## Preface

V

## Volume Editor's Preface

VII

## Table of Contents

XI

## Introduction

T. Imamoto ............................................................... 1

### 2.1 Product Class 1: Organometallic Complexes of Manganese

K. Oshima ................................................................ 13

### 2.2 Product Class 2: Organometallic Complexes of Technetium

I. D. Gridnev and T. Imamoto .............................................. 91

### 2.3 Product Class 3: Organometallic Complexes of Rhenium

F. E. Kühn, C. C. Romão, and W. A. Herrmann .......................... 111

### 2.4 Product Class 4: Arene Organometallic Complexes of Chromium, Molybdenum, and Tungsten

E. P. Kündig and S. H. Pache ................................................ 155

### 2.5 Product Class 5: Organometallic π-Complexes of Chromium, Molybdenum, and Tungsten Excluding Arenes

K. H. Theopold, A. Mommertz, and B. A. Salisbury ........................ 229

### 2.6 Product Class 6: Organometallic Complexes of Chromium, Molybdenum, and Tungsten without Carbonyl Ligands

R. Poli and K. M. Smith .................................................... 283

### 2.7 Product Class 7: Carbonyl Complexes of Chromium, Molybdenum, and Tungsten with σ-Bonded Ligands

T. Ito and M. Minato ......................................................... 333

### 2.8 Product Class 8: Organometallic Complexes of Vanadium

T. Imamoto and I. D. Gridnev ............................................... 385

### 2.9 Product Class 9: Organometallic Complexes of Niobium and Tantalum

K. Mashima and A. Nakamura ............................................. 415

### 2.10 Product Class 10: Organometallic Complexes of Titanium

K. Mikami, Y. Matsumoto, and T. Shiono ................................. 457
Table of Contents

Introduction
T. Imamoto

Introduction .............................................................. 1

2.1 Product Class 1: Organometallic Complexes of Manganese
K. Oshima

2.1 Product Class 1: Organometallic Complexes of Manganese 13
2.1.1 Product Subclass 1: Manganese–Cyclopentadienyl Complexes 13
Synthesis of Product Subclass 1 ...................................... 13
2.1.1.1 Method 1: By Reaction between Cyclopentadienyl Anions and Manganese Halides 13
2.1.1.1 Variation 1: From Lithium Cyclopentadienide Salts and Manganese(II) Chloride 14
2.1.1.2 Variation 2: From Cyclopentadienyl Salts and Carbonyl(halo)manganese Complexes 15
2.1.1.2 Method 2: By Reaction between 5-Acetyl-1,2,3,4,5-pentamethylcyclopentadiene and Decacarbonyldimanganese(0) 17
2.1.1.3 Method 3: By Substitution Reactions on the Manganese-Coordinated Cyclopentadienyl Ring 18
2.1.1.4 Method 4: By Insertion of 5-Diazocyclopenta-1,3-diene into a Manganese–Halogen Bond 18

2.1.2 Product Subclass 2: Manganese–Dienyl and –Diene Complexes 19
Synthesis of Product Subclass 2 ...................................... 19
2.1.2.1 Method 1: (η⁵-Pentadienyl)manganese Complexes from Pentadienyl Anions 19
2.1.2.1 Variation 1: A Tetrakis(pentadienyl)trimanganese Complex from Manganese(II) Chloride and 3-Methylpentadienyl Anion 21
2.1.2.2 Method 2: (η⁴-Butadiene)manganese Complexes from the Butadiene–magnesium–Bis(tetrahydrofuran) Complex and Manganese(II) Chloride 22
2.1.2.3 Method 3: (η⁵-Pentadienyl)manganese Complexes from Potassium Pentadienide Salts 22
2.1.2.4 Method 4: (η⁵-Cyclohexadienyl)manganese Complexes by Reaction between Decacarbonyldimanganese(0) and Cyclohexa-1,3-dienes or by Reduction of Manganese–Arene Complexes 23
2.1.3 **Product Subclass 3: Manganese–\(\eta^3\)-Allyl Complexes** ............................ 24
   Synthesis of Product Subclass 3 .............................................. 24
2.1.3.1 Method 1: From Carbonyl(halo)manganese Complexes and Allyl Bromide 24
2.1.3.2 Method 2: From (\(\eta^3\)-Alkene)- or (\(\eta^2\)-1,3-Diene)manganese Complexes 24
2.1.3.3 Method 3: From (\(\eta^1\)-Allyl)manganese Complexes by \(\eta^1\) to \(\eta^3\) Isomerization 25
   Applications of Product Subclass 3 in Organic Synthesis .................... 26
2.1.3.4 Method 4: Reaction of (\(\eta^3\)-Allyl)manganese Complexes with Nucleophiles 26
2.1.4 **Product Subclass 4: Manganese–Alkyne Complexes** ............................ 27
   Synthesis of Product Subclass 4 .............................................. 27
2.1.4.1 Method 1: By Ligand Substitution ...................................... 27
2.1.5 **Product Subclass 5: Manganese–Alkene Complexes** ............................ 29
   Synthesis of Product Subclass 5 .............................................. 29
2.1.5.1 Method 1: By Ligand Substitution ...................................... 29
2.1.5.2 Method 2: By Ligand Transformation .................................... 30
2.1.6 **Product Subclass 6: Manganese–Carbene Complexes** ............................ 30
   Synthesis of Product Subclass 6 .............................................. 30
2.1.6.1 Method 1: By Reaction between Alkylmetals and Carbonylmanganese Complexes 30
2.1.6.2 Method 2: Exocyclic Fischer Carbene Complexes by Reaction of Dibromoalkanes, Aziridines, or Oxiranes with Carbonylmanganese Complexes 33
2.1.6.3 Method 3: Manganese–Ethenylidene Complexes from Ethyldyne Complexes 34
2.1.6.4 Method 4: From Manganese–Acetylene Complexes ...................... 35
   Applications of Product Subclass 6 in Organic Synthesis .................... 36
2.1.6.5 Method 5: Reaction with Enynes, \(\alpha,\beta\)-Unsaturated Esters, or Alkynes .... 36
2.1.7 **Product Subclass 7: Manganese–Carbyne Complexes** ............................ 38
   Synthesis of Product Subclass 7 .............................................. 38
2.1.7.1 Method 1: From Manganese–Carbene Complexes ...................... 38
2.1.8 **Product Subclass 8: Manganese–\(\sigma\)-Alkyl Complexes** ............................ 39
   Synthesis of Product Subclass 8 .............................................. 39
2.1.8.1 Method 1: From Alkyl Halides and Sodium Pentacarbonylmanganate(–I) 39
2.1.8.2 Method 2: From Alkylmetals and Manganese(II) Halides .................. 40
2.1.8.2.1 Variation 1: Preparation of Tetraalkylmanganate(II) .................. 40
2.1.8.2.2 Variation 2: Preparation of Mono-, Di-, and Trialkylmanganate(II) Complexes 41
   Applications of Product Subclass 8 in Organic Synthesis .................... 43
2.1.8.3 Method 3: Use of Organomanganese Reagents ........................... 43
2.1.8.4 Method 4: Use of Alkylpentacarbonylmanganese(I) Complexes .......... 44
2.1.9 Product Subclass 9: Manganese–\( \eta^1 \)-Allyl Complexes

Synthesis of Product Subclass 9

2.1.9.1 Method 1: From Allyl Halides and Metallic Manganese or Low-Valent Manganese Generated by the Reduction of Manganese(II) Halides

2.1.9.2 Method 2: From Allylmagnesium Halides and Manganese(II) Halides

2.1.9.3 Method 3: From Allylic Halides and Tetrabutylmanganate(II)

2.1.9.4 Method 4: From 1,3-Dienes and Pentacarbonylhydridomanganese(I)

Applications of Product Subclass 9 in Organic Synthesis

2.1.9.5 Method 5: Allylation of Carbonyl and Other Unsaturated Compounds

2.1.10 Product Subclass 10: Manganese–Aryl, –Alkenyl, and –Alkynyl Complexes

Synthesis of Product Subclass 10

2.1.10.1 Method 1: Arylmanganese Complexes from Arylmetals and Manganese(II) Halides

2.1.10.2 Method 2: Arylmanganese Complexes from Acetophenones and Carboxyliermanganese Complexes

2.1.10.3 Method 3: Arylmanganese Complexes by Acylation–Decarbonylation

2.1.10.4 Method 4: Alkenylmanganese Complexes from Alkynes and Alkyl(carbonyl)manganese Complexes by Alkyn Insertion

2.1.10.5 Method 5: Alkynyl(carbonyl)manganese Complexes from Alkynes and Carbonyl(halo)manganese Complexes

Applications of Product Subclass 10 in Organic Synthesis

2.1.10.6 Method 6: Reaction of Alkenyl-, Aryl-, and Alkynylmanganese Halides with Acid Chlorides

2.1.10.7 Method 7: Demetalation of Aryl- and Alkenylmanganese Complexes

2.1.11 Product Subclass 11: Manganese–Hydrido Complexes

Synthesis of Product Subclass 11

2.1.11.1 Method 1: Preparation of Pentacarbonylhydridomanganese(I)

2.1.11.2 Method 2: Preparation of Substituted Carbonylhydridomanganese(I) Complexes

2.1.11.3 Method 3: Preparation of Tetracarbonylmanganate(–III) and Tris[tetracarbonylhydridomanganese(I)]

2.1.11.4 Method 4: Preparation of (\( \eta^5 \)-Arene)dicarbonylhydridomanganese(I) Complexes

2.1.11.5 Method 5: Preparation of (\( \eta^5 \)-Cyclopentadienyl)dihydridomanganese(III) Complexes

2.1.11.6 Method 6: Preparation of Hydrido(iodo)manganese(II)

Applications of Product Subclass 11 in Organic Synthesis

2.1.11.7 Method 7: Reduction of Activated C=C Bonds

2.1.12 Product Subclass 12: Neutral Dimanganese–Carbonyl Complexes

Synthesis of Product Subclass 12

2.1.12.1 Method 1: Homoleptic Dimanganese–Carbonyl Complexes by Reduction under Carbon Monoxide
<table>
<thead>
<tr>
<th>Section</th>
<th>Method</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1.12.2</td>
<td>Method 2:</td>
<td>Dimanganese–Carbonyl Complexes Substituted with Group 15 Ligands</td>
</tr>
<tr>
<td>2.1.12.3</td>
<td>Method 3:</td>
<td>Nonacarbonyldimanganese(0)–Aldehyde Complexes</td>
</tr>
<tr>
<td>2.1.13</td>
<td><strong>Product Subclass 13: Anionic Manganese–Carbonyl Complexes</strong></td>
<td></td>
</tr>
<tr>
<td>2.1.13.1</td>
<td>Method 1:</td>
<td>Synthesis of Product Subclass 13</td>
</tr>
<tr>
<td>2.1.13.2</td>
<td>Variation 1:</td>
<td>By Reduction</td>
</tr>
<tr>
<td>2.1.13.3</td>
<td>Variation 2:</td>
<td>With Sodium/Mercury Amalgam</td>
</tr>
<tr>
<td>2.1.13.4</td>
<td>Variation 3:</td>
<td>With Trialkylborohydride or Potassium Hydride</td>
</tr>
<tr>
<td>2.1.13.5</td>
<td>Variation 4:</td>
<td>With Sodium Bis(2-methoxyethoxy)aluminum Hydride</td>
</tr>
<tr>
<td>2.1.14</td>
<td><strong>Product Subclass 14: Cationic Manganese–Carbonyl Complexes</strong></td>
<td></td>
</tr>
<tr>
<td>2.1.14.1</td>
<td>Method 1:</td>
<td>Synthesis of Product Subclass 14</td>
</tr>
<tr>
<td>2.1.14.2</td>
<td>Method 2:</td>
<td>From Carbonyl(halo)manganese(I) Complexes by Substitution of a Halide for a Neutral Monohapto Ligand in the Presence of a Halide Acceptor</td>
</tr>
<tr>
<td>2.1.14.3</td>
<td>Method 3:</td>
<td>From (Alkoxycarbonyl)manganese Complexes by Treatment with Acid</td>
</tr>
<tr>
<td>2.1.14.4</td>
<td>Method 4:</td>
<td>By Oxidation of Decacarbonyldimanganese(0) by Nitrosium Hexafluorophosphate in the Presence of a Neutral Ligand</td>
</tr>
<tr>
<td>2.1.14.5</td>
<td>Method 5:</td>
<td>From Carbonyl(halo)manganese(I) Complexes by Substitution of a Halo for an Arene Ligand To Form Cationic (Arene)tricarbonylmanganese(I) Complexes</td>
</tr>
<tr>
<td>2.1.14.6</td>
<td>Method 6:</td>
<td>From Carbonylhydridomanganese(I) Complexes by Substitution of the Hydrido for a Neutral Ligand</td>
</tr>
<tr>
<td>2.1.15</td>
<td><strong>Product Subclass 15: Miscellaneous Complexes</strong></td>
<td></td>
</tr>
<tr>
<td>2.1.15.1</td>
<td>Method 1:</td>
<td>Synthesis of Product Subclass 15</td>
</tr>
<tr>
<td>2.1.15.2</td>
<td>Method 2:</td>
<td>Preparation of Carbonylmanganese–Halo Complexes</td>
</tr>
<tr>
<td>2.1.15.3</td>
<td>Method 3:</td>
<td>Preparation of Carbonylmanganese–Pseudohalo Complexes</td>
</tr>
<tr>
<td>2.1.15.4</td>
<td>Method 4:</td>
<td>Preparation of Nitrosylmanganese Complexes</td>
</tr>
<tr>
<td>2.1.15.5</td>
<td>Method 5:</td>
<td>Preparation of Isocyanidemanganese Complexes</td>
</tr>
<tr>
<td>2.1.15.6</td>
<td>Method 6:</td>
<td>Preparation of Silylmanganese Complexes</td>
</tr>
</tbody>
</table>
### 2.1.7 Method 7: Preparation of (1-Hydroxyalkyl)manganese Complexes

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preparation of (1-Hydroxyalkyl)manganese Complexes</td>
<td>84</td>
</tr>
</tbody>
</table>

### 2.1.8 Method 8: Preparation of Tetracarbonyl(octahydrotriborato(1–))manganese

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preparation of Tetracarbonyl(octahydrotriborato(1–))manganese</td>
<td>84</td>
</tr>
</tbody>
</table>

## 2.2 Product Class 2: Organometallic Complexes of Technetium

I. D. Gridnev and T. Imamoto

### 2.2.1 Product Subclass 1: Technetium–Arene Complexes

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesis of Product Subclass 1</td>
<td>92</td>
</tr>
</tbody>
</table>

#### 2.2.1.1 Method 1: By Interelement Synthesis

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>By Interelement Synthesis</td>
<td>92</td>
</tr>
</tbody>
</table>

#### 2.2.1.2 Method 2: From Technetium(IV) Chloride or Sodium Pertechnetate

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>From Technetium(IV) Chloride or Sodium Pertechnetate</td>
<td>92</td>
</tr>
</tbody>
</table>

#### 2.2.1.3 Method 3: Synthesis of Mixed Arene–Diene Complexes by Reduction of Bis(arene) Complexes

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesis of Mixed Arene–Diene Complexes by Reduction of Bis(arene) Complexes</td>
<td>93</td>
</tr>
</tbody>
</table>

#### 2.2.1.4 Method 4: Synthesis of (η¹-Benzene)tricarbonyltechnetium Chloride from Sodium Nonacarbonylheptamethoxytritechnetate(1–)

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesis of (η¹-Benzene)tricarbonyltechnetium Chloride from Sodium Nonacarbonylheptamethoxytritechnetate(1–)</td>
<td>93</td>
</tr>
</tbody>
</table>

### 2.2.2 Product Subclass 2: Technetium–Cyclopentadienyl and Substituted Cyclopentadienyl Complexes

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesis of Product Subclass 2</td>
<td>94</td>
</tr>
</tbody>
</table>

#### 2.2.2.1 Method 1: By the Reactions of Technetium Halides with Metal Cyclopentadienides

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>By the Reactions of Technetium Halides with Metal Cyclopentadienides</td>
<td>94</td>
</tr>
</tbody>
</table>

#### 2.2.2.2 Method 2: From Decacarbonylditechnetium

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>From Decacarbonylditechnetium</td>
<td>95</td>
</tr>
</tbody>
</table>

#### 2.2.2.3 Method 3: From Pentacarbonyltechnetium Iodide

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>From Pentacarbonyltechnetium Iodide</td>
<td>96</td>
</tr>
</tbody>
</table>

#### 2.2.2.4 Method 4: From Sodium Nonacarbonylheptamethoxytritechnetate(1–)

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>From Sodium Nonacarbonylheptamethoxytritechnetate(1–)</td>
<td>96</td>
</tr>
</tbody>
</table>

### 2.2.3 Product Subclass 3: Technetium–Carbene Complexes

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesis of Product Subclass 3</td>
<td>96</td>
</tr>
</tbody>
</table>

#### 2.2.3.1 Method 1: From Technetium–Carbonyls and Organolithium Compounds

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>From Technetium–Carbonyls and Organolithium Compounds</td>
<td>97</td>
</tr>
</tbody>
</table>

#### 2.2.3.2 Method 2: By the Reactions of Chlorobis[1,2-bis(diphenylphosphino)ethane]technetium with Terminal Alkynes

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>By the Reactions of Chlorobis[1,2-bis(diphenylphosphino)ethane]technetium with Terminal Alkynes</td>
<td>97</td>
</tr>
</tbody>
</table>

#### 2.2.3.3 Method 3: Reaction of a Benzoylcarbonyltechnetium Complex with Triethylxonium Tetrafluoroborate

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction of a Benzoylcarbonyltechnetium Complex with Triethylxonium Tetrafluoroborate</td>
<td>98</td>
</tr>
</tbody>
</table>

#### 2.2.3.4 Method 4: From Carbyne Complexes

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>From Carbyne Complexes</td>
<td>98</td>
</tr>
</tbody>
</table>

### 2.2.4 Product Subclass 4: Technetium–Carbyne Complexes

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesis of Product Subclass 4</td>
<td>99</td>
</tr>
</tbody>
</table>

#### 2.2.4.1 Method 1: By Protonation of Carbene Complexes

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>By Protonation of Carbene Complexes</td>
<td>99</td>
</tr>
</tbody>
</table>

#### 2.2.4.2 Method 2: By Reaction of Carbene Complexes with Boron Trichloride

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>By Reaction of Carbene Complexes with Boron Trichloride</td>
<td>100</td>
</tr>
</tbody>
</table>

### 2.2.5 Product Subclass 5: Technetium–σ-Alkyl Complexes

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesis of Product Subclass 5</td>
<td>100</td>
</tr>
</tbody>
</table>

#### 2.2.5.1 Method 1: Reaction of Technetium(VII) Oxide with Tetramethylstannane

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction of Technetium(VII) Oxide with Tetramethylstannane</td>
<td>100</td>
</tr>
</tbody>
</table>

#### 2.2.5.2 Method 2: Reaction of Technetium–Imido Complexes with Grignard Reagents

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction of Technetium–Imido Complexes with Grignard Reagents</td>
<td>101</td>
</tr>
</tbody>
</table>
2.2.6 **Product Subclass 6: Technetium–Carbonyl Complexes** ........................................... 102
   Synthesis of Product Subclass 6 ................................................................. 102
2.2.6.1 Method 1: Synthesis of Decacarbonylditechnetium ........................................ 102
2.2.6.2 Method 2: Synthesis of Pentacarbonylttechnetium Halides and Related Complexes .................................................................................. 102
2.2.6.3 Method 3: Synthesis of Technetium–Carbonyl Complexes Containing Triphenylphosphine and Other Ligands ...................................................... 104
2.2.6.4 Method 4: Synthesis of Technetium–Aquacarbonyl Complexes .......................... 104
2.2.7 **Product Subclass 7: Technetium–Isocyanide Complexes** ........................................ 105
   Synthesis of Product Subclass 7 ........................................................................ 105
2.2.7.1 Method 1: Reduction of Pertechnetate Ion in the Presence of Isocyanide Ligands .................................................................................. 105
2.2.7.2 Method 2: By Substitution Reactions .......................................................... 106
2.2.8 **Product Subclass 8: Miscellaneous Technetium Complexes** ................................ 107
   Synthesis of Product Subclass 8 ........................................................................ 107
2.2.8.1 Method 1: Synthesis of Hydridotechnetium Complexes .................................. 107
2.2.8.2 Method 2: Synthesis of Technetium Dinitrogen Complexes ............................. 107

2.3 **Product Class 3: Organometallic Complexes of Rhenium**
F. E. Kühn, C. C. Romão, and W. A. Herrmann

2.3 **Product Class 3: Organometallic Complexes of Rhenium** ......................................... 111
2.3.1 **Product Subclass 1: Rhenium–Arene Complexes** .............................................. 111
   Synthesis of Product Subclass 1 ......................................................................... 112
2.3.1.1 Method 1: Reductive Synthesis from Rhenium Halides ................................... 112
2.3.1.2 Method 2: Synthesis from Low-Oxidation-State Rhenium Precursors ............. 113
2.3.1.2.1 Variation 1: By Metal-Vapor Synthesis ..................................................... 113
2.3.1.2.2 Variation 2: By Ligand Substitution from Rhenium–Carbonyl Complexes ... 114
2.3.2 **Product Subclass 2: Rhenium–Dienyl Complexes** ............................................... 114
   Synthesis of Product Subclass 2 ......................................................................... 116
2.3.2.1 Method 1: Ligand Substitutions ...................................................................... 116
2.3.2.1.1 Variation 1: Synthesis from Trioxo($\eta^3$-pentamethylcyclopentadienyl)rhe-
   niuim(VII) and Tetrachloro($\eta^3$-pentamethylcyclopentadienyl)
   rhenium(V) ........................................................................................................ 117
2.3.2.1.2 Variation 2: Synthesis from Rhenium(VII) Oxide .................................... 119
2.3.2.2 Method 2: Oxidation Reactions ..................................................................... 119
2.3.2.2.1 Variation 1: Synthesis from Tricarbonyl($\eta^3$-pentamethylcyclopentadienyl)
   rhenium(I) .......................................................................................................... 120
2.3.2.2.2 Variation 2: Synthesis from Bis($\eta^2$-cyclopentadienyl)hydridorhenium(III) .. 121
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3.3</td>
<td>Product Subclass 3: Rhenium–Alkyne Complexes</td>
<td>121</td>
</tr>
<tr>
<td>2.3.3.1</td>
<td>Method 1: Reduction of Rhenium(VII) Precursors</td>
<td>121</td>
</tr>
<tr>
<td>2.3.4</td>
<td>Product Subclass 4: Rhenium–Alkene Complexes</td>
<td>122</td>
</tr>
<tr>
<td>2.3.4.1</td>
<td>Method 1: Nucleophilic Additions</td>
<td>122</td>
</tr>
<tr>
<td>2.3.4.2</td>
<td>Variation 1: Nucleophilic Addition to ((\eta^5\text{-Cyclopentadienyl})(\text{nitrosyl})(\text{tri-phenylphosphine})\text{rhenium}(1+))</td>
<td>122</td>
</tr>
<tr>
<td>2.3.4.2.2</td>
<td>Variation 2: Nucleophilic Addition to Pentacarbonylrhenium(1+)</td>
<td>123</td>
</tr>
<tr>
<td>2.3.5</td>
<td>Product Subclass 5: Rhenium–Carbene Complexes</td>
<td>124</td>
</tr>
<tr>
<td>2.3.5.1</td>
<td>Method 1: Photolysis of an Organorhenium(VII) Oxide</td>
<td>124</td>
</tr>
<tr>
<td>2.3.6</td>
<td>Product Subclass 6: Rhenium–Carbyne Complexes</td>
<td>125</td>
</tr>
<tr>
<td>2.3.6.1</td>
<td>Method 1: Ligand Substitution</td>
<td>125</td>
</tr>
<tr>
<td>2.3.6.2</td>
<td>Method 2: Alkene Metathesis</td>
<td>126</td>
</tr>
<tr>
<td>2.3.7</td>
<td>Product Subclass 7: Rhenium–Alkyl Complexes</td>
<td>127</td>
</tr>
<tr>
<td>2.3.7.1</td>
<td>Method 1: By Nucleophilic Reactions of Pentacarbonylrhenate(1–)</td>
<td>127</td>
</tr>
<tr>
<td>2.3.7.2</td>
<td>Method 2: Ligand Substitutions</td>
<td>128</td>
</tr>
<tr>
<td>2.3.7.2.1</td>
<td>Variation 1: From Rhenium(VII) Oxide</td>
<td>128</td>
</tr>
<tr>
<td>2.3.7.2.2</td>
<td>Variation 2: From Silver(I) Perrhenate</td>
<td>129</td>
</tr>
<tr>
<td>2.3.7.2.3</td>
<td>Variation 3: Synthesis of Alkyl(peroxo)rhenium(VII) Complexes</td>
<td>130</td>
</tr>
<tr>
<td>2.3.7.3</td>
<td>Method 3: Oxidation Catalysis</td>
<td>131</td>
</tr>
<tr>
<td>2.3.7.3.1</td>
<td>Variation 1: Alkene Epoxidation</td>
<td>131</td>
</tr>
<tr>
<td>2.3.7.3.2</td>
<td>Variation 2: Arene Oxidation</td>
<td>134</td>
</tr>
<tr>
<td>2.3.7.4</td>
<td>Method 4: Alkene Metathesis</td>
<td>136</td>
</tr>
<tr>
<td>2.3.7.5</td>
<td>Method 5: Alkenation of Aldehydes</td>
<td>137</td>
</tr>
<tr>
<td>2.3.8</td>
<td>Product Subclass 8: Rhenium–Hydride Complexes</td>
<td>139</td>
</tr>
<tr>
<td>2.3.8.1</td>
<td>Method 1: Substitution Reactions from Other Rhenium Hydrides</td>
<td>140</td>
</tr>
<tr>
<td>2.3.9</td>
<td>Product Subclass 9: Rhenium–Carbonyl Complexes</td>
<td>142</td>
</tr>
<tr>
<td>2.3.9.1</td>
<td>Method 1: From Decacarbonyldirhenium</td>
<td>142</td>
</tr>
<tr>
<td>2.3.9.1.1</td>
<td>Variation 1: Substitution Reactions</td>
<td>143</td>
</tr>
<tr>
<td>2.3.9.1.2</td>
<td>Variation 2: Redox Reactions</td>
<td>143</td>
</tr>
<tr>
<td>2.3.9.1.3</td>
<td>Variation 3: Nucleophilic Attack</td>
<td>144</td>
</tr>
</tbody>
</table>
2.3.9.4 Variation 4: Homolytic Cleavage ........................................ 144
2.3.9.2 Method 2: Nucleophilic Reactions of Pentacarbonylrhenate(1−) .......... 145
2.3.9.3 Method 3: Cationic Carbonylrhenium Complexes ........................ 146
2.3.9.4 Method 4: Carbonyl(halo)rhenium Complexes Prepared by Oxidative Addition .................................................. 146
2.3.9.5 Method 5: Carbonyl(halo)- and Carbonyl(pseudohalo)rhenium Complexes Prepared from Pentacarbonylrhenium(I) Tetrafluoroborate ........ 147

2.4 Product Class 4: Arene Organometallic Complexes of Chromium, Molybdenum, and Tungsten  
E. P. Kündig and S. H. Pache

2.4 Synthesis of Product Class 4 .................................................. 155
2.4.1 Method 1: Direct Synthesis of Metal–Bis(arene) Complexes via Metal Evaporation .............................................. 155
2.4.2 Method 2: Synthesis of Metal–Bis(arene) Complexes by Reductive Methods .................................................. 157
2.4.3 Method 3: Synthesis of Metal–Bis(arene) Complexes by Arene Exchange, by Arene Transformation Reactions, and by Cyclic Condensation Reactions ................................................. 158
2.4.4 Method 4: Synthesis of Tricarbonylmetal–Arene Complexes from Metal–Carbonyls ................................................. 159
2.4.4.1 Variation 1: From Hexacarbonylmetal Complexes ................................. 159
2.4.4.2 Variation 2: From [M(CO)3L3] Complexes ........................................... 162
2.4.4.3 Variation 3: By Arene and Heteroarene Exchange ................................ 163
2.4.4.4 Variation 4: From (Carbene)pentacarbonylmetal Complexes ............ 164
2.4.5 Method 5: Synthesis of Tricarbonylmetal–Arene Complexes by Arene Modification ........................................... 165
2.4.5.1 Variation 1: Via Lithiation and Reaction with Electrophiles ................. 166
2.4.5.2 Variation 2: Via Nucleophilic Substitution ........................................... 168
2.4.5.3 Variation 3: Via Palladium-Catalyzed Reactions .................................. 170
2.4.6 Method 6: Synthesis of Tricarbonylmetal–Arene Complexes by Side-Chain Modification ........................................... 172
2.4.6.1 Variation 1: Via Nucleophile Addition .............................................. 172
2.4.6.2 Variation 2: Via Benzylc Cations .................................................... 176
2.4.6.3 Variation 3: Via Benzylc Anions .................................................... 180
2.4.6.4 Variation 4: Via Cycloaddition Reactions ......................................... 182
2.4.6.5 Variation 5: Via Radical Coupling Reactions .................................... 186
2.4.6.6 Variation 6: Via Ring Expansion Rearrangements .............................. 187
2.4.7 Method 7: Synthesis of Optically Active Arene Complexes .................. 188
2.4.7.1 Variation 1: Resolution of Racemates ......................................... 188
2.4.7.2 Variation 2: Diastereoselective Complexation ................................... 189
2.4.7.3 Variation 3: Diastereo- and Enantioselective Lithiation–Electrophilic Addition Reactions ................................................... 191
2.4.7.4 Variation 4: Diastereo- or Enantioselective Nucleophile Addition Followed by endo-Hydride Abstraction .......................... 195
2.4.7.5 Variation 5: Palladium-Catalyzed Reactions ................................................... 196
2.4.7.6 Variation 6: Diastereo- or Enantioselective Benzannulation Reactions ................................................... 198
2.4.8 Method 8: Synthesis of [M(arene)(CO),(L),x] Complexes ................................................... 199
2.4.9 Method 9: Synthesis of Heteroarene Complexes ................................................... 203

Applications of Product Class 4 in Organic Synthesis ................................................... 207
2.4.10 Method 10: (Arene)tricarbonylchromium(0) Complexes as Catalysts ................................................... 207
2.4.11 Method 11: (Arene)tricarbonylchromium(0) Complexes as Auxiliaries and Building Blocks ................................................... 209
2.4.11.1 Variation 1: (Arene)tricarbonylchromium(0) Complexes as Chiral Ligands ................................................... 209
2.4.11.2 Variation 2: Arene Decomplexation ................................................... 210
2.4.11.3 Variation 3: Aromatic Substitution via Nucleophile Addition–Oxidation of (Arene)tricarbonylchromium(0) Complexes ................................................... 214
2.4.11.4 Variation 4: Dearomatization Reactions ................................................... 216

2.5 Product Class 5: Organometallic π-Complexes of Chromium, Molybdenum, and Tungsten Excluding Arenes
K. H. Theopold, A. Mommerz, and B. A. Salisbury

2.5 Product Class 5: Organometallic π-Complexes of Chromium, Molybdenum, and Tungsten Excluding Arenes ................................................... 229
2.5.1 Product Subclass 1: Metal–Triene and –Trienyl Complexes ................................................... 229

Synthesis of Product Subclass 1 ................................................... 229
2.5.1.1 Method 1: Ligand Substitution Reactions of Hexacarbonylchromium(0) or Hexacarbonylmolybdenum(0) with Trienes ................................................... 229
2.5.1.1.1 Variation 1: Substitution of Nitriles with Trienes ................................................... 231
2.5.1.2 Method 2: Synthesis of η⁶-Fulvene Complexes by Photocatalytic Substitution of Arenes in (η⁶-Arene)tricarbonylchromium(0) ................................................... 231
2.5.1.3 Method 3: Synthesis of η⁷-Cycloheptatrienyl Complexes by Abstraction of Hydride from Coordinated Cycloheptatriene ................................................... 232
2.5.1.3.1 Variation 1: Hydride Abstraction with Oxonium Salt ................................................... 233
2.5.1.4 Method 4: Reduction of Metal Halides in the Presence of Cycloheptatriene ................................................... 233
2.5.1.5 Method 5: Metal–Vapor Synthesis ................................................... 234

Applications of Product Subclass 1 in Organic Synthesis ................................................... 235
2.5.1.6 Method 6: Allylic Alkylation Catalyzed by a Tungsten–Cycloheptatriene Complex ................................................... 235

2.5.2 Product Subclass 2: Metal–Dienyl Complexes ................................................... 235

Synthesis of Product Subclass 2 ................................................... 236
2.5.2.1 Method 1: Ligand Substitution with Alkali Metal–Dienyl Complexes ................................................... 236
<table>
<thead>
<tr>
<th>Section</th>
<th>Method</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5.2.2</td>
<td>Method 2:</td>
<td>Ligand Substitution with Dienes</td>
</tr>
<tr>
<td>2.5.2.2.1</td>
<td>Variation 1:</td>
<td>Ligand Substitution of Metal Oxychlorides with Dienes</td>
</tr>
<tr>
<td>2.5.2.3</td>
<td>Method 3:</td>
<td>Intramolecular Reactions with Allylic Halides</td>
</tr>
<tr>
<td>2.5.2.4</td>
<td>Method 4:</td>
<td>Synthesis of Metal–Cycloadienyl Complexes from Metal–Arene or –Cycloheptatriene Complexes by Nucleophilic Addition</td>
</tr>
<tr>
<td>2.5.2.5</td>
<td>Method 5:</td>
<td>Protonation of Metal–Triene Complexes</td>
</tr>
<tr>
<td>2.5.2.6</td>
<td>Method 6:</td>
<td>Carbonyl Reduction with Molybdenum–Cyclopentadienyl Complexes</td>
</tr>
<tr>
<td>2.5.2.7</td>
<td>Method 7:</td>
<td>Hydrodehalogenation with Molybdenum–Cyclopentadienyl Complexes</td>
</tr>
<tr>
<td>2.5.2.8</td>
<td>Method 8:</td>
<td>Hydrogenation with Molybdenum–Cyclopentadienyl Complexes</td>
</tr>
<tr>
<td>2.5.3</td>
<td>Product Subclass 3: Metal–Diene Complexes</td>
<td>Synthesis of Product Subclass 3</td>
</tr>
<tr>
<td>2.5.3.1</td>
<td>Method 1:</td>
<td>Ligand Metathesis with Dienes</td>
</tr>
<tr>
<td>2.5.3.1.1</td>
<td>Variation 1:</td>
<td>Substitution of Electron-Deficient ( \eta^1 )-Acetylenes</td>
</tr>
<tr>
<td>2.5.3.1.2</td>
<td>Variation 2:</td>
<td>Substitution of Nitriles</td>
</tr>
<tr>
<td>2.5.3.2</td>
<td>Method 2:</td>
<td>Photolysis in the Presence of Dienes</td>
</tr>
<tr>
<td>2.5.3.3</td>
<td>Method 3:</td>
<td>Nucleophilic Addition to Metal–Cyclopentadienyl Complexes</td>
</tr>
<tr>
<td>2.5.3.4</td>
<td>Method 4:</td>
<td>Addition of Radicals to Metal–Cyclopentadienyl Complexes</td>
</tr>
<tr>
<td>2.5.3.5</td>
<td>Method 5:</td>
<td>Reduction of Metal Halides in the Presence of Dienes</td>
</tr>
<tr>
<td>2.5.3.6</td>
<td>Method 6:</td>
<td>Coupling of Metal-Bound Allyl Groups</td>
</tr>
<tr>
<td>2.5.3.7</td>
<td>Method 7:</td>
<td>([2 + 2]) Cycloadition of Metal-Bound Alkynes</td>
</tr>
<tr>
<td>2.5.3.8</td>
<td>Method 8:</td>
<td>Metal-Vapor Synthesis</td>
</tr>
<tr>
<td>2.5.4</td>
<td>Product Subclass 4: Metal–Allyl Complexes</td>
<td>Synthesis of Product Subclass 4</td>
</tr>
<tr>
<td>2.5.4.1</td>
<td>Method 1:</td>
<td>Substitution by Photolysis in the Presence of Alkynes</td>
</tr>
<tr>
<td>2.5.4.2</td>
<td>Method 2:</td>
<td>Deprotonation of Metal-Bound Dienes</td>
</tr>
<tr>
<td>2.5.4.3</td>
<td>Method 3:</td>
<td>Oxidative Addition of Allylic Compounds</td>
</tr>
<tr>
<td>2.5.4.4</td>
<td>Method 4:</td>
<td>Addition of Allylic Anions to Metal Complexes</td>
</tr>
<tr>
<td>2.5.4.5</td>
<td>Method 5:</td>
<td>Nucleophilic Substitution of Anionic Metal Complexes</td>
</tr>
<tr>
<td>2.5.4.6</td>
<td>Method 6:</td>
<td>Addition of Nucleophiles to Metal-Bound Dienes</td>
</tr>
<tr>
<td>2.5.5</td>
<td>Product Subclass 5: Metal–Alkyne Complexes</td>
<td>Synthesis of Product Subclass 5</td>
</tr>
<tr>
<td>2.5.5.1</td>
<td>Method 1:</td>
<td>Substitution by Photolysis of a Heteroleptic Metal–Carbonyl Complex in the Presence of Alkyne</td>
</tr>
<tr>
<td>2.5.5.2</td>
<td>Method 2:</td>
<td>Substitution Reactions</td>
</tr>
<tr>
<td>2.5.5.3</td>
<td>Method 3:</td>
<td>Reduction of Metal Halides in the Presence of Alkyne</td>
</tr>
<tr>
<td>2.5.5.3.1</td>
<td>Variation 1:</td>
<td>Reduction with Magnesium</td>
</tr>
</tbody>
</table>
### Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5.4</td>
<td>Method 4: Coupling of Two Isocyanide Ligands</td>
<td>267</td>
</tr>
<tr>
<td></td>
<td>Applications of Product Subclass 5 in Organic Synthesis</td>
<td>268</td>
</tr>
<tr>
<td>2.5.5</td>
<td>Method 5: Cycloaddition of Metal-Bound Alkynes with Cyclo-octatetraene</td>
<td>268</td>
</tr>
<tr>
<td>2.5.6</td>
<td><strong>Product Subclass 6: Metal–Alkene Complexes</strong></td>
<td>269</td>
</tr>
<tr>
<td></td>
<td>Synthesis of Product Subclass 6</td>
<td>270</td>
</tr>
<tr>
<td>2.5.6.1</td>
<td>Method 1: Photosubstitutions of Carbonyl Complexes</td>
<td>270</td>
</tr>
<tr>
<td>2.5.6.2</td>
<td>Method 2: Thermal Ligand Substitutions</td>
<td>271</td>
</tr>
<tr>
<td>2.5.6.2.1</td>
<td>Variation 1: Shifting the Equilibrium in Favor of the Alkene Complexes</td>
<td>273</td>
</tr>
<tr>
<td>2.5.6.3</td>
<td>Method 3: β-Hydride Elimination/Abstraction from Metal–Alkyl Complexes</td>
<td>274</td>
</tr>
<tr>
<td>2.5.6.4</td>
<td>Method 4: Nucleophilic Attack on Metal–Allyl Complexes</td>
<td>276</td>
</tr>
<tr>
<td>2.5.6.5</td>
<td>Method 5: Reduction of Metal Halides in the Presence of Alkene</td>
<td>276</td>
</tr>
<tr>
<td>2.6</td>
<td><strong>Product Class 6: Organometallic Complexes of Chromium, Molybdenum, and Tungsten without Carbonyl Ligands</strong></td>
<td>283</td>
</tr>
<tr>
<td></td>
<td>R. Poli and K. M. Smith</td>
<td>283</td>
</tr>
<tr>
<td>2.6.1</td>
<td><strong>Product Subclass 1: Metal–Carbene Complexes</strong></td>
<td>283</td>
</tr>
<tr>
<td></td>
<td>Synthesis of Product Subclass 1</td>
<td>284</td>
</tr>
<tr>
<td>2.6.1.1</td>
<td>Method 1: By α-Hydrogen Elimination from Alkyl Complexes</td>
<td>284</td>
</tr>
<tr>
<td>2.6.1.1.1</td>
<td>Variation 1: Alkylation of Chloride Precursors</td>
<td>284</td>
</tr>
<tr>
<td>2.6.1.1.2</td>
<td>Variation 2: Ligand Addition</td>
<td>285</td>
</tr>
<tr>
<td>2.6.1.1.3</td>
<td>Variation 3: Replacement of an Oxo or Imido Ligand</td>
<td>286</td>
</tr>
<tr>
<td>2.6.1.1.4</td>
<td>Variation 4: Deprotonation with an External Base</td>
<td>287</td>
</tr>
<tr>
<td>2.6.1.2</td>
<td>Method 2: By Stoichiometric Alkene Metathesis</td>
<td>287</td>
</tr>
<tr>
<td>2.6.1.3</td>
<td>Method 3: By Carbene Transfer</td>
<td>288</td>
</tr>
<tr>
<td>2.6.1.4</td>
<td>Method 4: From Carbene Complexes</td>
<td>289</td>
</tr>
<tr>
<td></td>
<td>Applications of Product Subclass 1 in Organic Synthesis</td>
<td>290</td>
</tr>
<tr>
<td>2.6.1.5</td>
<td>Method 5: Alkene Metathesis</td>
<td>290</td>
</tr>
<tr>
<td>2.6.1.5.1</td>
<td>Variation 1: Ring-Opening Metathesis Polymerization (ROMP)</td>
<td>291</td>
</tr>
<tr>
<td>2.6.1.5.2</td>
<td>Variation 2: Alkyne Polymerization</td>
<td>291</td>
</tr>
<tr>
<td>2.6.1.5.3</td>
<td>Variation 3: Ring-Closing Metathesis</td>
<td>292</td>
</tr>
<tr>
<td>2.6.1.5.4</td>
<td>Variation 4: Other Selective Metathesis Processes</td>
<td>294</td>
</tr>
<tr>
<td>2.6.1.6</td>
<td>Method 6: Carbonylmethylenation</td>
<td>295</td>
</tr>
<tr>
<td>2.6.2</td>
<td><strong>Product Subclass 2: Metal–Carbyne Complexes</strong></td>
<td>296</td>
</tr>
<tr>
<td></td>
<td>Synthesis of Product Subclass 2</td>
<td>297</td>
</tr>
<tr>
<td>2.6.2.1</td>
<td>Method 1: By α,α-Hydrogen Elimination from Alkyl Complexes</td>
<td>297</td>
</tr>
<tr>
<td>2.6.2.2</td>
<td>Method 2: By Addition of Alkynes to Compounds with Metal–Metal Triple Bonds</td>
<td>298</td>
</tr>
</tbody>
</table>

*Science of Synthesis Original Edition Volume 2 © Georg Thieme Verlag KG*

<table>
<thead>
<tr>
<th>Subclass</th>
<th>Method</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6.3</td>
<td>Method 3</td>
<td>By Stoichiometric Alkyne Metathesis</td>
</tr>
<tr>
<td>2.6.4</td>
<td>Method 4</td>
<td>By Oxidation of Fischer-Type Carbyne Complexes</td>
</tr>
<tr>
<td>2.6.5</td>
<td>Method 5</td>
<td>By Rearrangement of Vinyl Complexes</td>
</tr>
<tr>
<td>2.6.6</td>
<td>Method 6</td>
<td>By Other Rearrangement Processes</td>
</tr>
<tr>
<td>2.6.7</td>
<td>Method 7</td>
<td>Alkyne Metathesis</td>
</tr>
<tr>
<td>2.6.8</td>
<td>Product Subclass 3</td>
<td>Metal(\alpha)-Alkyl and (\alpha)-Aryl Homoleptic Complexes</td>
</tr>
<tr>
<td>2.6.9</td>
<td>Method 1</td>
<td>By Transmetalation</td>
</tr>
<tr>
<td>2.6.10</td>
<td>Product Subclass 4</td>
<td>Metal(\alpha)-Alkyl and (\alpha)-Aryl Non-homoleptic Complexes</td>
</tr>
<tr>
<td>2.6.11</td>
<td>Method 1</td>
<td>By Transmetalation</td>
</tr>
<tr>
<td>2.6.12</td>
<td>Method 2</td>
<td>By Oxidative Addition of Alkyl Halides</td>
</tr>
<tr>
<td>2.6.13</td>
<td>Method 3</td>
<td>By Oxidative Addition of Alkanes and Arenes</td>
</tr>
<tr>
<td>2.6.14</td>
<td>Method 4</td>
<td>By Protonation of Carbene and Carbyne Ligands</td>
</tr>
<tr>
<td>2.6.15</td>
<td>Product Subclass 5</td>
<td>Metallacyclic Complexes</td>
</tr>
<tr>
<td>2.6.16</td>
<td>Method 1</td>
<td>By Transmetalation</td>
</tr>
<tr>
<td>2.6.17</td>
<td>Method 2</td>
<td>By Reductive Coupling of Alkenes</td>
</tr>
<tr>
<td>2.6.18</td>
<td>Method 3</td>
<td>By Addition of Alkenes to Carbyne Complexes</td>
</tr>
<tr>
<td>2.6.19</td>
<td>Product Subclass 6</td>
<td>Complexes with Triply Bonded Heteroelement Ligands</td>
</tr>
<tr>
<td>2.6.20</td>
<td>Product Subclass 7</td>
<td>Complexes with Doubly Bonded Heteroelement Ligands</td>
</tr>
</tbody>
</table>

Applications of Product Subclass 2 in Organic Synthesis

Applications of Product Subclass 4 in Organic Synthesis

Application of Product Subclass 5 in Organic Synthesis

Application of Product Subclass 6 in Organic Synthesis

Application of Product Subclass 7 in Organic Synthesis
2.6.7.3 Method 3: From Complexes Containing Triply Bonded Heteroelement Ligands ........................................ 320
2.6.7.4 Method 4: By Oxidative Processes ........................................ 321
Applications of Product Subclass 7 in Organic Synthesis ..................... 322
2.6.7.5 Method 5: Catalytic Epoxidation of Alkenes .............................. 322

2.6.8 Product Subclass 8: Complexes with Singly Bonded Heteroelement Ligands

Synthesis of Product Subclass 8 ........................................ 323
2.6.8.1 Method 1: By Oxidative Addition of Compounds with Single Bonds between Heteroelements ..................... 323
2.6.8.2 Method 2: By Transmetalation ........................................ 324
2.6.8.3 Method 3: From α-Alkyl Complexes ...................................... 324
2.6.8.4 Method 4: From Carbene or Carbyne Complexes ....................... 325
2.6.8.5 Method 5: From Complexes Containing Doubly Bonded Heteroelement Ligands ........................................ 326

2.6.9 Product Subclass 9: Miscellaneous Complexes

Synthesis of Product Subclass 9 ........................................ 326
2.6.9.1 Method 1: Allylidene Complexes from Cyclopropenes .................. 326

2.7 Product Class 7: Carbonyl Complexes of Chromium, Molybdenum, and Tungsten with σ-Bonded Ligands

T. Ito and M. Minato

2.7.1 Product Subclass 1: Metal–Carbene Complexes .................................. 333
Synthesis of Product Subclass 1 ........................................ 333
2.7.1.1 Method 1: Fischer Method ........................................ 334
2.7.1.1.1 Variation 1: From Anionic Carbene Complexes ...................... 336
2.7.1.1.2 Variation 2: From Dianionic Complexes .............................. 337
2.7.1.1.3 Variation 3: From Acyloxycarbene Complexes ...................... 339
2.7.1.1.4 Variation 4: Synthesis of Miscellaneous Carbene Complexes ........ 340
Application of Product Subclass 1 in Organic Synthesis ..................... 341
2.7.1.2 Method 2: Cyclohexadiene and Cyclohexadienone Annulation ........ 341

2.7.2 Product Subclass 2: Metal–Carbyne Complexes .................................. 343
Synthesis of Product Subclass 2 ........................................ 343
2.7.2.1 Method 1: From Fischer-Type Carbene Complexes ...................... 343
2.7.2.1.1 Variation 1: By Formal Oxygen Abstraction from Acyl Ligands ........ 344
2.7.2.1.2 Variation 2: From Acetylides ........................................ 345
2.7.2.1.3 Variation 3: Synthesis of Miscellaneous Carbyne Complexes ........ 345
Applications of Product Subclass 2 in Organic Synthesis .......................... 348

2.7.2.2 Method 2: Synthesis of Phenol Derivatives ........................... 348

2.7.3 Product Subclass 3: Metal–Isocyanide Complexes ........................ 349

Synthesis of Product Subclass 3 .................................................. 349

2.7.3.1 Method 1: By Substitution of Carbonyl Complexes ..................... 350

2.7.3.1.1 Variation 1: By Catalytic Substitution Using Palladium(II) Oxide ..... 350

2.7.3.1.2 Variation 2: From Cyano Anionic Complexes .......................... 351

2.7.3.1.3 Variation 3: Synthesis of Miscellaneous Isocyanide Complexes .... 352

Applications of Product Subclass 3 in Organic Synthesis ......................... 353

2.7.3.2 Method 2: Synthesis of Functionalized Isocyanides .................... 353

2.7.4 Product Subclass 4: Metal–Nitrile Complexes and –Cyanide Complexes 354

Synthesis of Product Subclass 4 .................................................. 354

2.7.4.1 Method 1: Synthesis of Nitrile Complexes ............................ 354

2.7.4.1.1 Variation 1: Synthesis of Acrylonitrile–Carbonyl Complexes ........... 355

2.7.4.2 Method 2: Synthesis of Cyanide Complexes ........................... 355

2.7.4.2.1 Variation 1: By Reaction of Hexacarbonyl Complexes with Sodium Bis(trimethylsilyl)amide .................................................. 356

2.7.5 Product Subclass 5: Metal–Carbonyl Complexes with Ligands Containing Group 15 Elements .................................................. 357

Synthesis of Product Subclass 5 .................................................. 357

2.7.5.1 Method 1: Synthesis of Carbonyl Complexes of Phosphine, Arsine, or Stibine ............................................................... 357

2.7.5.1.1 Variation 1: Synthesis of Phosphine Complexes ....................... 358

2.7.5.1.2 Variation 2: Synthesis of Complexes with Chelating Ligands ........ 358

2.7.5.2 Method 2: Synthesis of Amino Acid Complexes ........................ 359

Applications of Product Subclass 5 in Organic Synthesis ........................ 360

2.7.5.3 Method 3: Ring-Opening Polymerization ................................ 360

2.7.6 Product Subclass 6: Metal–Carbonyl Complexes with Ligands Containing Group 16 Elements .................................................. 360

Synthesis of Product Subclass 6 .................................................. 360

2.7.6.1 Method 1: Synthesis of Pentacarbonyl(dialkyl sulfide) Complexes ...... 361

2.7.6.2 Method 2: Synthesis of Alkoxide Complexes ........................... 361

2.7.6.2.1 Variation 1: Synthesis of Hydroxide Complexes ....................... 362

2.7.6.2.2 Variation 2: Synthesis of Aryloxo Complexes ........................ 363

2.7.6.2.3 Variation 3: Synthesis of Catecholato Complexes ..................... 364

2.7.6.2.4 Variation 4: Synthesis of Miscellaneous Complexes ................ 365

2.7.7 Product Subclass 7: Carbonyl Halides ...................................... 366

Synthesis of Product Subclass 7 .................................................. 366

2.7.7.1 Method 1: By Reaction of Metal–Hexacarbonyl Complexes with Chlorine or Bromine .................................................. 366

2.7.7.1.1 Variation 1: From Metal–Hexacarbonyl Complexes ................... 367
2.7.1.2 Variation 2: Using a Phase-Transfer Agent ........................................ 368
2.7.1.3 Variation 3: By Photoreaction in the Presence of Crown Ethers ............... 369
2.7.1.4 Variation 4: Synthesis of Miscellaneous Complexes ........................... 370

2.7.8 **Product Subclass 8: Carbonyl Hydrides** ............................................ 370

Synthesis of Product Subclass 8 ........................................................................ 370

2.7.8.1 Method 1: By Reduction of Hexacarbonyl Complexes with Sodium Borohydride ................................................................. 370

2.7.8.1.1 Variation 1: By Ion-Pair Extraction .................................................. 371

2.7.8.1.2 Variation 2: By Reaction of Hydridochromium Pentacarbonyl Anion with Metal Pentacarbonyl(piperidine) Complexes ................. 372

2.7.8.2 Method 2: From Carbonylmetalate Tetraanions ..................................... 372

2.7.8.3 Method 3: Utilizing a Phase-Transfer Agent .......................................... 373

Applications of Product Subclass 8 in Organic Synthesis ................................. 373

2.7.9 **Product Subclass 9: Anionic Carbonyl Complexes** ............................... 374

Synthesis of Product Subclass 9 ........................................................................ 374

2.7.9.1 Method 1: By Reduction of Hexacarbonyl Complexes with Sodium in Liquid Ammonia ................................................................. 375

2.7.9.1.1 Variation 1: By Reduction with Alkali Metal Amalgam ....................... 376

2.7.9.2 Method 2: By Reduction of Hexacarbonylchromium(0) with Potassium-Graphite ........................................................................... 376

2.7.9.3 Method 3: From Carbonyl Derivatives .................................................. 377

2.8 **Product Class 8: Organometallic Complexes of Vanadium**
T. Imamoto and I. D. Gridnev

2.8 **Product Class 8: Organometallic Complexes of Vanadium** ..................... 385

2.8.1 **Product Subclass 1: Vanadium–Arene Complexes** ............................... 385

Synthesis of Product Subclass 1 ........................................................................ 386

2.8.1.1 Method 1: Reduction of Vanadium Chlorides ...................................... 386

2.8.1.2 Method 2: By Metal-Vapor Deposition ................................................ 387

2.8.1.3 Method 3: By Ring Substitution ............................................................ 388

2.8.1.4 Method 4: From Vanadocene ............................................................... 388

2.8.2 **Product Subclass 2: Vanadium–Cyclopentadienyland Substituted Cyclopentadienyl Complexes** .............................................................. 389

Synthesis of Product Subclass 2 ........................................................................ 389

2.8.2.1 Method 1: Synthesis of Bis(\(\eta^5\)-cyclopentadienyl)vanadium(II)
(\(\eta^5\)-Cyclopentadiene) and Ring-Substituted Derivatives ......................... 389

2.8.2.2 Method 2: Synthesis of Vanadocene Halides and Ring-Substituted Derivatives .......................................................... 390

2.8.2.3 Method 3: Synthesis of Ring-Bridged Vanadocene Dichlorides ............. 390

2.8.2.4 Method 4: Synthesis of Tetracarbonyl(\(\eta^5\)-cyclopentadienyl)vanadium and Ring-Substituted Derivatives ................................. 391
2.8.5 Method 5: By the Reaction of Pentafulvenes with Alkylstannyl(carbonyl)-
vanadium Complexes ........................................ 392
2.8.6 Method 6: Synthesis of Mono(η\(^5\)-cyclopentadienyl)vanadium Halides .. 393
2.8.7 Method 7: Synthesis of Tripledecker (η\(^5\)-Cyclopentadienyl)vanadium
Complexes .................................................. 394
Applications of Product Subclass 2 in Organic Synthesis .................. 395

2.8.3 Product Subclass 3: Vanadium–Alkyne Complexes ....................... 395
Synthesis of Product Subclass 3 .................................. 395
2.8.3.1 Method 1: From Vanadocene .................................. 395
2.8.3.2 Method 2: Synthesis of Mono(η\(^5\)-cyclopentadienyl)vanadium(I)–Alkyne
Complexes .................................................. 396

2.8.4 Product Subclass 4: Vanadium–Alkene Complexes ....................... 396
Synthesis of Product Subclass 4 .................................. 396
2.8.4.1 Method 1: Reaction of Vanadocene with Electron-Deficient Alkenes ...... 396
2.8.4.2 Method 2: Synthesis of η\(^2\)-Ethene Complexes from a 1,4-Di-Grignard
Species ................................................... 397

2.8.5 Product Subclass 5: Vanadium–Carbene Complexes ....................... 398
Synthesis of Product Subclass 5 .................................. 398
2.8.5.1 Method 1: Synthesis of Fischer-Type Vanadium–Carbene Complexes .... 398
2.8.5.2 Method 2: Synthesis of Schrock-Type Vanadium–Carbene Complexes .. 399

2.8.6 Product Subclass 6: Vanadium–σ-Alkyl and –σ-Aryl Complexes ........ 400
Synthesis of Product Subclass 6 .................................. 400
2.8.6.1 Method 1: Synthesis of Homoleptic Complexes ..................... 400
2.8.6.2 Method 2: Synthesis of Non-homoleptic Complexes .................. 401
2.8.6.2.1 Variation 1: Photochemical Insertion of Alkenes into a V–H Bond ...... 402
2.8.6.2.2 Variation 2: By the Reaction of Vanadocene with Iodomethane or
Bromomethane ................................................ 402
Applications of Product Subclass 6 in Organic Synthesis .................. 403
2.8.6.3 Method 3: Reaction of Organovanadium Complexes with Aldehydes .... 403
2.8.6.4 Method 4: Synthesis of 1H-1,2-Azaphospholes from Imidovanadium(V)
Complexes and Phosphaalkynes .................................. 403

2.8.7 Product Subclass 7: Vanadium–Carbonyl Complexes without
Cyclopentadienyl and Related Groups ................................ 404
Synthesis of Product Subclass 7 .................................. 404
2.8.7.1 Method 1: Synthesis of Hexacarbonylvanadium ....................... 404
2.8.7.2 Method 2: Synthesis of Hexacarbonylvanadate(1–) Complexes .......... 405

2.8.8 Product Subclass 8: Vanadium–Isocyanide Complexes .................... 406
Synthesis of Product Subclass 8 .................................. 406
2.8.8.1 Method 1: By Ligand Substitution .................................. 406
2.8.2 Method 2: Complex Formation Accompanying Oxidation or Reduction of the Central Vanadium Atom ............................... 407

2.8.9 Product Subclass 9: Hydridovanadium Complexes ........................................... 407

Synthesis of Product Subclass 9 ........................................... 408

2.8.9.1 Method 1: Synthesis of Carbonylhydridovanadium Complexes Stabilized by Oligotertiary Phosphines ............................... 408

2.8.9.2 Method 2: Synthesis of Bis(η^5-pentamethylcyclopentadienyl)hydridovanadium(III) ............................................. 409

2.8.9.3 Method 3: Synthesis of Anionic Hydridovanadium(1−) Complexes .................. 409

Applications of Product Subclass 9 in Organic Synthesis ........................................... 410

2.8.9.4 Method 4: Reduction of Organic Halides by Tricarbonyl(η^5-cyclopentadienyl)hydridovanadate(1−) Anion under Phase-Transfer Conditions ........................................... 410

2.9 Product Class 9: Organometallic Complexes of Niobium and Tantalum

K. Mashima and A. Nakamura

2.9.1 Product Subclass 1: Metal–Arene Complexes ........................................... 419

Synthesis of Product Subclass 1 ........................................... 419

2.9.1.1 Method 1: By Reduction of Metal Halides ..................................... 419

2.9.1.2 Method 2: Via Alkyne Cyclotrimerization ..................................... 421

2.9.2 Product Subclass 2: Metal–Triene and Metal–Tetraene Complexes ............... 421

Synthesis of Product Subclass 2 ........................................... 422

2.9.2.1 Method 1: Reductive Synthesis from Metal(V) Halides ...................... 422

2.9.2.2 Method 2: Using Dipotassium Cyclooctatetraene .............................. 422

2.9.2.3 Method 3: From Tetrachloro(η^5-cyclopentadienyl)niobium .................... 423

2.9.2.4 Method 4: From Niobium Hydride Derivatives ................................. 423

2.9.3 Product Subclass 3: Metal–Cyclopentadienyl and Metal–Tris(pyrazolyl)borate Complexes ....................................................... 423

Synthesis of Product Subclass 3 ........................................... 423

2.9.3.1 Method 1: From Metal(V) Halides ..................................... 423

2.9.3.2 Method 2: Via Halide–Ligand Exchange ..................................... 424

2.9.3.3 Method 3: By Sodium Reduction ..................................... 425

2.9.3.4 Method 4: Tris(pyrazolyl)borate Complexes ................................. 425

2.9.4 Product Subclass 4: Metal–Diene Complexes ........................................... 426

Synthesis of Product Subclass 4 ........................................... 427

2.9.4.1 Method 1: By Reaction of Magnesium Butadiene .............................. 427

2.9.4.2 Method 2: Via Halide–Ligand Exchange ..................................... 428
2.9.5 **Product Subclass 5: Metal–Allyl Complexes** ........................................... 428
Synthesis of Product Subclass 5 ........................................... 429
2.9.5.1 Method 1: From Allyl Grignard Reagents ........................................ 429
2.9.5.2 Method 2: From Butadiene ........................................... 429
2.9.6 **Product Subclass 6: Metal–Alkyne Complexes** ........................................... 430
Synthesis of Product Subclass 6 ........................................... 430
2.9.6.1 Method 1: Via Ligand Exchange ........................................... 430
2.9.6.2 Method 2: By Reduction ........................................... 433
Applications of Product Subclass 6 in Organic Synthesis ................. 434
2.9.7 **Product Subclass 7: Metal–Alkene Complexes** ........................................... 434
Synthesis of Product Subclass 7 ........................................... 434
2.9.7.1 Method 1: By Alkylation Reactions ........................................... 434
2.9.7.2 Method 2: By Reaction of Ethene and an Alkylidene Complex ........... 436
Applications of Product Subclass 7 in Organic Synthesis ................. 436
2.9.8 **Product Subclass 8: Metal–Alkylidene Complexes** ........................................... 436
Synthesis of Product Subclass 8 ........................................... 437
2.9.8.1 Method 1: Via α-Hydrogen Elimination ........................................... 437
2.9.8.2 Method 2: By Addition of a Chelating Ligand .................................... 437
2.9.8.3 Method 3: By Proton Abstraction ........................................... 438
2.9.8.4 Method 4: By Alkylation of Tetrachloro(η5-pentamethylcyclopentadienyl) tntalam ........................................... 438
2.9.8.5 Method 5: By Ligand Exchange ........................................... 439
2.9.8.6 Method 6: By Sodium Reduction ........................................... 440
2.9.8.7 Method 7: Dialkylation Followed by Alkane Elimination ............... 440
Applications of Product Subclass 8 in Organic Synthesis ................. 440
2.9.9 **Product Subclass 9: Metal–Alkylidyne Complexes** ........................................... 441
Synthesis of Product Subclass 9 ........................................... 441
2.9.9.1 Method 1: From Carbene Complex by Addition of Trimethylaluminum ... 441
2.9.9.1.1 Variation 1: By Addition of Trimethylphosphine ......................... 442
Applications of Product Subclass 9 in Organic Synthesis ................. 442
2.9.10 **Product Subclass 10: Metal–α-Alkyl Homoleptic Complexes** ....................... 442
Synthesis of Product Subclass 10 ........................................... 443
2.9.10.1 Method 1: By Alkylation ........................................... 443
2.9.11 **Product Subclass 11: Metal–α-Alkyl Non-homoleptic Complexes** ............... 444
Synthesis of Product Subclass 11 ........................................... 445
2.9.11.1 Method 1: By Alkylation ........................................... 445
2.9.11.2 Method 2: By Addition of Cyclopentadienyl Ligands ...................... 446
Applications of Product Subclass 11 in Organic Synthesis ................. 447
## Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.9.12</td>
<td>Product Subclass 12: Metal–Hydride Complexes</td>
<td>447</td>
</tr>
<tr>
<td>2.9.12.1</td>
<td>Method 1: From Niobium(V) Chloride</td>
<td>448</td>
</tr>
<tr>
<td>2.9.13</td>
<td>Product Subclass 13: Metal–Carbonyl Complexes</td>
<td>448</td>
</tr>
<tr>
<td>2.9.14</td>
<td>Product Subclass 14: Metal–Alkoxy Complexes</td>
<td>451</td>
</tr>
<tr>
<td>2.10</td>
<td>Product Class 10: Organometallic Complexes of Titanium</td>
<td>457</td>
</tr>
<tr>
<td>2.10.1</td>
<td>Product Subclass 1: Titanium–Arene Complexes</td>
<td>458</td>
</tr>
<tr>
<td>2.10.1.1</td>
<td>Method 1: Titanium(0)–Arene Complexes</td>
<td>458</td>
</tr>
<tr>
<td>2.10.1.2</td>
<td>Method 2: Titanium(II)–Arene Complexes</td>
<td>458</td>
</tr>
<tr>
<td>2.10.1.2.1</td>
<td>Variation 1: Titanium(II)–Arene Complexes by the Fischer–Hafner Method</td>
<td>459</td>
</tr>
<tr>
<td>2.10.1.2.2</td>
<td>Variation 2: Titanium(II)–Arene Complexes by Ligand Exchange of Aluminum–Titanium(II) Halide Complexes with Arenes</td>
<td>459</td>
</tr>
<tr>
<td>2.10.1.2.3</td>
<td>Variation 3: Titanium(II)–Arene Complexes by Ligand Exchange with Aluminum Reagents</td>
<td>460</td>
</tr>
<tr>
<td>2.10.1.3</td>
<td>Method 3: Titanium(IV)–Arene Complexes by Cationic Complex Formation</td>
<td>460</td>
</tr>
<tr>
<td>2.10.2</td>
<td>Product Subclass 2: Titanium–Triene, –Trienyl, and –Tetraene Complexes</td>
<td>461</td>
</tr>
<tr>
<td>2.10.2.1</td>
<td>Method 1: Titanium–Tetraene Complexes by Reaction of Tetrabutoxytitanium(IV) with Cyclooctatetraene</td>
<td>461</td>
</tr>
<tr>
<td>2.10.2.2</td>
<td>Method 2: Titanium–Tetraene Complexes by Reaction of Trichloro(pentamethylcyclopentadienyl)titanium(IV) with Dipotassium Cyclooctatetraene</td>
<td>461</td>
</tr>
<tr>
<td>2.10.2.3</td>
<td>Method 3: Titanium–Tetraene and –Triene Complexes by Reaction of Trichloro(η^5-cyclopentadienyl)titanium(IV) Complexes with Cyclooctatetraene or Cycloheptatriene in the Presence of Magnesium</td>
<td>462</td>
</tr>
<tr>
<td>Section</td>
<td>Method</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>2.10.2.4</td>
<td>Method 4:</td>
<td>Titanium–Trienyl Complexes by Functionalization of the Cycloheptatrienyl Ligand</td>
</tr>
<tr>
<td>2.10.2.5</td>
<td>Method 5:</td>
<td>Titanium(II)–Trienyl Complexes by Reaction of Titanium(II) with Cycloheptatriene</td>
</tr>
<tr>
<td>2.10.3</td>
<td>Product Subclass 3:</td>
<td>Bis(η²-cyclopentadienyl)titanium Complexes without Allyl Functionalities or Titanacycles</td>
</tr>
<tr>
<td>2.10.3.1</td>
<td>Method 1:</td>
<td>Salt Elimination Reactions between Cyclopentadienyllithium Compounds and Titanium(IV) Chloride</td>
</tr>
<tr>
<td>2.10.3.1.1</td>
<td>Variation 1:</td>
<td>Salt Elimination Reactions between Sodium Cyclopentadienide Compounds and Titanium(III) Chloride</td>
</tr>
<tr>
<td>2.10.3.1.2</td>
<td>Variation 2:</td>
<td>Salt Elimination Reactions between Titanium(IV)–Chloro Complexes, Potassium, and Cyclopentadienes</td>
</tr>
<tr>
<td>2.10.3.1.3</td>
<td>Variation 3:</td>
<td>Salt Elimination Reactions between Thallium Cyclopentadienide Compounds and Trichloro(η²-cyclopentadienyl)titanium(IV) Complexes</td>
</tr>
<tr>
<td>2.10.3.1.4</td>
<td>Variation 4:</td>
<td>Transmetalation between Tin Cyclopentadienide Complexes and Titanium Complexes</td>
</tr>
<tr>
<td>2.10.3.2</td>
<td>Method 2:</td>
<td>Transmetalation between Metal Cyclopentadienide Complexes and Titanium(III) Chloride, Followed by Oxidation</td>
</tr>
<tr>
<td>2.10.3.2.1</td>
<td>Variation 1:</td>
<td>Transmetalation between Magnesium Cyclopentadienide Salts and Titanium(III) Chloride</td>
</tr>
<tr>
<td>2.10.3.3</td>
<td>Method 3:</td>
<td>Hydrogenation of the Indenyl Ligand in Titanium(IV) Complexes</td>
</tr>
<tr>
<td>2.10.3.4</td>
<td>Method 4:</td>
<td>Titanium(IV) Complexes by Oxidation of Allylbis(η²-cyclopentadienyl)titanium(III) Complexes by Lead(II) Chloride</td>
</tr>
<tr>
<td>2.10.3.5</td>
<td>Method 5:</td>
<td>Halide Exchange between Titanium(IV)–Halo Complexes and Alkali Metal Halides</td>
</tr>
<tr>
<td>2.10.3.5.1</td>
<td>Variation 1:</td>
<td>Halide Exchange with Hydrogen Halides</td>
</tr>
<tr>
<td>2.10.3.5.2</td>
<td>Variation 2:</td>
<td>Halide Exchange with Boron Halides</td>
</tr>
<tr>
<td>2.10.3.6</td>
<td>Method 6:</td>
<td>Bis(η²-cyclopentadienyl)titanium Complexes as Alkene Polymerization Catalysts</td>
</tr>
<tr>
<td>2.10.4</td>
<td>Product Subclass 4:</td>
<td>Mono(η²-cyclopentadienyl)titanium Complexes</td>
</tr>
<tr>
<td>2.10.4.1</td>
<td>Method 1:</td>
<td>Reaction between Titanium(IV) Chloride and Metal Cyclopentadienide Compounds</td>
</tr>
<tr>
<td>2.10.4.1.1</td>
<td>Variation 1:</td>
<td>Reaction between Titanium(IV) Chloride and Silyl-Substituted Cyclopentadienyl Reagents</td>
</tr>
<tr>
<td>2.10.4.1.2</td>
<td>Variation 2:</td>
<td>Reaction between Titanium(III) Chloride and Lithium Cyclopentadienide Compounds, Followed by Oxidation</td>
</tr>
<tr>
<td>2.10.4.2</td>
<td>Method 2:</td>
<td>Reaction between Titanium(IV) Chloride and Unsaturated Hydrocarbons</td>
</tr>
</tbody>
</table>

Table of Contents

Science of Synthesis Original Edition Volume 2
© Georg Thieme Verlag KG
### Table of Contents

#### 2.10.3 Method 3: Trichloro(η⁵-cyclopentadienyl)titanium(IV) Complexes by Redistribution Reactions

- 2.10.4 Method 4: Trihalo(η⁵-cyclopentadienyl)titanium(IV) Complexes by Halogenation of Mono- and Bis(η⁵-cyclopentadienyl)titanium(IV) Complexes

- 2.10.5 Method 5: Replacement of Alkoxy Ligands in Alkoxy(η⁵-cyclopentadienyl)titanium Complexes by Halides

- 2.10.6 Method 6: Reaction between Tetraalkoxytitanium(IV) or Tetraamidotitanium(IV) Complexes and Cyclopentadienes

- 2.10.7 Method 7: Halide Exchange between Cyclopentadienyl(halo)titanium Complexes and Trimethyltin Fluoride or Arsenic Trifluoride

Applying Method 4 in Organic Synthesis

- 2.10.8 Method 8: Mono(η⁵-cyclopentadienyl)titanium Complexes as Styrene Polymerization Catalysts

- 2.10.9 Method 9: Mono(η⁵-cyclopentadienyl)titanium Complexes as Buta-1,3-diene Polymerization Catalysts

- 2.10.10 Method 10: Mono(η⁵-cyclopentadienyl)titanium Complexes as Alkene Polymerization Catalysts

#### 2.10.5 Product Subclass 5: Trivalent Titanium(III) Complexes Including Bis- and Mono(η⁵-cyclopentadienyl)titanium–Hydrido Complexes

- Synthesis of Product Subclass 5

- 2.10.5.1 Method 1: Titanium–Hydrido Complexes by Reduction of Titanium(IV)–Methyl Complexes by Hydrogen

- 2.10.5.1.1 Variation 1: Hydridotitanium Complexes by Reduction of Alkyltitanium(IV) Complexes by Silanes

- 2.10.5.1.2 Variation 2: Hydridotitanium Complexes by Reduction of Chlorotitanium(IV) Complexes by Potassium or Sodium

- 2.10.5.2 Method 2: Titanium(III) Complexes by Reduction of Titanium(IV) Complexes by Lithium Nitride

- 2.10.5.2.1 Variation 1: Titanium(III) Complexes by Reduction of Titanium(IV) Complexes by Zinc and Magnesium

- 2.10.5.2.2 Variation 2: Titanium(III) Complexes by Reduction of Cobalt(II) Complexes

Applying Method 5 in Organic Synthesis

- 2.10.5.3 Method 3: Preparation of Alkene Hydrogenation Catalysts by Reduction with Aluminum Hydrides

- 2.10.5.3.1 Variation 1: Preparation of Alkene Hydrogenation Catalysts by Reduction with Alkyllithium Compounds

- 2.10.5.3.2 Variation 2: Preparation of Alkene Hydrogenation Catalysts by Reduction with Grignard Reagents

#### 2.10.6 Product Subclass 6: Bis- or Mono(η⁵-cyclopentadienyl)titanium(II) Complexes

- Synthesis of Product Subclass 6

- 2.10.6.1 Method 1: Titanocenes by Reduction of Titanium(IV) Complexes
2.10.2 Method 2: Titanocene by Photochemical Reaction of Bis(η⁵-cyclopentadienyl)dimethyltitanium(IV)  

2.10.3 Method 3: Dicarbonyl(η⁵-cyclopentadienyl)titanium(II) Complexes from Titanium–Alkyl and –Aryl Complexes  

2.10.4 Method 4: Dicarbonyl(η⁵-cyclopentadienyl)titanium(II) Complexes by Photolysis of Titanium–Alkyl and –Aryl Complexes  

2.10.5 Method 5: Titanium(II)–Carbonyl Complexes by Reduction of Chlorotitanium(IV) Complexes with Aluminum under Carbon Monoxide  

2.10.6.1 Variation 1: Reduction with Sodium–Naphthalene  

2.10.6.2 Variation 2: Reduction with Cobaltocene  

2.10.6.3 Method 6: Dicarbonyl(η⁵-cyclopentadienyl)bistrimethylphosphine)titanium(II) by Reduction of Dichlorobis(η⁵-cyclopentadienyl)titanium(IV) with Magnesium  

2.10.6.4 Method 7: Titanium(II)–Phosphine Complexes by Photolysis of Dicarbonyl(η⁵-cyclopentadienyl)titanium(II)  

Applications of Product Subclass 6 in Organic Synthesis  

2.10.6.8 Method 8: Titanium(II)–Carbonyl Complexes as Catalysts in the Pauson–Khand Reaction  

2.10.7 Product Subclass 7: Titanium–Allyl, –Allenyl, and –Propargyl Complexes  

2.10.7.1 Method 1: (η¹-Allyl)titanium(III) Complexes by Reaction between Chlorotitanium(III) Complexes and Allyl Grignard Reagents  

2.10.7.2 Method 2: (η¹-Allyl)titanium(III) Complexes by Reaction between Chlorotitanium(IV) Complexes and Allyl Grignard Reagents  

2.10.7.2.1 Variation 1: (η¹-Allyl)bis(η⁵-cyclopentadienyl)titanium(III) Complexes by Reaction of Dichlorobis(η⁵-cyclopentadienyl)titanium(IV) with a Grignard Reagent and a Diene  

2.10.7.2.2 Variation 2: (η¹-Allyl)bis(η⁵-cyclopentadienyl)titanium(III) by Rearrangement of Bis(η⁵-cyclopentadienyl)(η²-ethene)(η²-vinyl)titanium(III)  

2.10.7.3 Method 3: (η¹-Allyl)bis(η⁵-cyclopentadienyl)halotitanium(IV) Complexes by Reaction of (η¹-Allyl)bis(η⁵-cyclopentadienyl)titanium(III) Complexes with 1-Halobut-2-enes  

2.10.7.4 Method 4: (η¹-Allyl)bis(η⁵-cyclopentadienyl)titanium(IV) Complexes by Reaction of Vinyl Halides, Vinyl Esters, or Carboxylic Esters with the Dichlorobis(η⁵-cyclopentadienyl)titanium(IV)–Trimethylaluminum Complex  

2.10.7.5 Method 5: (η¹-Allyl)bis(isopropoxy)titanium(IV) Complexes by Reaction of Low-Valent Titanium Complexes with Allylic Halides, Acetates, Carbonates, Phosphates, Sulfonates, or Aryl Ethers  

2.10.7.6 Method 6: Bis(isopropoxy)titanium(IV)–Propargyl or –Allenyl Complexes by Transmetalation of Titanium(IV) Complexes with Propargyl- or Allenyllithium Compounds
Method 7: Bis(isopropoxy)titanium(IV)–Propargyl or –Allenyl Complexes by Reaction of Low-Valent Titanium Complexes with Propargyl Halides, Acetates, Carbonates, Phosphates, or Sulfonates

Applications of Product Subclass 7 in Organic Synthesis

Method 8: Allylation of Carbonyl Compounds by Allyltris(amido)titanium(IV) Complexes

Method 9: Reactions of Bis(isopropoxy)titanium(IV)–Propargyl or –Allenyl Complexes with Electrophiles

Product Subclass 8: Titanium–Diene and Titanacyclopentene Complexes

Synthesis of Product Subclass 8

Method 1: [Bis(dimethylphosphino)ethane]bis(butadiene)titanium(0) by Reduction of [Bis(dimethylphosphino)ethane]tetrachlorotitanium(IV) by Sodium Amalgam in the Presence of Butadiene

Method 2: Chloro(η⁵-pentamethylcyclopentadienyl)titanium(II)–Diene Complexes by Reaction of Trichloro(η⁵-pentamethylcyclopentadienyl)titanium(IV) with the Magnesium–Diene Complex

Method 3: Titanium–Buta-1,3-diene Complexes from Titanium–η⁵-Methallyl Complexes

Method 4: Titanium–Cyclobutadiene Complexes by Reaction between Titanium–Arene Complexes and Alkynes

Product Subclass 9: Titanacycles

Synthesis of Product Subclass 9

Method 1: Reaction of Bis(η⁵-cyclopentadienyl)titanium(II)–Phosphine Complexes with Alkynes or Allenes

Method 2: Reduction of Dichlorobis(η⁵-cyclopentadienyl)titanium(IV) Complexes by Grignard Reagents in the Presence of Alkenes or Alkynes

Variation 1: Reactions of Bis(arylxy)dichlorotitanium(IV) Complexes with Butyllithium in the Presence of Dienes

Variation 2: Reduction of Titanium(IV)–Chloro Complexes by Sodium Amalgam in the Presence of Alkenes or Alkynes

Variation 3: Reaction of Dichlorobis(η⁵-cyclopentadienyl)titanium(IV) with Lithium Naphthalene in the Presence of an Alkene

Variation 4: Reduction of Dichlorobis(η⁵-cyclopentadienyl)titanium(IV) by Magnesium in the Presence of Alkynes

Method 3: Photolysis of Bis(η⁵-cyclopentadienyl)dimethyltitanium(IV) in the Presence of an Alkyne

Method 4: Substitution Reaction of Dichlorobis(η⁵-cyclopentadienyl)titanium(IV) with an Alkenediylidilithium Reagent

Method 5: Insertion Reactions of Alkenes with Alkyne- or Alkenediylidilithium Reagent and Titanacyclopentene Complexes
2.10.9.5.1 Variation 1: Reactions of Alkynes, Dialkynes, or Carbonyl Compounds with Alkyne- or Alkenetitanium Complexes .................................................. 545

2.10.9.6 Method 6: Titanacycles from Ligand Exchange Reactions of Titanacypentanes ................................................................. 547

2.10.9.6.1 Variation 1: Large Metallacycles by Insertion Reactions of Smaller Titanacycles ................................................................. 548

2.10.9.7 Method 7: Titanacyclobutanes from Tebbe’s Reagent ................................................................. 549

2.10.9.7.1 Variation 1: Titanacyclobutanes via Vinylealuminum Complexes ................................................................. 551

2.10.9.7.2 Variation 2: Titanacyclobutanes by Reaction of Dichlorobis(η5-cyclopentadienyl)titanium(IV) with a Dimagnesium Reagent ................................................................. 551

2.10.9.7.3 Variation 3: Ligand Exchange of Titanacyclobutanes with Alkenes, Alkynes, or Allenes To Form Other Titanacyclobutanes or Titanacyclobutenes ................................................................. 552

Applications of Product Subclass 9 in Organic Synthesis ................................................................. 553

2.10.9.8 Method 8: Ring-Opening Metathesis Polymerization ................................................................. 553

2.10.9 Product Subclass 10: Titanium–Alkyne Complexes ................................................................. 555

Synthesis of Product Subclass 10 ................................................................. 557

2.10.10.1 Method 1: Reaction of an Alkyne with a Titanium(II)–Carbonyl Complex ................................................................. 557

2.10.10.1.1 Variation 1: Reaction of an Alkyne with a Titanium(II)–Phosphine Complex ................................................................. 557

2.10.10.2 Method 2: Reduction of Dichlorobis(η5-cyclopentadienyl)titanium(IV) by Magnesium in the Presence of an Alkyne ................................................................. 558

2.10.10.2.1 Variation 1: Reaction of Titanium(II) Complexes with Diynes or Polyynes ................................................................. 559

2.10.10.3 Method 3: Reaction of an Alkyne with Bis(isopropoxy)(η2-propene)titanium(II) ................................................................. 560

2.10.10.4 Method 4: Benzynetitanium Complexes by Thermolysis of Aryltitanium Complexes ................................................................. 560

2.10.10.4.1 Variation 1: Benzynetitanium Complexes by Thermolysis of Arylmethylene Complexes ................................................................. 561

2.10.10.4.2 Variation 2: A Benzynetitanium Complex from 1-Bromo-2-fluorobenzene and Dichlorobis(η5-cyclopentadienyl)titanium(IV) ................................................................. 562

2.10.11 Product Subclass 11: Titanium–Alkene Complexes ................................................................. 563

Synthesis of Product Subclass 11 ................................................................. 564

2.10.11.1 Method 1: (η2-Alkene)bis(η5-cyclopentadienyl)titanium(II) Complexes by Substitution of Bis(η5-cyclopentadienyl)bis(trimethylphosphine)titanium(II) by Alkenes ................................................................. 564

2.10.11.1.1 Variation 1: (η2-Ethene)bis(η5-pentamethylcyclopentadienyl)titanium(II) Complexes by Reaction of (-Dinitrogen)bisis[bis(η5-pentamethylcyclopentadienyl)titanium(II)] with Ethene ................................................................. 564

2.10.11.2 Method 2: (η2-Alkene)bis(η5-pentamethylcyclopentadienyl)titanium(II) Complexes by Reduction of
Dichlorobis(η⁵-pentamethylcyclopentadienyl)titanium(IV) by Sodium Amalgam in the Presence of an Alkene .......... 565

2.10.11.2.1 Variation 1: (η²-Alkene)bis(η⁵-pentamethylcyclopentadienyl)titanium(II) Complexes by Reduction of Dichlorobis(η⁵-pentamethylcyclopentadienyl)titanium(IV) by an Alkyllithium in the Presence of an Alkene .......... 565

2.10.11.2.2 Variation 2: (η²-Alkene)titanium(II) Complexes by Reduction of Titanium(IV) Complexes by Grignard Reagents in the Presence of an Alkene ........................................ 565

2.10.11.3 Method 3: (η²-Alkene)titanium(II) Complexes by Ligand-Exchange Reactions ........................................... 566

Applications of Product Subclass 11 in Organic Synthesis .................. 566

2.10.11.4 Method 4: Titanium-Mediated Cyclization of Enynes ............ 566

2.10.11.5 Method 5: Preparation of Cyclopropanols from Dialkoxotitanacyclopropanes .......................... 567

2.10.12 Product Subclass 12: Titanium–Carbene Complexes .................. 567

Synthesis of Product Subclass 12 ........................................ 567

2.10.12.1 Method 1: Preparation of Tebbe’s Reagent ..................... 567

Applications of Product Subclass 12 in Organic Synthesis .................. 568

2.10.12.2 Method 2: Methyleneation of Amides, Esters, Ketones, and Aldehydes by Tebbe’s Reagent ....................... 568

2.10.12.2.1 Variation 1: Alkenation of Carbonyl Compounds by the Lead(II) Chloride/Dihaloalkane/Titanium(IV) Chloride/Zinc Reagent .......... 569

2.10.12.2.2 Variation 2: Alkylidenation with Magnesium Analogues of Tebbe’s Reagent ........................................... 570

2.10.12.2.3 Variation 3: Other Applications of Titanium–Carbene Complexes .......... 570

2.10.13 Product Subclass 13: Titanium–Alkenyl, –Alkynyl, and –Aryl Complexes ........................................... 572

Synthesis of Product Subclass 13 ........................................ 572

2.10.13.1 Method 1: Alkenyltitanium Complexes by Reaction of Chlorotitanium Complexes with Vinyllithium Reagents ...................... 572

2.10.13.2 Method 2: Alkenyltitanium Complexes by Hydrotitanation ........ 573

2.10.13.2.1 Variation 1: Alkenyltitanium Complexes by Carbotitanation .......... 574

2.10.13.2.2 Variation 2: Alkenyltitanium Complexes by Silyltitanation ............. 575

2.10.13.2.3 Variation 3: Alkenyltitanium Complexes by Partial Hydrolysis of Titanium–Silylalkyne and–Stannyalkyne Complexes ................ 576

2.10.13.3 Method 3: Alkenyltitanium Heterotitanacycles by [2 + 2] Cycloadditions of Titanium(IV) Complexes with Alkynes .............................. 577

2.10.13.4 Method 4: Alkynyltitanium Complexes by Reaction of Titanium(IV) Complexes with Alkynes .............................. 577

2.10.13.5 Method 5: Aryltitanium Complexes by Reaction of Titanium Complexes with Arylmetal Reagents ...................... 578

2.10.13.5.1 Variation 1: Tetraaryltitanium(IV) Complexes by Reaction of Titanium(IV) Complexes with Grignard Reagents .............................. 579
2.10.14 **Product Subclass 14: Titanium–ω-Alkyl Complexes** ........................................ 579

Synthesis of Product Subclass 14 ................................................................. 585

2.10.14.1 Method 1: Alkyltitanium Complexes by Transmetalation of
Chlorotitanium Complexes with Grignard Reagents ..................... 585

2.10.14.1.1 Variation 1: Alkylation of Alkoxy(halo)titanium Complexes by
Grignard Reagents .............................................................. 587

2.10.14.1.2 Variation 2: Alkyltitanium Complexes by Reaction of Titanium Complexes
with Alkyl lithium Reagents .............................................. 587

2.10.14.1.3 Variation 3: Alkytris(alkoxy)titanium(IV) Complexes by Reaction of
Alkoxytitanium Complexes with Alkyl lithium Reagents .............. 589

2.10.14.1.4 Variation 4: Alkyltitanium Complexes by Reaction of Titanium Complexes
with Dialkylaluminum Reagents ........................................ 590

2.10.14.1.5 Variation 5: Alkyltitanium Complexes by Alkylation of Titanium Halides
with Dialkyl zinc Reagents .................................................. 590

2.10.14.1.6 Variation 6: Alkyl- or Aryltitanium Complexes by Reaction of
Tetramethyltitanium(IV) with Alkyl- or Arylboranes ................. 591

2.10.14.1.7 Variation 7: Alkyltitanium Complexes by Alkylation and Oxidation of
Titanium Complexes by Dimethyl cadmium(II) ......................... 591

2.10.14.2 Method 2: Acyltitanium Complexes by Oxidative Addition of Alkyl- or
Acyl Halides to Dicarbonylbis(η5-cyclopentadienyl)titanium(II) ....... 592

2.10.14.3 Method 3: Alkyltitanium Complexes by Hydrotitanation of Alkenyl
Sulfides ...................................................................................... 592

2.10.14.4 Method 4: Alkyltitanium Complexes by Redistribution ............. 593

2.10.14.5 Method 5: Alkyltitanium Complexes by Insertion ..................... 594

2.10.14.6 Method 6: Cationic Alkyltitanium Complexes ............................ 595

2.10.14.7 Method 7: Benzyl(halo)titanium Complexes from Tetrabenzyltitanium(IV)
and a Halide Source ............................................................... 595

Applications of Product Subclass 14 in Polymerization ...................... 596

2.10.14.8 Method 8: Alkyltitanium Complexes as Catalysts for Alkene
Polymerization ....................................................................... 596

2.10.14.9 Method 9: Alkyltitanium Complexes as Catalysts for Styrene
Polymerization ....................................................................... 598

2.10.14.10 Method 10: Alkyltitanium Complexes as Cocatalysts in Alkene
Polymerization ..................................................................... 599

2.10.15 **Product Subclass 15: Titanium–Alkoxy Complexes** ........................................ 600

Synthesis of Product Subclass 15 ......................................................... 601

2.10.15.1 Method 1: Titanium–Phenoxy Complexes from Alkyltitanium Complexes
by Ligand Exchange with Phenols ........................................... 601

2.10.15.2 Method 2: Titanium–Alkoxy and –Phenoxy Complexes from
Chlorotitanium Complexes by Ligand Exchange with Alcohols
or Phenols in the Presence of Amines .................................... 602

2.10.15.2.1 Variation 1: Titanium–Alkoxy and –Phenoxy Complexes from
Chlorotitanium Complexes by Ligand Exchange with Alcohols
or Phenols ............................................................................... 602
<table>
<thead>
<tr>
<th>Section</th>
<th>Method</th>
<th>Reaction Type</th>
<th>Key Reagents</th>
<th>Product Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.10.2</td>
<td>Variation 2</td>
<td>Cyclopentadienyltitanium–Alkoxy Complexes for Enantio- and Diastereomeric Reactions by Hydrolysis of Chlorotitanium Complexes with Alcohols</td>
<td></td>
<td>603</td>
<td></td>
</tr>
<tr>
<td>2.10.3</td>
<td>Variation 3</td>
<td>Titanium–Alkoxy and –Phenoxy Complexes from Chlorotitanium Complexes by Ligand Exchange with Lithium Alkoxides or Phenoxides</td>
<td></td>
<td>604</td>
<td></td>
</tr>
<tr>
<td>2.10.4</td>
<td>Variation 4</td>
<td>Titanium–Alkoxy and –Phenoxy Complexes from Chlorotitanium Complexes by Ligand Exchange with Sodium Alkoxides or Phenoxides</td>
<td></td>
<td>607</td>
<td></td>
</tr>
<tr>
<td>2.10.5</td>
<td>Variation 5</td>
<td>Titanium–Phenoxy Complexes from Chlorotitanium Complexes by Ligand Exchange with Aryl Silyl Ethers</td>
<td></td>
<td>607</td>
<td></td>
</tr>
<tr>
<td>2.10.6</td>
<td>Variation 6</td>
<td>Titanium–Phenoxy Complexes from Titanium–Alkoxy Complexes by Ligand Replacement with Esters</td>
<td></td>
<td>608</td>
<td></td>
</tr>
<tr>
<td>2.10.7</td>
<td>Method 3</td>
<td>Chiral Titanium–Phenoxy Complexes from Achiral Titanium–Alkoxy Complexes by Ligand Replacement with Esters</td>
<td></td>
<td>608</td>
<td></td>
</tr>
<tr>
<td>2.10.8</td>
<td>Method 4</td>
<td>Titanium–Alkoxy and –Phenoxy Complexes from Amidotitanium Complexes by Ligand Replacement with Alcohols or Phenols</td>
<td></td>
<td>609</td>
<td></td>
</tr>
<tr>
<td>2.10.9</td>
<td>Method 5</td>
<td>Titanium–Sulfanyl Complexes by Ligand Exchange with Alcohols or Phenols</td>
<td></td>
<td>610</td>
<td></td>
</tr>
<tr>
<td>2.10.10</td>
<td>Method 6</td>
<td>Catalytic Asymmetric Alkylation of Aldehydes</td>
<td></td>
<td>610</td>
<td></td>
</tr>
<tr>
<td>2.10.11</td>
<td>Method 7</td>
<td>Catalytic Asymmetric Alkylation</td>
<td></td>
<td>616</td>
<td></td>
</tr>
<tr>
<td>2.10.12</td>
<td>Method 8</td>
<td>Catalytic Asymmetric Ene Reaction</td>
<td></td>
<td>617</td>
<td></td>
</tr>
<tr>
<td>2.10.13</td>
<td>Method 9</td>
<td>Catalytic Asymmetric Mukaiyama Aldol Reaction</td>
<td></td>
<td>620</td>
<td></td>
</tr>
<tr>
<td>2.10.14</td>
<td>Method 10</td>
<td>Catalytic Asymmetric Diels–Alder and Hetero-Diels–Alder Reactions</td>
<td></td>
<td>621</td>
<td></td>
</tr>
<tr>
<td>2.10.15</td>
<td>Method 11</td>
<td>Catalytic Asymmetric [2 + 2]- and [2 + 3] Cycloaditions</td>
<td></td>
<td>624</td>
<td></td>
</tr>
<tr>
<td>2.10.16</td>
<td>Method 12</td>
<td>Catalytic Asymmetric Cyanization</td>
<td></td>
<td>625</td>
<td></td>
</tr>
<tr>
<td>2.10.17</td>
<td>Method 13</td>
<td>Other Catalytic Asymmetric Reactions</td>
<td></td>
<td>628</td>
<td></td>
</tr>
<tr>
<td>2.10.18</td>
<td>Method 14</td>
<td>Sharpless Epoxidation</td>
<td></td>
<td>628</td>
<td></td>
</tr>
<tr>
<td>2.10.19</td>
<td>Application</td>
<td>Applications of Product Subclass 15 in Organic Synthesis</td>
<td></td>
<td>612</td>
<td></td>
</tr>
<tr>
<td>2.10.20</td>
<td>Application</td>
<td>Applications of Product Subclass 15 in Polymerization</td>
<td></td>
<td>631</td>
<td></td>
</tr>
<tr>
<td>2.10.21</td>
<td>Method 15</td>
<td>Alkoxytitanium Complexes as Catalysts for Living Polymerization of Polar Monomers</td>
<td></td>
<td>632</td>
<td></td>
</tr>
<tr>
<td>2.10.22</td>
<td>Method 16</td>
<td>Chelating Bis(phenoxo)titanium Complexes as Catalysts for Alkene Polymerization</td>
<td></td>
<td>634</td>
<td></td>
</tr>
<tr>
<td>2.10.23</td>
<td>Product Subclass 16</td>
<td>Titanium–Amido Complexes</td>
<td></td>
<td>637</td>
<td></td>
</tr>
</tbody>
</table>

Synthesis of Product Subclass 16: 

638
2.10.16.1 Method 1: Amidotitanium Complexes from Chlorotitanium Complexes by Transmetalation with Lithium or Magnesium Amides ................................................... 638

2.10.16.1.1 Variation 1: Amidotitanium Complexes from Halotitanium Complexes and Silylamines ........................................... 639

2.10.16.1.2 Variation 2: Titanium Complexes with Chelating Cyclopentadienyl–Amido Ligands from Titanium(III) or Titanium(IV) Halides by Transmetalation with Metal Amides ........................ 640

Applications of Product Subclass 16 in Organic Synthesis .......................... 644

2.10.16.2 Method 2: Stereoselective Organic Reactions Promoted by Amidotitanium Complexes ........................................... 644

2.10.16.3 Method 3: Fixation of Atmospheric Nitrogen by Titanium Complexes ........................ 646

Applications of Product Subclass 16 in Polymerization .............................. 650

2.10.16.4 Method 4: Diamidotitanium Complexes as Alkene Polymerization Catalysts .......................................................... 650

2.10.16.5 Method 5: Titanium Complexes with Monocyclopentadienyl–Amido Ligands Bridged by Silylene Groups as Alkene Polymerization Catalysts .......................................................... 652

2.10.17 Product Subclass 17: Miscellaneous Titanium Complexes .......................... 654

Applications of Product Subclass 17 in Organic Synthesis .......................... 654

2.10.17.1 Method 1: McMurry Coupling ........................................ 654

2.10.17.2 Method 2: Pinacol Coupling .......................................... 656

2.10.17.3 Method 3: Carbonyl Coupling of Carbamoyl(oxo) Compounds Promoted by Low-Valent Titanium ................................... 657

2.10.17.4 Method 4: Dimerization of Imines and Iminium Salts Promoted by Low-Valent Titanium Species ...................................... 659

2.10.17.5 Method 5: Reactions of Epoxides Promoted by Titanium Complexes .................. 659

2.10.17.6 Method 6: Addition of Alkyl Halides to Alkenes Promoted by Titanium Complexes .......................................................... 660

2.11 Product Class 11: Organometallic Complexes of Zirconium and Hafnium E.-i. Negishi and T. Takahashi

2.11 Product Class 11: Organometallic Complexes of Zirconium and Hafnium .... 681

2.11.1 Product Subclass 1: Metal–η^8-Arene and –η^7-Arene Complexes .............. 683

Synthesis of Product Subclass 1 .......................................................... 683

2.11.1.1 Method 1: By π-Complexation .......................................... 683

2.11.1.2 Method 2: By Transmetalation ........................................ 683

2.11.1.3 Method 3: Miscellaneous Transformations ................................ 685

Applications of Product Subclass 1 in Organic Synthesis .............................. 686

2.11.1.4 Method 4: Reactions of (η^8-Cyclooctatetraene)zirconium Derivatives .... 686
2.11.2 Product Subclass 2: Metal–$\eta^5$-Arene Complexes

Synthesis of Product Subclass 2

2.11.2.1 Method 1: By $\pi$-Complexation

2.11.2.1.1 Variation 1: Co-condensation of Metal Vapors with Arenes

2.11.2.1.2 Variation 2: Reduction of Zirconium(IV) and Hafnium(IV) Compounds

2.11.2.1.3 Variation 3: Complexation with Activated Zirconium(IV) and Hafnium(IV) Compounds of Low Electron Count

2.11.2.2 Method 2: By Transmetalation

2.11.2.3 Method 3: Other Methods

Applications of Product Subclass 2 in Organic Synthesis

2.11.3 Product Subclass 3: Metal–Triene Complexes

2.11.4 Product Subclass 4: Metal–$\eta^5$-cyclopentadienyl) Complexes and Related Derivatives of Oxidation State Four

Synthesis of Product Subclass 4

2.11.4.1 Bis($\eta^5$-cyclopentadienyl)Metal(IV) Complexes Containing Two Electronegative Heteroatom Groups

2.11.4.1.1 Method 1: Synthesis of Bis($\eta^5$-cyclopentadienyl)Dihalometal(IV) Complexes

2.11.4.1.2 Method 2: Synthesis of Bis($\eta^5$-cyclopentadienyl)Dihalometal(IV) Complexes and Their Derivatives with Modified Cyclopentadienyl Ligands

2.11.4.1.3 Method 3: Synthesis of Bis($\eta^5$-cyclopentadienyl)Metal(IV) Complexes Containing Monohalo and/or Group 16 or 15 Atom Ligands and Their Derivatives with Modified Cyclopentadienyl Ligands

2.11.4.2 Bis($\eta^5$-cyclopentadienyl)Hydridometal(IV) Complexes

2.11.4.2.1 Method 1: By Transmetalation

2.11.4.3 Bis($\eta^5$-cyclopentadienyl)Monometallo- and Bis($\eta^5$-cyclopentadienyl)Dimetallo-Zirconium Complexes (Excluding Hydrido Derivatives)

2.11.4.4 Bis($\eta^5$-cyclopentadienyl)Monooorganometal Complexes

2.11.4.4.1 Method 1: By Transmetalation

2.11.4.4.2 Method 2: By Hydrometalation

2.11.4.4.3 Method 3: By Carbometalation

2.11.4.4.4 Method 4: By Oxidative Addition

2.11.4.4.5 Method 5: Miscellaneous Methods

2.11.4.5 Bis($\eta^5$-cyclopentadienyl)Diorganometal Complexes

2.11.4.5.1 Method 1: Synthesis of Bis($\eta^5$-cyclopentadienyl)Diorganometal Complexes and Their Derivatives

Applications of Product Subclass 4 in Organic Synthesis

2.11.4.6 Bis($\eta^5$-cyclopentadienyl)Hydridometal(IV) Complexes
2.11.4.6.1 Method 1: Stoichiometric Reactions of Bis(η^5-cyclopentadienyl)hydridozirconium(IV) and Bis(η^5-cyclopentadienyl)dihydridozirconium(IV) Complexes and Related Reagents ................................................. 712
2.11.4.6.1.1 Variation 1: Hydrozirconation and Hydrogen-Transfer Hydrozirconation .............................................. 712
2.11.4.6.1.2 Variation 2: Other Stoichiometric Reactions .......... 715
2.11.4.6.1.3 Variation 3: Catalytic Reactions Involving Bis(η^5-cyclopentadienyl)hydridozirconium Derivatives ...................... 716
2.11.4.7 Bis(η^5-cyclopentadienyl)monoorganometal Complexes .................................................. 718
2.11.4.7.1 Method 1: Protonolysis, Halogenolysis, Oxidation, and Related Heteroatom—Carbon Bond Formation ................. 719
2.11.4.7.1.1 Variation 1: Protonolysis and Deuterolysis .............. 719
2.11.4.7.1.2 Variation 2: Halogenolysis ......................................... 720
2.11.4.7.1.3 Variation 3: Oxidation .............................................. 720
2.11.4.7.2 Method 2: C—C Bond Formation via Polar Reactions of Chlorobis-(η^5-cyclopentadienyl)monoorganozirconium Complexes with Carbon Electrophiles ........................................... 721
2.11.4.7.2.1 Variation 1: Reactions of Allylbis(η^5-cyclopentadienyl)zirconium Derivatives with Aldehydes .......................... 721
2.11.4.7.3 Method 3: C—C Bond Formation via Carbonylation and Other Migratory Insertion Reactions of Bis(η^5-cyclopentadienyl)monoorganozirconium Complexes ............................................. 722
2.11.4.7.3.1 Variation 1: Carbonylation .......................................... 723
2.11.4.7.3.2 Variation 2: Isocyanide Insertion ............................ 723
2.11.4.7.3.3 Variation 3: Other Migratory Insertion Reactions ........... 725
2.11.4.7.4 Method 4: C—C Bond Formation via Stoichiometric Transmetalation ................................................... 726
2.11.4.7.5 Method 5: C—C Bond Formation via Metal-Catalyzed Reactions of Bis(η^5-cyclopentadienyl)monoorganozirconium Complexes with Organic Electrophiles ................................................... 727
2.11.4.7.5.1 Variation 1: Nickel- or Palladium-Catalyzed Cross Coupling of Alkenylchlorobis(η^5-cyclopentadienyl)zirconium Complexes ............................................................ 728
2.11.4.7.5.2 Variation 2: Nickel-Catalyzed Conjugate Addition of Alkenylchlorobis(η^5-cyclopentadienyl)zirconium Complexes ......................................................... 729
2.11.4.7.5.3 Variation 3: Copper-Catalyzed Conjugate Addition of Chlorobis(η^5-cyclopentadienyl)monoorganozirconium Complexes .............................................................. 730
2.11.4.7.6 Method 6: C—C Bond Formation Reactions of Organometals Catalyzed by Bis(η^5-cyclopentadienyl)monoorganozirconium Complexes ............................................................. 732
2.11.4.7.6.1 Variation 1: Zirconium-Catalyzed Carboalumination of Alkynes ................................................................. 732
2.11.4.7.6.2 Variation 2: Zirconium-Catalyzed Enantioselective Carboalumination of Alkenes .............................................. 734
2.11.4.7.6.3 Variation 3: Other Zirconium-Catalyzed Carbometalation Reactions of Alkynes and Alkenes ......................... 736
2.11.4.8 Bis(η^5-cyclopentadienyl)diorganometal Complexes ........................................................................... 736
2.11.4.8.1 Method 1: By β-Hydrogen Abstraction .................................................................................. 736
2.11.5 Product Subclass 5: Five-Membered Metallocycle–Bis(η^5-cyclopentadienyl) Derivatives of Oxidation State Four ........................................ 739

Synthesis of Product Subclass 5 ............................................ 740
2.11.5.1 Method 1: By Transmetalation ........................................ 740
2.11.5.2 Method 2: Carbometalative Ring-Expansion Reactions of Three- Membered Zirconocene and Hafnocene Derivatives ................. 741
2.11.5.2.1 Variation 1: The Erker–Buchwald Protocol ......................... 747
2.11.5.2.2 Variation 2: The Negishi–Takahashi Protocol ....................... 750
2.11.5.2.3 Variation 3: Other Protocols for the Synthesis of Five-Membered Zirconacycles and Hafnacycles .............................. 753

Applications of Product Subclass 5 in Organic Synthesis ............... 754
2.11.5.3 Method 3: Reactions of Five-Membered Zirconacycles Leading to the Formation of C–H(D) and C–X Bonds .................. 755
2.11.5.3.1 Variation 1: Protonolysis, Deuterolysis, and Halogenolysis ......... 755
2.11.5.3.2 Variation 2: Synthesis of Five-Membered Heterocycles ........... 759
2.11.5.3.3 Variation 3: Reactions with Organometals Containing Electropositive Metals .................................................. 759
2.11.5.4 Method 4: C–C Bond Formation via Polar Reactions of Five-Membered Zirconacycles with Carbon Electrophiles and Related π-Compounds ............................................. 761
2.11.5.4.1 Variation 1: Reactions of Zirconocene–Conjugated Diene Complexes with π-Compounds ............................................. 761
2.11.5.4.2 Variation 2: Ring Expansion of Zirconacyclopentenes and Zirconacyclo- pentanes with Aldehydes ............................................... 763
2.11.5.4.3 Variation 3: Reactions of Zirconacyclopentenes with Allyl and Alkenyl Ethers and Halides ............................................... 764
2.11.5.5 Method 5: C–C Bond Formation by the Reactions of Five-Membered Zirconacycles with Carbon Monoxide, Isocyanides, and Related Carbon Nucleophiles ......................... 765
2.11.5.5.1 Variation 1: Migratory Insertion Reactions of Zirconacycles with Carbon Monoxide and Isocyanides ......................... 765
2.11.5.6 Method 6: C–C Bond Formation by the Transition-Metal-Catalyzed Reaction of Five-Membered Zirconacycles ................ 769
2.11.5.6.1 Variation 1: Copper-Catalyzed Allylation of Zirconacyclopentadienes ................................................................. 769
2.11.5.6.2 Variation 2: Copper-Catalyzed Allylation of Zirconacyclopentenes ................................................................. 770
2.11.5.6.3 Variation 3: Copper-Catalyzed Acylation of Zirconacycles ................................................................. 771
2.11.5.6.4 Variation 4: Synthesis of Arenes from Three Different Alkynes by Copper- or Nickel-Mediated Reactions of Alkynes with Zirconacyclopentadienes ................................................................. 772
2.11.5.6.5 Variation 5: Coupling Reaction of Diiodobenzene with Zirconacyclopentadienes ................................................................. 773
2.11.5.7 Method 7: Organometallic Reactions Catalyzed by Five-Membered Zirconacycles ................................................................. 774
2.11.6 Product Subclass 6: Metal–Bis(η^5-cyclopentadienyl) Derivatives Containing Carbene, Nitrène, and Other Doubly Bonded Ligands

Synthesis of Product Subclass 6

2.11.6.1 Method 1: By α-Hydrogen Elimination

2.11.6.1.1 Variation 1: Formation of Imido- or Hydrazidozirconium Complexes

2.11.6.1.2 Variation 2: Formation of Oxo-, Thioxo-, or Phosphinidenezirconium Complexes

2.11.6.1.3 Variation 3: Formation of Oxo-, Carbene, or Nitrène Complexes

2.11.6.2 Method 2: Zirconium–Nitrène Complexes by Cleavage of Metallacycles

2.11.6.3 Method 3: Oxo-, Thioxo-, Selenoxo-, or Telluroxozirconium Complexes by the Oxidative Reaction of a Zirconium(II) Complex

2.11.6.4 Method 4: Miscellaneous Reactions

Applications of Product Subclass 6 in Organic Synthesis

2.11.7 Product Subclass 7: Cationic Metal–Bis(η^5-cyclopentadienyl) Derivatives of Oxidation State Four

Synthesis of Product Subclass 7

2.11.7.1 Method 1: By Halogen or Alkyl Abstraction from Bis(η^5-cyclopentadienyl)organozirconium Complexes

2.11.7.1.1 Variation 1: Cationic Alkylbis(η^5-cyclopentadienyl)zirconium Complexes by Halogen Abstraction from Bis(η^5-cyclopentadienyl)halo-(methyl)zirconium

2.11.7.1.2 Variation 2: One-Electron Oxidation of Bis(η^5-cyclopentadienyl)dioorganozirconium Complexes

2.11.7.1.3 Variation 3: Cationic Alkylbis(η^5-cyclopentadienyl)zirconium Complexes by Alkyl Abstraction Using a Lewis Acid

2.11.7.2 Method 2: By Ligand Exchange of Cationic Alkylbis(η^5-cyclopentadienyl)zirconium Complexes

2.11.7.3 Method 3: By Insertion Reactions of Cationic Alkylbis(η^5-cyclopentadienyl)zirconium Complexes

Applications of Product Subclass 7 in Organic Synthesis

2.11.7.4 Method 4: Coupling of Propene and 2-Methylpyridine Catalyzed by Cationic Bis(η^5-cyclopentadienyl)zirconium Complexes

2.11.7.5 Method 5: Catalytic Oligomerization of Terminal Alkynes

2.11.7.6 Method 6: Addition of Alkyl(chloro)bis(η^5-cyclopentadienyl)zirconium Complexes to Aldehydes

2.11.8 Product Subclass 8: Metal–Bis(η^5-cyclopentadienyl) Derivatives of Oxidation States Two and Three

Synthesis of Product Subclass 8

2.11.8.1 Method 1: By Reduction with Metals
### Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Method</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.11.8.2</td>
<td>Method 2:</td>
<td>By β-Hydrogen Abstraction</td>
</tr>
<tr>
<td>2.11.8.2.1</td>
<td>Variation 1:</td>
<td>Formation of Bis(η⁵-cyclopentadienyl)zirconium Complexes with Allenes, Silenes, Imines, and Diphenyl diazene Derivatives</td>
</tr>
<tr>
<td>2.11.8.2.2</td>
<td>Variation 2:</td>
<td>Formation of Bis(η⁵-cyclopentadienyl)zirconium–Benzyne Complexes</td>
</tr>
<tr>
<td>2.11.8.2.3</td>
<td>Variation 3:</td>
<td>Formation of Bis(η⁵-cyclopentadienyl)zirconium–Alkyne Complexes</td>
</tr>
<tr>
<td>2.11.8.2.4</td>
<td>Variation 4:</td>
<td>Formation of Bis(η⁵-cyclopentadienyl)zirconium–Alkene Complexes</td>
</tr>
<tr>
<td>2.11.8.3</td>
<td>Method 3:</td>
<td>By π-Complexation</td>
</tr>
<tr>
<td>2.11.8.4</td>
<td>Method 4:</td>
<td>By Transmetalation</td>
</tr>
<tr>
<td>2.11.8.5</td>
<td>Method 5:</td>
<td>By Reductive Elimination or Migration</td>
</tr>
<tr>
<td>2.11.8.6</td>
<td>Method 6:</td>
<td>By β,γ-C=C Bond Cleavage</td>
</tr>
<tr>
<td>2.11.8.7</td>
<td>Method 7:</td>
<td>Formation of Bis(η⁵-cyclopentadienyl)zirconium(III) Complexes</td>
</tr>
<tr>
<td>2.11.8.8</td>
<td>Method 8:</td>
<td>Bis(η²-cyclopentadienyl)zirconium(II)-Catalyzed C=C Bond Formation</td>
</tr>
<tr>
<td>2.11.8.8.1</td>
<td>Variation 1:</td>
<td>Using Grignard or Other Magnesium Reagents</td>
</tr>
<tr>
<td>2.11.8.8.2</td>
<td>Variation 2:</td>
<td>Using Organoaluminum Reagents</td>
</tr>
<tr>
<td>2.11.8.8.3</td>
<td>Variation 3:</td>
<td>Using Organozinc Reagents</td>
</tr>
<tr>
<td>2.11.8.9</td>
<td>Method 9:</td>
<td>Bis(η²-cyclopentadienyl)zirconium(II)-Catalyzed Hydrosilylation of Alkenes</td>
</tr>
<tr>
<td>2.11.9</td>
<td>Product Subclass 9: Metal–Mono(η⁵-cyclopentadienyl) and –Tris(η⁵-cyclopentadienyl) Complexes and Related Derivatives</td>
<td></td>
</tr>
<tr>
<td>2.11.9.1</td>
<td>Method 1:</td>
<td>By Transmetalation</td>
</tr>
<tr>
<td>2.11.9.1.1</td>
<td>Variation 1:</td>
<td>Formation of Trichloromono(η⁵-cyclopentadienyl)metal Derivatives from Metal(IV) Tetrachloride–Bis(dimethyl sulfide) Complexes</td>
</tr>
<tr>
<td>2.11.9.1.2</td>
<td>Variation 2:</td>
<td>Formation of Trichloro(η⁵-cyclopentadienyl)zirconium from Thallium(I) Methylcyclopentadienide and Zirconium(IV) Chloride–Bis(tetrahydrofuran) Complex</td>
</tr>
<tr>
<td>2.11.9.1.3</td>
<td>Variation 3:</td>
<td>Formation of Zirconium Complexes Containing an Amido-Linked Cyclopentadienyl Ligand</td>
</tr>
<tr>
<td>2.11.9.1.4</td>
<td>Variation 4:</td>
<td>Formation of Tris(η⁵-cyclopentadienyl)metal Complexes</td>
</tr>
<tr>
<td>2.11.9.2</td>
<td>Method 2:</td>
<td>By Radical Chlorination of Dichlorobis(η⁵-cyclopentadienyl)-zirconium</td>
</tr>
<tr>
<td>2.11.9.3</td>
<td>Method 3:</td>
<td>By Amine Elimination</td>
</tr>
<tr>
<td>2.11.9.4</td>
<td>Method 4:</td>
<td>Aldol-Type Reactions of 1-Naphthol Catalyzed by Trichloro(η²-cyclopentadienyl)zirconium Derivatives</td>
</tr>
</tbody>
</table>

---

*Science of Synthesis Original Edition Volume 2 © Georg Thieme Verlag KG*
2.11.10 Product Subclass 10: “Ate” Complexes of Metal–Bis(η^5-cyclopentadieny1) and Other Derivatives ................................................... 812
Synthesis of Product Subclass 10 .............................................. 813
2.11.10.1 Method 1: Synthesis of Bis(η^5-cyclopentadieny1)metal(IV) “Ate” Complexes ................................................... 813
2.11.10.1.1 Variation 1: Reactions of Bis(η^5-cyclopentadieny1)zirconium(IV) Derivatives with Alkyl- and Arylmetals Containing Lithium or Magnesium, or with Metal Hydrides .............................................. 813
Applications of Product Subclass 10 in Organic Synthesis ................ 815
2.11.10.2 Method 2: “Ate” Complexes of Bis(η^5-cyclopentadieny1)metal(IV) Derivatives ................................................... 815
2.11.10.2.1 Variation 1: Reactions of Bis(η^5-cyclopentadieny1)zirconium(IV) Derivatives with Alkynylmetals Containing Lithium and Magnesium 815
2.11.10.2.2 Variation 2: Reactions of Bis(η^5-cyclopentadieny1)metal(IV) Derivatives with α- and γ-Hetero-Substituted Alkyl- and Alkenyllithiums 819
2.11.10.2.3 Variation 3: Zwitterionic Bis(η^5-cyclopentadieny1)zirconium(IV) Derivatives ................................................... 822
2.11.10.3 Method 3: Zirconate Complexes of Bis(η^5-cyclopentadieny1)zirconium(II) Derivatives ................................................... 823
2.11.11 Product Subclass 11: Metal π-Complexes Containing η^5-Ligands Other than η^5-Cyclopentadienyl ................................................ 825
Synthesis of Product Subclass 11 .............................................. 826
2.11.11.1 Method 1: By Transmetalation ...................................... 826
2.11.11.2 Method 2: By Protonation with Carborane ...................... 827
2.11.12 Product Subclass 12: Metal π-Complexes Containing η^4, η^3, and η^2-Ligands .......................................................................... 827
Synthesis of Product Subclass 12 .............................................. 828
2.11.12.1 Method 1: By π-Complexation ....................................... 828
2.11.12.2 Method 2: By Transmetalation ...................................... 828
2.11.13 Product Subclass 13: Metal σ-Complexes without π-Ligands of Oxidation State Four ................................................... 829
Synthesis of Product Subclass 13 .............................................. 830
2.11.13.1 Method 1: By Transmetalation ...................................... 830
2.11.13.2 Method 2: Miscellaneous Methods ................................ 832
Applications of Product Subclass 13 in Organic Synthesis .............. 833
2.11.13.3 Method 3: Carbonyl Addition and Related Addition Reactions of σ-Organozirconium Complexes ....................................... 833
2.11.13.4 Method 4: Migratory Insertion of Isocyanides and Carbon Monoxide ................................................... 834
2.11.14 Product Subclass 14: Metal σ-Complexes of Oxidation States below Four ................................................... 835
2.11.14.1 Method 1: By Reduction .............................................. 835
2.11.14.2 Method 2: By Reductive Carbonylation ......................... 836
2.12 Product Class 12: Organometallic Complexes of Scandium, Yttrium and the Lanthanides
Z. Hou and Y. Wakatsuki

2.12.1 Product Subclass 1: Complexes in the Zero Oxidation State
Synthesis of Product Subclass 1

2.12.1.1 Method 1: By Co-condensation of Metal Vapor with a Ligand Compound

2.12.1.2 Method 2: By Reduction of Lanthanide(II) Species
Applications of Product Subclass 1 in Organic Synthesis

2.12.1.3 Method 3: Catalytic Conversion of Carbon Dioxide and Epoxides into Dioxolan-2-ones

2.12.2 Product Subclass 2: Lanthanide(II) Complexes with α-Organo Ligands
Synthesis of Product Subclass 2

2.12.2.1 Method 1: By Reduction of Appropriate Organic Compounds with Lanthanide Metals

2.12.2.1.1 Variation 1: By Reduction of Organic Iodides

2.12.2.1.2 Variation 2: By Reduction of Aromatic Ketones, Thioketones, and Imines

2.12.2.2 Method 2: By Transmetalation

2.12.2.2.1 Variation 1: From Lanthanide(II) Iodides

2.12.2.2.2 Variation 2: From Lanthanide Metals
Applications of Product Subclass 2 in Organic Synthesis

2.12.2.3 Method 3: Cross-Coupling Reactions with Organic Electrophiles

2.12.3 Product Subclass 3: Mono- and Bis(cyclopentadienyl)lanthanide(II) Complexes
Synthesis of Product Subclass 3

2.12.3.1 Method 1: By Transmetalation
Applications of Product Subclass 3 in Organic Synthesis

2.12.3.2 Method 2: Formation of Nucleophilic Allyl- and Benzylsamarium(III) Species

2.12.4 Product Subclass 4: Mono- and Bis(pentamethylcyclopentadienyl)lanthanide(II) Complexes
Synthesis of Product Subclass 4

2.12.4.1 Method 1: By Transmetalation
Applications of Product Subclass 4 in Organic Synthesis

2.12.4.2 Method 2: Reductive Coupling Reactions

2.12.4.2.1 Variation 1: Homocoupling Reactions

2.12.4.2.2 Variation 2: Cross-Coupling Reactions

2.12.4.3 Method 3: Acylation of Alcohols and Amines
### Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.12.4.4</td>
<td>Method 4: Polymerization</td>
<td>866</td>
</tr>
<tr>
<td>2.12.4.4.1</td>
<td>Variation 1: Synthesis of (Meth)acrylate Triblock Copolymers</td>
<td>866</td>
</tr>
<tr>
<td>2.12.4.4.2</td>
<td>Variation 2: Block Copolymerization of Ethene and Styrene</td>
<td>867</td>
</tr>
<tr>
<td>2.12.5</td>
<td>Product Subclass 5: Lanthanide(II) Complexes with Other Modified Cyclopentadienyl Ligands</td>
<td>868</td>
</tr>
<tr>
<td>2.12.5.1</td>
<td>Method 1: By Transmetalation</td>
<td>868</td>
</tr>
<tr>
<td>2.12.5.2</td>
<td>Method 2: Alkene Polymerization</td>
<td>870</td>
</tr>
<tr>
<td>2.12.6</td>
<td>Product Subclass 6: Miscellaneous Lanthanide(II) Complexes</td>
<td>871</td>
</tr>
<tr>
<td>2.12.6.1</td>
<td>Method 1: By Oxidation of Lanthanide Metals</td>
<td>871</td>
</tr>
<tr>
<td>2.12.6.2</td>
<td>Method 2: By Transmetalation</td>
<td>872</td>
</tr>
<tr>
<td>2.12.6.3</td>
<td>Method 3: Reversible Pinacol-Coupling Reactions</td>
<td>874</td>
</tr>
<tr>
<td>2.12.6.4</td>
<td>Method 4: Ring-Opening Polymerization and Copolymerization of Lactones</td>
<td>875</td>
</tr>
<tr>
<td>2.12.7</td>
<td>Product Subclass 7: Scandium(III)–, Yttrium(III)–, and Lanthanide(III)–α-Organo Complexes without Anionic π-Ligands</td>
<td>876</td>
</tr>
<tr>
<td>2.12.7.1</td>
<td>Method 1: By Transmetalation</td>
<td>876</td>
</tr>
<tr>
<td>2.12.7.2</td>
<td>Method 2: By Deprotonation of Terminal Alkynes</td>
<td>880</td>
</tr>
<tr>
<td>2.12.7.3</td>
<td>Method 3: Nucleophilic Addition</td>
<td>881</td>
</tr>
<tr>
<td>2.12.7.4</td>
<td>Method 4: Catalytic Dimerization of Alk-1-ynes and Polymerization of Ethene</td>
<td>882</td>
</tr>
<tr>
<td>2.12.8</td>
<td>Product Subclass 8: Mono- and Bis(cyclopentadienyl) Complexes of Scandium(III), Yttrium(III), and Lanthanides(III) Bearing α-Organo or Other Anionic Ligands</td>
<td>883</td>
</tr>
<tr>
<td>2.12.8.1</td>
<td>Method 1: By Transmetalation</td>
<td>883</td>
</tr>
<tr>
<td>2.12.8.1.1</td>
<td>Variation 1: From Rare Earth Trihalides</td>
<td>883</td>
</tr>
<tr>
<td>2.12.8.1.2</td>
<td>Variation 2: From Cyclopentadienyl Rare Earth Chlorides</td>
<td>885</td>
</tr>
<tr>
<td>2.12.8.2</td>
<td>Method 2: By Hydrogenolysis or Protonation of Rare Earth Metal–Carbon Bonds</td>
<td>887</td>
</tr>
<tr>
<td>2.12.8.3</td>
<td>Method 3: Addition of Ln—X (X = H, Alkyl, Silyl, or Germyl) to Unsaturated C—C, C—N, or C—O Bonds</td>
<td>889</td>
</tr>
</tbody>
</table>
2.12.9 Product Subclass 9: Tris(substituted or unsubstituted cyclopentadienyl) Complexes .......................................................... 891
    Synthesis of Product Subclass 9 ........................................ 891
    Method 1: By Transmetalation ............................................. 891
    Applications of Product Subclass 9 in Organic Synthesis .......... 893
    Method 2: Coupling Reactions between Pentamethylcyclopentadienide Anion and Electrophilic Substrates ............................. 893
2.12.10 Product Subclass 10: Mono- and Bis(pentamethylcyclopentadienyl) Complexes of Scandium(III), Yttrium(III), and the Lanthanides(III) Bearing α-Organo or Other Anionic Ligands ........................................ 895
    Synthesis of Product Subclass 10 ........................................ 895
    Method 1: By Transmetalation ............................................. 895
    Variation 1: From Rare Earth Trihalides or Tris(aryloxides) ......... 895
    Variation 2: From Pentamethylcyclopentadienyl Rare Earth Halides or Aryloxides .................................................. 897
    Method 2: By Hydrogenolysis or Protonation of Rare Earth Metal—Organo or Metal—Amide Bonds ...................................... 898
    Method 3: By Oxidation of Bis(pentamethylcyclopentadienyl)Lanthanide(II) Complexes ................................................ 900
    Applications of Product Subclass 10 in Organic Synthesis .......... 901
    Method 4: Catalytic Dimerization of Alk-1- or Alk-2-yynes .......... 901
    Method 5: Catalytic Hydrogenation, Hydrosilylation, and Hydroboration of Alkenes or Alkynes .............................................. 903
    Method 6: Catalytic Cyclization Reactions ............................... 904
    Method 7: Polymerization Reactions ...................................... 906
2.12.11 Product Subclass 11: Other Modified Cyclopentadienyl Complexes in Oxidation State Three ................................................ 907
    Synthesis of Product Subclass 11 ........................................ 907
    Method 1: By Transmetalation ............................................. 907
    Method 2: By Deprotonation ................................................. 915
    Applications of Product Subclass 11 in Organic Synthesis .......... 916
    Method 3: Catalytic Cyclization—Silylation of Hindered Dienes and Trienes ................................................................. 917
    Method 4: Asymmetric Catalysis ........................................... 917
    Method 5: Dimerization and Polymerization of Alk-1-enes .......... 918
2.12.12 Product Subclass 12: Cyclooctatetraenyl Complexes in Oxidation States Two and Three .......................................................... 919
    Synthesis of Product Subclass 12 ........................................ 919
    Method 1: By Transmetalation ................................................ 919
    Method 2: By Oxidation of Low-Valent Lanthanides .................. 921
2.12.13  
Product Subclass 13: Miscellaneous Complexes in Oxidation State Three  
Synthesis of Product Subclass 13  .......................................................... 922
2.12.13.1  
Method 1:  By Transmetalation  ............................................................... 923
2.12.13.2  
Method 2:  By Oxidation of Low-Valent Lanthanides  ................................ 925
2.12.13.3  
Method 3:  Polymerization of Buta-1,3-diene, Methyl Methacrylate, and Lactones .......................................................... 927
2.12.13.4  
Method 4:  Catalytic Asymmetric C—C, C—O, and C—P Bond Formation  ........ 928
2.12.14  
Product Subclass 14: Complexes in Oxidation State Four  ...................... 929
Synthesis of Product Subclass 14  .......................................................... 929
2.12.14.1  
Method 1:  By Transmetalation  ............................................................... 929
2.12.14.2  
Method 2:  By Oxidation of Cerium(III) Compounds  ............................. 931

2.13  
Product Class 13: Organometallic Complexes of the Actinides  
A. Dormond and D. Barbier-Baudry

2.13  
Product Class 13: Organometallic Complexes of the Actinides  ............... 943
2.13.1  
Product Subclass 1: Actinide–Cyclooctatetraenyl Complexes  ................. 943
Synthesis of Product Subclass 1  .............................................................. 944
2.13.1.1  
Method 1:  Preparation of Actinide–Cyclooctatetraenyl Complexes by Ligand Substitution .......................................................... 944
2.13.2  
Product Subclass 2: Actinide–Cycloheptatrienyl Complexes  ................. 946
Synthesis of Product Subclass 2  .............................................................. 947
2.13.2.1  
Method 1:  Preparation of Uranium–Cycloheptatrienyl Complexes by Ligand Substitution .......................................................... 947
2.13.3  
Product Subclass 3: Actinide–Arene Complexes  .................................. 947
Synthesis of Product Subclass 3  .............................................................. 947
2.13.3.1  
Method 1:  Preparation of Uranium(III) Arene Complexes by Reduction of Uranium(IV) Complexes .......................................................... 947
2.13.4  
Product Subclass 4: Actinide–Cyclopentadienyland Substituted 
Cyclopentadienyl Complexes  ............................................................... 948
Synthesis of Product Subclass 4  .............................................................. 948
2.13.4.1  
Method 1:  Preparation of Actinide Cyclopentadienyl Halide and Amide Complexes by Ligand Substitution .......................................................... 948
2.13.4.2  
Method 2:  Preparation of Actinide Cyclopentadienyl Alkyl Complexes by Ligand Substitution .......................................................... 950
2.13.4.3  
Method 3:  Preparation of Other Actinide Cyclopentadienyl Complexes by Ligand Substitution .......................................................... 952
2.13.4.4  
Method 4:  Preparation of (Cyclopentadienyl)actinide(III) Complexes by Reduction .......................................................... 953
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.13.5</td>
<td><strong>Product Subclass 5: Actinide–Pentamethylcyclopentadienyl Complexes</strong></td>
<td>954</td>
</tr>
<tr>
<td></td>
<td>Synthesis of Product Subclass 5</td>
<td>954</td>
</tr>
<tr>
<td>2.13.5.1</td>
<td>Method 1: Preparation of (Pentamethylcyclopentadienyl)actinide(IV)</td>
<td>954</td>
</tr>
<tr>
<td></td>
<td>Halide and Alkyl Complexes by Ligand Substitution</td>
<td></td>
</tr>
<tr>
<td>2.13.5.2</td>
<td>Method 2: Preparation of (Pentamethylcyclopentadienyl)uranium(III)</td>
<td>958</td>
</tr>
<tr>
<td></td>
<td>Complexes by Reduction</td>
<td></td>
</tr>
<tr>
<td>2.13.5.3</td>
<td>Method 3: Preparation of (Tetramethylcyclopentadienyl)actinide Adduct</td>
<td>959</td>
</tr>
<tr>
<td></td>
<td>Complexes by Ligand Addition</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Applications of Product Subclass 5 in Organic Synthesis</td>
<td>959</td>
</tr>
<tr>
<td>2.13.5.4</td>
<td>Method 4: Catalytic Synthesis of Imines by Addition</td>
<td>959</td>
</tr>
<tr>
<td>2.13.6</td>
<td>**Product Subclass 6: Actinide–Tetramethylphospholyl Complexes</td>
<td>960</td>
</tr>
<tr>
<td></td>
<td>Synthesis of Product Subclass 6</td>
<td>960</td>
</tr>
<tr>
<td>2.13.6.1</td>
<td>Method 1: Preparation of (Tetramethylphospholyl)uranium Complexes</td>
<td>960</td>
</tr>
<tr>
<td></td>
<td>by Ligand Substitution</td>
<td></td>
</tr>
<tr>
<td>2.13.7</td>
<td>**Product Subclass 7: Actinide–Hexadienyl and –Pentadienyl Complexes</td>
<td>961</td>
</tr>
<tr>
<td></td>
<td>Synthesis of Product Subclass 7</td>
<td>961</td>
</tr>
<tr>
<td>2.13.7.1</td>
<td>Method 1: Preparation of (Hexadienyl)- and (Pentadienyl)actinide</td>
<td>961</td>
</tr>
<tr>
<td></td>
<td>Complexes by Ligand Substitution</td>
<td></td>
</tr>
<tr>
<td>2.13.8</td>
<td>**Product Subclass 8: Actinide–Allyl Complexes</td>
<td>962</td>
</tr>
<tr>
<td></td>
<td>Synthesis of Product Subclass 8</td>
<td>962</td>
</tr>
<tr>
<td>2.13.8.1</td>
<td>Method 1: Preparation of Actinide–Allyl Complexes by Ligand</td>
<td>962</td>
</tr>
<tr>
<td></td>
<td>Substitution</td>
<td></td>
</tr>
<tr>
<td>2.13.9</td>
<td>**Product Subclass 9: Actinide–(\sigma)-Organo Complexes without</td>
<td>963</td>
</tr>
<tr>
<td></td>
<td>Anionic (\pi)-Ligands</td>
<td>964</td>
</tr>
<tr>
<td></td>
<td>Synthesis of Product Subclass 9</td>
<td>964</td>
</tr>
<tr>
<td>2.13.9.1</td>
<td>Method 1: Preparation of Actinide Alkyl Pyrazolylborate Complexes</td>
<td>964</td>
</tr>
<tr>
<td></td>
<td>by Ligand Substitution</td>
<td></td>
</tr>
<tr>
<td>2.13.9.2</td>
<td>Method 2: Preparation of Actinide Alkyl Aryloxy Complexes by Ligand</td>
<td>964</td>
</tr>
<tr>
<td></td>
<td>Substitution</td>
<td></td>
</tr>
<tr>
<td>2.13.9.3</td>
<td>Method 3: Preparation of Actinide Alkyl Silylamido Complexes by Ligand</td>
<td>965</td>
</tr>
<tr>
<td></td>
<td>Substitution</td>
<td></td>
</tr>
<tr>
<td>2.13.9.4</td>
<td>Method 4: Preparation of Actinide Metallacycles by Elimination</td>
<td>966</td>
</tr>
<tr>
<td></td>
<td>Reactions</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Applications of Product Subclass 9 in Organic Synthesis</td>
<td>967</td>
</tr>
<tr>
<td>2.13.9.5</td>
<td>Method 5: Selective Nucleophilic Addition to Carbonyl Compounds</td>
<td>967</td>
</tr>
<tr>
<td>2.13.9.6</td>
<td>Method 6: Nucleophilic Addition to Unsaturated Compounds</td>
<td>967</td>
</tr>
<tr>
<td>2.13.10</td>
<td>**Product Subclass 10: Miscellaneous Complexes</td>
<td>969</td>
</tr>
<tr>
<td></td>
<td>Synthesis of Product Subclass 10</td>
<td>969</td>
</tr>
<tr>
<td>2.13.10.1</td>
<td>Method 1: Preparation of Uranium(IV) Borohydride by Ligand</td>
<td>969</td>
</tr>
<tr>
<td></td>
<td>Substitution</td>
<td></td>
</tr>
</tbody>
</table>
Table of Contents

Keyword Index .......................................................... 975
Author Index ............................................................ 1011
Abbreviations ........................................................ 1065