synthesis of Iridium–Alkynyl Complexes:<br>$[\text{Ir}(\text{C}\equiv\text{CPh})(\eta^4\text{-cod})(\text{PCy}_3)]$ .....                                     | 691 |
| 1.6.3.5.10 | Variation 10: | Synthesis of Iridium–Alkyl Complexes:<br>$[\text{Ir}(\text{Me})(\eta^4\text{-1,3-C}_6\text{H}_8)_2]$ .....  | 691 |
| 1.6.3.5.11 | Variation 11: | Synthesis of $[\text{Ir}(\eta^4\text{-cod})(\text{py})(\text{PCy}_3)]\text{PF}_6$ .....   | 692 |
| 1.6.3.5.12 | Variation 12: | Synthesis of a Phosphinodihydrooxazole Complex:<br>$[\text{Ir}(\eta^4\text{-cod})(\text{NP})]\text{BARF}$ .....   | 692 |
| 1.6.3.5.13 | Variation 13: | Synthesis of a Neutral Phosphine Complex:<br>$[\text{IrCl}(\eta^4\text{-cod})(\text{PPh}_3)]$ .....   | 693 |
| 1.6.3.5.14 | Variation 14: | Synthesis of Neutral Phosphine Complexes with Retention<br>of the Diene Ligand: $[\text{IrCl}(\eta^4\text{-cod})\{(-)\text{-Chiraphos}\}]$ .....              | 694 |
| 1.6.3.5.15 | Variation 15: | Synthesis of $[\text{Ir}(\eta^4\text{-cod})(\text{PPh}_3)_2]\text{BF}_4$ .....  | 695 |
| 1.6.3.5.16 | Variation 16: | Synthesis of $[\text{Ir}(\eta^4\text{-cod})(\text{PMe}_3)_3]\text{Cl}$ .....  | 696 |
| 1.6.3.5.17 | Variation 17: | Synthesis of $[\text{Ir}(\eta^4\text{-cod})\{(+)\text{-degusph}\}]\text{BF}_4$ .....  | 697 |
|            |               | Applications of Product Subclass 3 in Organic Synthesis .....   | 698 |
| 1.6.3.6    | Method 6:     | Iridium–Diene Complexes as Catalyst Precursors .....  | 698 |
| 1.6.3.6.1  | Variation 1:  | Hydrogenation of Carbonyl Compounds via<br>Hydrogen Atom Transfer from Propan-2-ol .....  | 698 |
| 1.6.3.6.2  | Variation 2:  | Hydrogenation of Ketones with Hydrogen .....  | 700 |
| 1.6.3.6.3  | Variation 3:  | Asymmetric Hydrosilylation of Ketones .....   | 703 |
| 1.6.3.6.4  | Variation 4:  | Asymmetric Hydrogenation of Imines .....  | 705 |
| 1.6.3.6.5  | Variation 5:  | Hydrogenation of Alkenes with $[\text{Ir}(\eta^4\text{-cod})(\text{py})(\text{PCy}_3)]\text{PF}_6$ ....   | 709 |
| 1.6.3.6.6  | Variation 6:  | Asymmetric Hydrogenation of Alkenes .....   | 710 |
| 1.6.3.6.7  | Variation 7:  | Allylic Alkylation .....  | 711 |

|           |  |     |
|-----------|--|-----|
| 1.6.3.6.8 | Variation 8: Isomerization of Allyl Ethers   | 712 |
| 1.6.4     | <b>Product Subclass 4: Iridium–Allyl Complexes</b>   | 714 |
|           | Synthesis of Product Subclass 4  | 715 |
| 1.6.4.1   | Method 1: Preparation of Iridium–Allyl Complexes by Ligand Substitution  | 715 |
| 1.6.4.1.1 | Variation 1: From Iridium Halides and Grignard or Organolithium Reagents   | 715 |
| 1.6.4.1.2 | Variation 2: Synthesis of the Cyclopropenyl Complex $[\text{Ir}(\eta^3\text{-C}_3\text{t-Bu}_3)(\text{CO})_3]$                                     | 716 |
| 1.6.4.2   | Method 2: Preparation of Iridium–Allyl Complexes by Addition   | 717 |
| 1.6.4.2.1 | Variation 1: From Iridium(I) Precursors and Allyl Halides  | 717 |
| 1.6.4.2.2 | Variation 2: From $[\text{Ir}_2(\mu\text{-Cl})_2(\eta^2\text{-coe})_4]$ and Allylbenzene   | 718 |
| 1.6.4.2.3 | Variation 3: From Diene Insertion into Ir–H Bonds  | 718 |
| 1.6.4.2.4 | Variation 4: From Nucleophilic Attack on a $\eta^1$ -Allenyl Ligand  | 719 |
| 1.6.4.3   | Method 3: Preparation of Iridium–Allyl Complexes by Elimination  | 720 |
| 1.6.4.3.1 | Variation 1: From $[\text{Ir}_2(\text{Cp}^*)_2(\mu\text{-Cl})_2\text{Cl}_2]$ and Dienes in the Presence of Alcohol and Base                        | 720 |
| 1.6.4.3.2 | Variation 2: From $[\text{Ir}_2(\text{Cp}^*)_2(\mu\text{-Cl})_2\text{Cl}_2]$ , Silver(I) Salts, and an Alkene                                      | 721 |
|           | Applications of Product Subclass 4 in Organic Synthesis  | 722 |
| 1.6.4.4   | Method 4: Nucleophilic Attack on $\pi$ -Allyl Intermediates  | 722 |
| 1.6.5     | <b>Product Subclass 5: Iridium–Alkyne Complexes</b>  | 722 |
|           | Synthesis of Product Subclass 5  | 723 |
| 1.6.5.1   | Method 1: Preparation of Iridium–Alkyne Complexes by Ligand Substitution   | 723 |
| 1.6.5.2   | Method 2: Preparation of Iridium–Alkyne Complexes by Addition  | 724 |
| 1.6.6     | <b>Product Subclass 6: Iridium–Alkene Complexes</b>  | 725 |
|           | Synthesis of Product Subclass 6  | 726 |
| 1.6.6.1   | Method 1: Preparation of Iridium–Alkene Complexes by Ligand Substitution   | 726 |
| 1.6.6.2   | Method 2: Preparation of Iridium–Alkene Complexes by Addition  | 727 |
| 1.6.6.3   | Method 3: Preparation of Iridium–Alkene Complexes by Elimination   | 728 |
|           | Applications of Product Subclass 6 in Organic Synthesis  | 729 |
| 1.6.6.4   | Method 4: Iridium–Alkene Complexes in Catalysis  | 729 |
| 1.6.7     | <b>Product Subclass 7: Iridium–Carbene Complexes</b>   | 729 |
|           | Synthesis of Product Subclass 7  | 730 |
| 1.6.7.1   | Method 1: Preparation of Iridium–Carbene Complexes by Ligand Substitution  | 730 |
| 1.6.7.1.1 | Variation 1: From $[\text{Ir}(\text{R}^1\text{C}=\text{CR}^1\text{CR}^1=\text{CR}^1)(\text{NCMe})_2(\text{PPh}_3)_2]\text{BF}_4$ and But-3-yn-1-ol | 730 |
| 1.6.7.1.2 | Variation 2: A Vinylidene Complex from $[\text{Ir}[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_3](\eta^2\text{-coe})]$ and Acetylene            | 731 |
| 1.6.7.1.3 | Variation 3: A Vinylidene Complex from $[\text{Ir}_2(\mu\text{-Cl})_2(\eta^2\text{-coe})_4]$ and Sodium/1-Chloro-2-methylprop-1-ene                | 731 |
| 1.6.7.2   | Method 2: Preparation of Iridium–Carbene Complexes by Addition   | 732 |

|           |  |   |     |
|-----------|--|---|-----|
| 1.6.7.2.1 | Variation 1:   | From [IrCl(CO)(PPh <sub>3</sub> ) <sub>2</sub> ] and<br>(Chloromethylene)dimethylammonium Chloride        | 732 |
| 1.6.7.2.2 | Variation 2:   | From [IrClH(OTf)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ] and<br>Benzylidyne(methyl)ammonium Triflate        | 733 |
| 1.6.7.3   | Method 3:  | Preparation of Iridium–Carbene Complexes by Elimination   | 733 |
| 1.6.7.3.1 | Variation 1:   | From [IrCl(CO)(PPh <sub>3</sub> ) <sub>2</sub> ] and Electron-Rich Alkenes                                | 733 |
| 1.6.7.3.2 | Variation 2:   | From [IrCl <sub>2</sub> H(PPh <sub>3</sub> ) <sub>3</sub> ] and Bis(trichloromethyl)mercury(II)           | 734 |
| 1.6.7.3.3 | Variation 3:   | From [IrClH <sub>2</sub> (P-iPr <sub>3</sub> ) <sub>2</sub> ] and Acetylene                               | 734 |
| 1.6.7.3.4 | Variation 4:   | An Iridium–Allenylidene Complex from<br>[Ir(C≡CPh <sub>2</sub> OH)ClH(P-iPr <sub>3</sub> ) <sub>2</sub> ] | 735 |
| 1.6.7.4   | Method 4:  | Preparation of Iridium–Vinylidene Complexes by<br>Rearrangement   | 736 |
| 1.6.8     | <b>Product Subclass 8: Iridium–Carbyne Complexes</b>     |   | 736 |
|           | Synthesis of Product Subclass 8                          |   | 736 |
| 1.7       | <b>Product Class 7: Organometallic Complexes of Iron</b> |   |     |
|           | G. R. Stephenson   |   |     |
| 1.7       | <b>Product Class 7: Organometallic Complexes of Iron</b> |   |     |
| 1.7.1     | <b>Product Subclass 1: Iron–Arene Complexes</b>          |   |     |
|           | Synthesis of Product Subclass 1                          |   |     |
| 1.7.1.1   | Method 1:  | Direct Complexation of Arenes   | 749 |
| 1.7.1.2   | Method 2:  | Modification of η <sup>6</sup> -Complexes   | 750 |
| 1.7.1.2.1 | Variation 1:   | Replacement of Chloride in Chlorobenzene Complexes by<br>Nucleophiles                                     | 751 |
| 1.7.1.2.2 | Variation 2:   | Use of Palladium-Catalyzed Coupling in the Presence<br>of Cationic Iron–Cyclopentadienyl Complexes        | 752 |
| 1.7.1.2.3 | Variation 3:   | Use of Nucleophilic Complexes Obtained by Deprotonation<br>of Arene–Cyclopentadienyliron Complexes        | 752 |
| 1.7.1.2.4 | Variation 4:   | Nucleophile Addition to a Carbonyl Ligand   | 753 |
| 1.7.1.2.5 | Variation 5:   | Hydrogenation of Ligands in the Presence of<br>Cationic Iron–Cyclopentadienyl Complexes                   | 753 |
|           | Applications of Product Subclass 1 in Organic Synthesis  |   |     |
| 1.7.1.3   | Method 3:  | Metal Removal To Give Organic Products  | 753 |
| 1.7.2     | <b>Product Subclass 2: Iron–Dienyl Complexes</b>         |   |     |
|           | Synthesis of Product Subclass 2                          |   |     |
| 1.7.2.1   | Method 1:  | Direct Complexation   | 755 |
| 1.7.2.1.1 | Variation 1:   | Reaction of Cyclopentadienyl Anions with Iron Salts   | 755 |
| 1.7.2.1.2 | Variation 2:   | Transfer of Cyclopentadienyliron  | 756 |
| 1.7.2.1.3 | Variation 3:   | From Neutral Cyclopentadiene Derivatives  | 756 |
| 1.7.2.2   | Method 2:  | Modification of η <sup>5</sup> -Cyclopentadienyl Complexes  | 757 |
| 1.7.2.2.1 | Variation 1:   | Friedel–Crafts Acylation of Ferrocene Complexes   | 757 |
| 1.7.2.2.2 | Variation 2:   | Metalation of Ferrocene Complexes   | 758 |

|            |   |   |     |
|------------|---|---|-----|
| 1.7.2.2.3  | Variation 3:                                    | Modification of Substituents on Ferrocene Complexes   | 758 |
| 1.7.2.2.4  | Variation 4:                                    | Redox Chemistry at the Metal of Ferrocene Complexes   | 759 |
| 1.7.2.2.5  | Variation 5:                                    | Protonation at Iron   | 759 |
| 1.7.2.2.6  | Variation 6:                                    | Manipulation of Di- $\mu$ -carbonyldicarbonylbis( $\eta^5$ -cyclopentadienyl)diiron                   | 759 |
| 1.7.2.3    | Method 3:                                       | Preparation by Hydride Abstraction  | 760 |
| 1.7.2.3.1  | Variation 1:                                    | Regioisomer Preparation without Rearrangement   | 761 |
| 1.7.2.3.2  | Variation 2:                                    | Regioisomer Preparation with Rearrangement  | 762 |
| 1.7.2.4    | Method 4:                                       | Preparation from $\eta^4$ -Triene Complexes with Electrophiles  | 762 |
| 1.7.2.5    | Method 5:                                       | Preparation from Dienol Complexes with Acid   | 763 |
| 1.7.2.5.1  | Variation 1:                                    | Without Rearrangement   | 764 |
| 1.7.2.5.2  | Variation 2:                                    | With Rearrangement  | 765 |
| 1.7.2.6    | Method 6:                                       | Preparation by Demethoxylation in Acid  | 765 |
| 1.7.2.7    | Method 7:                                       | Preparation by Oxidation with Thallium(III) Salts   | 767 |
| 1.7.2.8    | Method 8:                                       | Preparation from Dienone Complexes  | 767 |
| 1.7.2.9    | Method 9:                                       | Preparation from $\eta^6$ -Complexes  | 768 |
| 1.7.2.9.1  | Variation 1:                                    | Nucleophile Addition to $\eta^6$ -Complexes at the $\pi$ -System                                      | 768 |
| 1.7.2.9.2  | Variation 2:                                    | Dealkoxylation of $\eta^6$ -Complexes   | 770 |
| 1.7.2.10   | Method 10:                                      | Nucleophile Addition to $\eta^5$ -Complexes   | 770 |
| 1.7.2.10.1 | Variation 1:                                    | Addition at the $\pi$ -System   | 770 |
| 1.7.2.10.2 | Variation 2:                                    | Addition next to the $\pi$ -System  | 770 |
| 1.7.2.10.3 | Variation 3:                                    | Addition at a Carbonyl Group  | 771 |
| 1.7.2.11   | Method 11:                                      | Access to Salts by a Sequence of Nucleophile Addition and Leaving-Group Removal                       | 771 |
| 1.7.2.11.1 | Variation 1:                                    | Without Rearrangement   | 772 |
| 1.7.2.11.2 | Variation 2:                                    | With Rearrangement  | 773 |
| 1.7.2.12   | Method 12:                                      | Opening Cyclopropane Rings  | 774 |
| 1.7.2.13   | Method 13:                                      | Preparation of Nonracemic Complexes   | 774 |
| 1.7.2.13.1 | Variation 1:                                    | From Ferrocene Complexes by Asymmetric Induction  | 774 |
| 1.7.2.13.2 | Variation 2:                                    | From Complexes Originating from Resolution or Asymmetric Induction                                    | 775 |
| 1.7.2.13.3 | Variation 3:                                    | From Complexes Originating from Biological Sources  | 776 |
|            |   | Applications of Product Subclass 2 in Organic Synthesis   | 777 |
| 1.7.2.14   | Method 14:                                      | Metal Removal To Give Organic Products  | 777 |
| 1.7.2.14.1 | Variation 1:                                    | From Ferrocene Complexes  | 777 |
| 1.7.2.14.2 | Variation 2:                                    | From Cationic $\eta^5$ -Ligated Tricarbonyliron Complexes   | 777 |
| 1.7.2.14.3 | Variation 3:                                    | From $\eta^5$ -Cyclopentadienyl-Iron Complexes Formed by Nucleophilic Addition to $\eta^6$ -Complexes | 778 |
| 1.7.3      | <b>Product Subclass 3: Iron-Diene Complexes</b> |   | 778 |
|            |   | Synthesis of Product Subclass 3   | 778 |
| 1.7.3.1    | Method 1:                                       | Preparation by Complexation   | 778 |
| 1.7.3.1.1  | Variation 1:                                    | From Dienes without Rearrangement   | 778 |
| 1.7.3.1.2  | Variation 2:                                    | From Dienes with Rearrangement  | 780 |
| 1.7.3.1.3  | Variation 3:                                    | From Dienes and Alkynes by Reaction with $\eta^1$ -Complexes  | 781 |
| 1.7.3.1.4  | Variation 4:                                    | From Cyclohexadienones by Reduction   | 782 |



|            |               |   |     |
|------------|---------------|---|-----|
| 1.7.3.1.5  | Variation 5:  | From Dihydrothiophene 1,1-Dioxides                                      | 782 |
| 1.7.3.1.6  | Variation 6:  | From Allyl Alcohols   | 782 |
| 1.7.3.1.7  | Variation 7:  | From Dihalides, Allyl Halides, and Phosphate Esters                     | 782 |
| 1.7.3.1.8  | Variation 8:  | From Pyrones  | 783 |
| 1.7.3.1.9  | Variation 9:  | From Dimethylcyclopropenes  | 783 |
| 1.7.3.1.10 | Variation 10: | From Vinylcyclopropanes   | 784 |
| 1.7.3.1.11 | Variation 11: | From Allenes via Trimethylenemethane Lactones                           | 784 |
| 1.7.3.2    | Method 2:     | Preparation from $\eta^3, \eta^1$ -Complexes                            | 784 |
| 1.7.3.2.1  | Variation 1:  | From Ferralactone Complexes   | 785 |
| 1.7.3.2.2  | Variation 2:  | From $\eta^3, \eta^1$ -Allenyl Complexes                                | 785 |
| 1.7.3.2.3  | Variation 3:  | Nucleophile Addition to Cationic $\eta^3, \eta^1$ -Carbene Complexes    | 786 |
| 1.7.3.3    | Method 3:     | Cyclodimerization of $\eta^2$ -Ligands                                  | 786 |
| 1.7.3.4    | Method 4:     | Nucleophile Addition to $\eta^5$ -Complexes at the $\pi$ -System        | 787 |
| 1.7.3.4.1  | Variation 1:  | Cyclohexadienyl Complexes   | 787 |
| 1.7.3.4.2  | Variation 2:  | Cycloheptadienyl Complexes  | 794 |
| 1.7.3.4.3  | Variation 3:  | Cyclooctadienyl Complexes   | 795 |
| 1.7.3.4.4  | Variation 4:  | Acyclic Dienyl Complexes  | 795 |
| 1.7.3.4.5  | Variation 5:  | In Situ Generation of Acyclic Dienyl Complexes                          | 797 |
| 1.7.3.4.6  | Variation 6:  | Cyclopentadienyl Complexes  | 799 |
| 1.7.3.5    | Method 5:     | Metal-Centered Reduction of $\eta^5$ -Complexes at the $\pi$ -System    | 799 |
| 1.7.3.6    | Method 6:     | Modification of $\eta^4$ -Complexes                                     | 799 |
| 1.7.3.6.1  | Variation 1:  | By Acylation  | 799 |
| 1.7.3.6.2  | Variation 2:  | By Lithiation and Addition of Electrophiles                             | 800 |
| 1.7.3.6.3  | Variation 3:  | By Palladium Coupling   | 801 |
| 1.7.3.6.4  | Variation 4:  | Nucleophile Addition to $\eta^4$ -Complexes at the $\pi$ -System        | 802 |
| 1.7.3.6.5  | Variation 5:  | Nucleophile Addition to $\eta^4$ -Complexes at a Carbonyl Ligand        | 802 |
| 1.7.3.6.6  | Variation 6:  | Nucleophile Addition to $\eta^4$ -Complexes next to the $\pi$ -System   | 803 |
| 1.7.3.6.7  | Variation 7:  | Reactions of Enolates and Silyl Enol Ethers                             | 806 |
| 1.7.3.6.8  | Variation 8:  | Epoxide Formation and Cyclopropanation next to the $\pi$ -System        | 807 |
| 1.7.3.6.9  | Variation 9:  | Diol Synthesis next to the $\pi$ -System                                | 808 |
| 1.7.3.6.10 | Variation 10: | Cycloaddition Reactions next to the $\pi$ -System                       | 808 |
| 1.7.3.6.11 | Variation 11: | Functionalization of Cycloheptatriene Complexes                         | 810 |
| 1.7.3.7    | Method 7:     | Complexation of Heterodienes  | 810 |
| 1.7.3.8    | Method 8:     | Additional Methods for the Formation of $\eta^4$ -Complexes             | 811 |
| 1.7.3.8.1  | Variation 1:  | Alkylation of $\eta^3$ -Anions  | 811 |
| 1.7.3.8.2  | Variation 2:  | From Pentacarbonyliron by Nucleophile Addition at Carbonyl              | 812 |
| 1.7.3.8.3  | Variation 3:  | Exchange of Carbonyl for Phosphines, Phosphites, and Nitrosonium        | 812 |
| 1.7.3.9    | Method 9:     | Preparation of Nonracemic Complexes                                     | 813 |
| 1.7.3.9.1  | Variation 1:  | Asymmetric Complexation   | 813 |
| 1.7.3.9.2  | Variation 2:  | Asymmetric Modification of Prochiral $\eta^4$ -Complexes                | 815 |
| 1.7.3.9.3  | Variation 3:  | By Asymmetric Induction and Kinetic Resolution with $\eta^5$ -Complexes | 816 |
| 1.7.3.9.4  | Variation 4:  | Classical Resolution of Chiral $\eta^4$ -Complexes                      | 817 |
| 1.7.3.9.5  | Variation 5:  | Kinetic Resolution of Chiral $\eta^4$ -Complexes                        | 818 |

|            |  |     |
|------------|--|-----|
|            | Applications of Product Subclass 3 in Organic Synthesis                                      | 818 |
| 1.7.3.10   | Method 10: Metal Removal To Give Organic Products  | 818 |
| 1.7.3.10.1 | Variation 1: Decomplexation without Ligand Modification                                      | 818 |
| 1.7.3.10.2 | Variation 2: Decomplexation with Ligand Modification   | 822 |
| 1.7.3.11   | Method 11: Reactions next to $\eta^3$ -Complexes, Followed by Rearrangement                  | 826 |
| 1.7.4      | <b>Product Subclass 4: Iron–Allyl Complexes</b>  | 826 |
|            | Synthesis of Product Subclass 4  | 826 |
| 1.7.4.1    | Method 1: Protonation of Diene Complexes   | 826 |
| 1.7.4.1.1  | Variation 1: From $\eta^2$ -Complexes  | 827 |
| 1.7.4.1.2  | Variation 2: From $\eta^4$ -Complexes  | 827 |
| 1.7.4.1.3  | Variation 3: During Direct Complexation of Allyl Alcohols and Dienes in the Presence of Acid | 827 |
| 1.7.4.2    | Method 2: Preparation by Leaving-Group Displacement from $\eta^2$ -Complexes                 | 827 |
| 1.7.4.3    | Method 3: Preparation by Opening Vinyl Epoxides and Cyclopropanes                            | 828 |
| 1.7.4.3.1  | Variation 1: From Epoxides   | 828 |
| 1.7.4.3.2  | Variation 2: From Aziridines   | 830 |
| 1.7.4.3.3  | Variation 3: From Cyclopropanes  | 830 |
| 1.7.4.4    | Method 4: Nucleophile Addition at a Complexed $\pi$ -System                                  | 830 |
| 1.7.4.4.1  | Variation 1: Nucleophile Addition to $\eta^4$ -Complexes                                     | 830 |
| 1.7.4.4.2  | Variation 2: Nucleophile Addition to $\eta^5$ -Complexes                                     | 831 |
| 1.7.4.5    | Method 5: Nucleophile Addition to $\eta^3$ -Complexes next to the $\pi$ -System              | 832 |
| 1.7.4.6    | Method 6: Nucleophile Addition at a Carbonyl Ligand  | 833 |
| 1.7.4.6.1  | Variation 1: Nucleophile Addition to $\eta^4$ -Complexes                                     | 833 |
| 1.7.4.6.2  | Variation 2: Nucleophile Addition to $\eta^2, \eta^2$ -Complexes                             | 834 |
| 1.7.4.7    | Method 7: Additional Methods for the Formation of $\eta^3$ -Complexes                        | 834 |
| 1.7.4.7.1  | Variation 1: From $\eta^5$ - to $\eta^3$ -Diene Complexes by Carbonyl Insertion              | 834 |
| 1.7.4.7.2  | Variation 2: Alkene Insertion  | 834 |
| 1.7.4.7.3  | Variation 3: From $\eta^4$ -Vinylketene Complexes  | 835 |
| 1.7.4.7.4  | Variation 4: Reductive Methods To Make Anionic $\eta^3$ -Complexes                           | 835 |
| 1.7.4.7.5  | Variation 5: Exchange of Carbonyl for Nitrosonium  | 835 |
| 1.7.4.8    | Method 8: Preparation of Nonracemic Complexes  | 835 |
|            | Applications of Product Subclass 4 in Organic Synthesis                                      | 836 |
| 1.7.4.9    | Method 9: Metal Removal To Give Organic Products   | 836 |
| 1.7.5      | <b>Product Subclass 5: Iron–Alkene Complexes</b>   | 839 |
|            | Synthesis of Product Subclass 5  | 839 |
| 1.7.5.1    | Method 1: Direct Complexation of Alkenes   | 839 |
| 1.7.5.1.1  | Variation 1: Ligand Exchange with a Butene Complex   | 839 |
| 1.7.5.1.2  | Variation 2: Reaction with Nonacarbonyliron  | 839 |
| 1.7.5.1.3  | Variation 3: Reaction with Pentacarbonyliron   | 840 |
| 1.7.5.2    | Method 2: Preparation by Protonation of $\eta^1$ -Complexes                                  | 840 |
| 1.7.5.2.1  | Variation 1: Protonation of $\eta^1$ -Allyl Complexes  | 840 |
| 1.7.5.2.2  | Variation 2: Removal of Leaving Groups from $\eta^1$ -Alkyl Complexes                        | 841 |
| 1.7.5.2.3  | Variation 3: Protonation at Iron   | 841 |

|           |              |   |     |
|-----------|--------------|---|-----|
| 1.7.5.3   | Method 3:    | Reactions of $\eta^1$ -Allyl Complexes with Electrophiles           | 841 |
| 1.7.5.3.1 | Variation 1: | Reaction with Aldehydes and Ketones in the Presence of a Lewis Acid | 841 |
| 1.7.5.3.2 | Variation 2: | Reaction with Activated Alkenes                                     | 842 |
| 1.7.5.3.3 | Variation 3: | Reaction with $\eta^2$ -Alkene Complexes                            | 843 |
| 1.7.5.3.4 | Variation 4: | Reaction with $\eta^5$ -Dienyl Complexes                            | 843 |
| 1.7.5.4   | Method 4:    | Nucleophile Addition at a Complexed $\pi$ -System                   | 843 |
| 1.7.5.4.1 | Variation 1: | Nucleophile Addition to $\eta^3$ -Complexes                         | 843 |
| 1.7.5.4.2 | Variation 2: | Nucleophile Addition to $\eta^4$ -Complexes                         | 843 |
| 1.7.5.4.3 | Variation 3: | Nucleophile Addition to $\eta^5$ -Complexes                         | 844 |
| 1.7.5.5   | Method 5:    | Preparation of Nonracemic Complexes                                 | 844 |
|           |              | Applications of Product Subclass 5 in Organic Synthesis             | 845 |
| 1.7.5.6   | Method 6:    | Metal Removal To Give Organic Products                              | 845 |
| 1.7.6     |              | <b>Product Subclass 6: Iron–Carbene Complexes</b>                   | 846 |
|           |              | Synthesis of Product Subclass 6                                     | 846 |
| 1.7.6.1   | Method 1:    | Preparation by the Fischer Carbene Method                           | 846 |
| 1.7.6.2   | Method 2:    | Removal of Leaving Groups from Metal–Alkyl Complexes                | 847 |
| 1.7.6.3   | Method 3:    | Modification of Other Carbene Complexes                             | 848 |
| 1.7.6.3.1 | Variation 1: | Exchange of Substituents at the Carbene Complex                     | 848 |
| 1.7.6.3.2 | Variation 2: | Reactions at Functional Groups Adjacent to the Carbene Complexes    | 848 |
| 1.7.6.4   | Method 4:    | Preparation by Ring Expansion                                       | 849 |
| 1.7.6.5   | Method 5:    | Preparation of Bridging Carbene Complexes                           | 849 |
| 1.7.6.6   | Method 6:    | Preparation of Nonracemic Complexes                                 | 851 |
|           |              | Applications of Product Subclass 6 in Organic Synthesis             | 852 |
| 1.7.6.7   | Method 7:    | Cyclopropanation by Transfer of Diazoesters                         | 852 |
| 1.7.6.8   | Method 8:    | C–H Insertion Reactions   | 852 |
| 1.7.6.9   | Method 9:    | Cyclization with Alkynes To Form Naphthols                          | 852 |
| 1.7.6.10  | Method 10:   | Removal of the Metal by Oxidation                                   | 853 |
| 1.7.7     |              | <b>Product Subclass 7: Iron–Alkyl Complexes</b>                     | 853 |
|           |              | Synthesis of Product Subclass 7                                     | 853 |
| 1.7.7.1   | Method 1:    | Metal Addition to Organic Electrophiles                             | 853 |
| 1.7.7.2   | Method 2:    | Metal Addition to Organic Nucleophiles/Lewis Bases                  | 854 |
| 1.7.7.3   | Method 3:    | Nucleophile Addition to $\eta^2$ -Alkene Complexes                  | 854 |
| 1.7.7.4   | Method 4:    | Additional Methods for the Formation of $\eta^1$ -Alkyl Complexes   | 855 |
| 1.7.7.4.1 | Variation 1: | Nucleophile Addition to $\eta^1$ -Carbene Complexes                 | 855 |
| 1.7.7.4.2 | Variation 2: | Nucleophile Addition to $\eta^2$ -Alkyne Complexes                  | 855 |
| 1.7.7.4.3 | Variation 3: | Nucleophile Addition to Carbonyl Complexes                          | 855 |
| 1.7.7.4.4 | Variation 4: | Deprotonation of $\eta^2$ -Alkene Complexes                         | 856 |
| 1.7.7.5   | Method 5:    | Reactions of Allyl Complexes  | 856 |
| 1.7.7.5.1 | Variation 1: | $\eta^1$ -Allyl Complexes   | 856 |
| 1.7.7.5.2 | Variation 2: | $\eta^3$ -Allyl Complexes   | 857 |
| 1.7.7.6   | Method 6:    | Modification of Ligands in $\eta^1$ -Complexes                      | 857 |
| 1.7.7.7   | Method 7:    | Preparation of Nonracemic Complexes                                 | 859 |

|            |  |     |
|------------|--|-----|
|            | Applications of Product Subclass 7 in Organic Synthesis  | 860 |
| 1.7.7.8    | Method 8: Oxidation of $\eta^1$ -Products  | 860 |
| 1.7.7.8.1  | Variation 1: Metal Removal To Generate a Carboxylic Acid   | 860 |
| 1.7.7.8.2  | Variation 2: Metal Removal To Generate an Ester  | 861 |
| 1.7.7.8.3  | Variation 3: Metal Removal To Generate an Amide  | 862 |
| 1.7.7.8.4  | Variation 4: Metal Removal To Generate Alkyl Bromides or Epoxides  | 862 |
| 1.7.7.8.5  | Variation 5: Metal Removal To Generate Cyclic Ketones  | 863 |
| 1.7.7.8.6  | Variation 6: Metal Removal with Transmetalation to Mercury   | 863 |
| 1.7.7.9    | Method 9: Additional Methods for Decomplexation of $\eta^1$ -Alkyl Complexes   | 864 |
| 1.7.7.9.1  | Variation 1: Disproportionation of $\eta^1$ -Products  | 864 |
| 1.7.7.9.2  | Variation 2: Photochemical Dimerization  | 864 |
| 1.7.7.9.3  | Variation 3: Asymmetric Cycloaddition  | 864 |
| 1.7.7.10   | Method 10: Formation and Reaction of Oxyallyl Cation Complexes   | 864 |
| 1.7.7.10.1 | Variation 1: [4+3] Cycloaddition   | 864 |
| 1.7.7.10.2 | Variation 2: [2+3] Cycloaddition   | 865 |
| 1.7.7.10.3 | Variation 3: Electrophilic Substitution  | 865 |
| 1.7.7.11   | Method 11: Application of Collman's Reagent  | 865 |
| 1.7.7.11.1 | Variation 1: Cyclization to Alkenes  | 866 |
| 1.7.7.11.2 | Variation 2: Reductions with the Tetracarbonylhydroferrate Complex   | 867 |
| 1.7.8      | <b>Product Subclass 8: Ferrocenes</b><br>M. Perseghini and A. Togni  |     |
| 1.7.8      | <b>Product Subclass 8: Ferrocenes</b>  | 889 |
|            | Synthesis of Product Subclass 8  | 890 |
| 1.7.8.1    | Method 1: Monosubstituted and 1,1'-Disubstituted Ferrocenes via Metalated Intermediates  | 890 |
| 1.7.8.1.1  | Variation 1: Synthesis of Halogenated Ferrocenes   | 890 |
| 1.7.8.1.2  | Variation 2: Synthesis of Hydroxyferrocene and 1,1'-Dihydroxyferrocene via the Ferroceneboronic Acids                            | 891 |
| 1.7.8.1.3  | Variation 3: Synthesis of Aminoferrocene and 1,1'-Diaminoferrocene   | 892 |
| 1.7.8.1.4  | Variation 4: Synthesis of Carboxyferrocene, Formylferrocene, 1,1'-Dicarboxyferrocene, and 1,1'-Diformylferrocene                 | 894 |
| 1.7.8.2    | Method 2: Acylferrocenes under Friedel-Crafts Conditions   | 895 |
| 1.7.8.3    | Method 3: Chiral 1-Ferrocenylalkyl Alcohols and 1-Ferrocenylalkylamines  | 895 |
| 1.7.8.3.1  | Variation 1: Via Stereoselective Alkylation of Formylferrocene   | 896 |
| 1.7.8.3.2  | Variation 2: Via Stereoselective Reduction of Acyl Intermediates   | 896 |
| 1.7.8.3.3  | Variation 3: Via Enzymatic Methods   | 897 |
| 1.7.8.3.4  | Variation 4: Via Racemate Resolution: Preparation of ( <i>R</i> )- and ( <i>S</i> )-1-Ferrocenyl- <i>N,N</i> -dimethylethylamine | 897 |
| 1.7.8.4    | Method 4: Chiral (4,5-Dihydrooxazol-2-yl)ferrocenes  | 898 |
| 1.7.8.5    | Method 5: Chiral Ferrocenyl Acetals  | 900 |
| 1.7.8.6    | Method 6: Chiral Ferrocenyl Sulfoxides   | 902 |

|              |   |  |     |
|--------------|---|--|-----|
| 1.7.8.7      | Method 7:   | Chiral 1,2-Disubstituted Ferrocenes by Diastereoselective Functionalization            | 903 |
| 1.7.8.7.1    | Variation 1:  | From 1-Ferrocenyl- <i>N,N</i> -dimethylethylamine                                      | 903 |
| 1.7.8.7.2    | Variation 2:  | From (4,5-Dihydrooxazol-2-yl)ferrocenes  | 907 |
| 1.7.8.7.3    | Variation 3:  | From Chiral Ferrocenyl Acetals   | 908 |
| 1.7.8.7.4    | Variation 4:  | From Chiral Ferrocenyl Sulfoxides  | 909 |
| 1.7.8.8      | Method 8:   | Chiral 1,2-Disubstituted Ferrocenes via Enantioselective Sparteine-Mediated Lithiation | 910 |
| 1.7.8.9      | Method 9:   | 1,1',2-Trisubstituted Ferrocenes (BPPFA Ligand Type)                                   | 911 |
| 1.7.8.10     | Method 10:  | Tetra- to Decasubstituted Ferrocenes   | 913 |
| 1.7.8.10.1   | Variation 1:  | From 1,1'-Bis(1-aminoalkyl)ferrocenes  | 913 |
| 1.7.8.10.2   | Variation 2:  | From 1,1'-Bis(4,5-dihydrooxazol-2-yl)ferrocenes  | 915 |
| 1.7.8.10.3   | Variation 3:  | Via Enantioselective Sparteine-Mediated Lithiation                                     | 916 |
| 1.7.8.10.4   | Variation 4:  | Synthesis of 4-(Dimethylamino)pyridine Analogues via Racemate Resolution               | 916 |
| 1.7.8.10.5   | Variation 5:  | From Chiral Fulvene Derivatives  | 917 |
| 1.7.8.10.6   | Variation 6:  | From Fully Substituted Cyclopentadienyl Salts  | 919 |
| 1.7.8.11     | Method 11:  | Chiral Biferrocenes  | 921 |
|              |   | Applications of Product Subclass 8 in Organic Synthesis                                | 923 |
| 1.7.8.12     | Method 12:  | Catalytic Enantioselective Hydrogenation   | 923 |
| 1.7.8.13     | Method 13:  | Catalytic Enantioselective Hydroboration   | 923 |
| 1.7.8.14     | Method 14:  | Catalytic Enantioselective Hydrosilylation   | 924 |
| 1.7.8.15     | Method 15:  | Catalytic Enantioselective Allylic Substitution  | 924 |
| 1.7.8.16     | Method 16:  | Catalytic Enantioselective Aldol Reactions   | 924 |
| <b>1.8</b>   | <b>Product Class 8: Organometallic Complexes of Ruthenium</b>                             |  |     |
|              | N. Chatani  |  |     |
| <b>1.8</b>   | <b>Product Class 8: Organometallic Complexes of Ruthenium</b>                             |  | 931 |
| <b>1.8.1</b> | <b>Product Subclass 1: Ruthenium–Arene Complexes</b>                                      |  | 931 |
|              | Synthesis of Product Subclass 1   |  | 932 |
| 1.8.1.1      | Method 1:   | Preparation of Ruthenium(II)–Arene Complexes   | 932 |
| 1.8.1.1.1    | Variation 1:  | From Dienes  | 933 |
| 1.8.1.1.2    | Variation 2:  | By Ligand Exchange   | 934 |
| 1.8.1.2      | Method 2:   | Preparation of Ruthenium(0)–Arene Complexes  | 934 |
| 1.8.1.2.1    | Variation 1:  | From Ruthenium(II) Complexes   | 935 |
| 1.8.1.2.2    | Variation 2:  | By Ligand Exchange   | 936 |
|              | Applications of Product Subclass 1 in Organic Synthesis                                   |  | 937 |
| 1.8.1.3      | Method 3:   | Reactions Involving Ruthenium–Arene Complexes  | 937 |
| <b>1.8.2</b> | <b>Product Subclass 2: Ruthenium–Cyclopentadienyl and Ruthenium–Pentadienyl Complexes</b> |  | 939 |
|              | Synthesis of Product Subclass 2   |  | 941 |
| 1.8.2.1      | Method 1:   | Preparation of Ruthenium–Cyclopentadienyl Complexes                                    | 941 |

---

|           |              |   |     |
|-----------|--------------|---|-----|
| 1.8.2.1.1 | Variation 1: | From Cyclopentadienes (CpH) .....                                       | 942 |
| 1.8.2.1.2 | Variation 2: | From Organometallic Cyclopentadienyl Reagents (MCp) ....                | 944 |
| 1.8.2.1.3 | Variation 3: | By Ligand Exchange .....  | 945 |
| 1.8.2.1.4 | Variation 4: | By Ligand Substitution .....  | 946 |
| 1.8.2.2   | Method 2:    | Preparation of Cationic Ruthenium–Cyclopentadienyl<br>Complexes .....   | 946 |
|           |              | Applications of Product Subclass 2 in Organic Synthesis .....           | 947 |
| 1.8.2.3   | Method 3:    | Reactions with Alkylolithium Reagents .....                             | 947 |
| 1.8.2.4   | Method 4:    | Electrophilic Substitution (Friedel–Crafts-type Reaction) ....          | 947 |
| 1.8.2.5   | Method 5:    | Preparation of Ruthenium–Vinylidene–Cyclopentadienyl<br>Complexes ..... | 948 |
| 1.8.3     |              | <b>Product Subclass 3: Ruthenium–Diene Complexes</b> .....              | 949 |
|           |              | Synthesis of Product Subclass 3 .....                                   | 951 |
| 1.8.3.1   | Method 1:    | Preparation of Ruthenium–Diene Complexes by<br>Ligand Exchange .....    | 951 |
|           |              | Applications of Product Subclass 3 in Organic Synthesis .....           | 951 |
| 1.8.3.2   | Method 2:    | Reactions Involving Ruthenium–Diene Complexes .....                     | 951 |
| 1.8.4     |              | <b>Product Subclass 4: Ruthenium–Allyl Complexes</b> .....              | 952 |
|           |              | Synthesis of Product Subclass 4 .....                                   | 953 |
| 1.8.4.1   | Method 1:    | Preparation of Ruthenium–Allyl Complexes .....                          | 953 |
|           |              | Applications of Product Subclass 4 in Organic Synthesis .....           | 954 |
| 1.8.4.2   | Method 2:    | Reactions Involving Ruthenium–Allyl Complexes .....                     | 954 |
| 1.8.5     |              | <b>Product Subclass 5: Ruthenium–Alkyne Complexes</b> .....             | 956 |
|           |              | Synthesis of Product Subclass 5 .....                                   | 959 |
| 1.8.5.1   | Method 1:    | Preparation of Ruthenium–Alkyne Complexes by Irradiation .              | 959 |
|           |              | Applications of Product Subclass 5 in Organic Synthesis .....           | 959 |
| 1.8.5.2   | Method 2:    | Reactions Involving Ruthenium–Alkyne Complexes .....                    | 959 |
| 1.8.6     |              | <b>Product Subclass 6: Ruthenium–Alkene Complexes</b> .....             | 963 |
|           |              | Synthesis of Product Subclass 6 .....                                   | 965 |
| 1.8.6.1   | Method 1:    | Preparation of Ruthenium(II)–Alkene Complexes .....                     | 965 |
| 1.8.6.2   | Method 2:    | Preparation of Ruthenium(0)–Alkene Complexes .....                      | 965 |
|           |              | Applications of Product Subclass 6 in Organic Synthesis .....           | 967 |
| 1.8.6.3   | Method 3:    | Reactions Involving Ruthenium–Alkene Complexes .....                    | 967 |

---

|                  |  |      |
|------------------|--|------|
| <b>1.9</b>       | <b>Product Class 9: Organometallic Complexes of Osmium</b><br>J. Gonzalez and W. D. Harman                       |      |
| <b>1.9</b>       | <b>Product Class 9: Organometallic Complexes of Osmium</b> .....   | 973  |
| <b>1.9.1</b>     | <b>Product Subclass 1: Osmium-<math>\eta^2</math>-Arene and -<math>\eta^2</math>-Heteroarene Complexes</b> ..... | 977  |
|                  | Synthesis of Product Subclass 1 .....  | 981  |
| <b>1.9.1.1</b>   | Method 1: Exchange of a Trifluoromethanesulfonate Anion for<br>an Organic Ligand .....                           | 981  |
| <b>1.9.1.2</b>   | Method 2: Electrophilic Aromatic Substitution on the Ligand .....  | 983  |
|                  | Applications of Product Subclass 1 in Organic Synthesis .....  | 984  |
| <b>1.9.1.3</b>   | Method 3: Electrophilic Addition and Substitution .....  | 984  |
| <b>1.9.1.4</b>   | Method 4: Sequential Addition of Electrophiles and Nucleophiles .....  | 987  |
| <b>1.9.1.4.1</b> | Variation 1: [4+2]-Cycloaddition Reactions .....   | 990  |
| <b>1.9.1.4.2</b> | Variation 2: 1,3-Dipolar Cycloadditions .....  | 993  |
| <b>1.9.1.4.3</b> | Variation 3: Michael-Michael Ring Closures and<br>Related Annulation Reactions .....                             | 997  |
| <b>1.9.1.5</b>   | Method 5: Addition of Nucleophiles to S-Alkylthiophenium Complexes .....   | 1002 |
| <b>1.9.2</b>     | <b>Product Subclass 2: Osmium-Allyl Complexes</b> .....  | 1003 |
|                  | Synthesis of Product Subclass 2 .....  | 1003 |
| <b>1.9.2.1</b>   | Method 1: Elimination of Labile Allylic Substituents .....   | 1003 |
| <b>1.9.2.2</b>   | Method 2: Addition of Electrophiles to Diene and Arene Complexes .....   | 1004 |
|                  | Applications of Product Subclass 2 in Organic Synthesis .....  | 1005 |
| <b>1.9.2.3</b>   | Method 3: Addition of Carbon Nucleophiles and<br>Tandem Difunctionalizations .....                               | 1005 |
| <b>1.9.3</b>     | <b>Product Subclass 3: Osmium-Carbonyl Complexes</b> .....   | 1007 |
| <b>1.9.4</b>     | <b>Product Subclass 4: Osmate Esters and Related Species</b> .....   | 1008 |
|                  | <b>Keyword Index</b> .....   | 1017 |
|                  | <b>Author Index</b> .....  | 1055 |
|                  | <b>Abbreviations</b> .....   | 1107 |

