Table of Contents

Volume 1:
Compounds with Transition Metal—Carbon π-Bonds and Compounds of Groups 10–8 (Ni, Pd, Pt, Co, Rh, Ir, Fe, Ru, Os)

1.1 Product Class 1: Organometallic Complexes of Nickel

1.1.5 **Organometallic Complexes of Nickel** 2013
R. M. Stolley and J. Louie

1.1.5 **Organometallic Complexes of Nickel** 1
1.1.5.1 Nickel Complexes of 1,3-Dienes 1
1.1.5.1.1 Method 1: Applications in Diene–Diene Cycloadditions 1
1.1.5.1.2 Method 2: Diene–Aldehyde Reductive Coupling 3
1.1.5.1.2.1 Variation 1: Triethylsilane-Mediated Reactions 3
1.1.5.1.2.2 Variation 2: Triethylborane-Mediated Reactions 4
1.1.5.1.2.3 Variation 3: Organoaluminum-Mediated Reactions 5
1.1.5.1.2.4 Variation 4: Bismetalative Reductive Coupling Mediated by Main Group Bimetallic Reagents 7
1.1.5.1.2.5 Variation 5: Reductive Coupling of Dienes with Other Carbonyl Compounds or Imines 9
1.1.5.1.3 Method 3: Addition of Main Group Elements to Dienes 12
1.1.5.1.3.1 Variation 1: Hydroelement Addition to Dienes 12
1.1.5.1.3.2 Variation 2: Interelement Addition to Dienes 13
1.1.5.1.3.3 Variation 3: Main Group Element/Carbon Nucleophile Addition to Dienes 14
1.1.5.1.3.4 Variation 4: Addition of C—H Bonds to Dienes 15
1.1.5.2 Nickel–Allyl Complexes 16
1.1.5.2.1 Method 1: Oxidative Addition of But-3-enenitriles in the Presence of Lewis Acids 16
1.1.5.2.2 Method 2: Oxidative Addition of Allylic Chalcogenides 17
1.1.5.2.3 Method 3: Oxidative Heterocoupling of Carbonyl Compounds and Dienes 18
1.1.5.2.4 Method 4: Reaction of Nickel–Allyl Complexes with Main Group Organometallics 18
1.1.5.2.5 Method 5: Alkyne Insertion with Nickel–Allyl Complexes 19
1.1.5.2.5.1 Variation 1: But-3-enenitrile-Derived Nickel–Allyl Complexes 20
1.1.5.2.5.2 Variation 2: Allyl Chalcogenide Derived Nickel–Allyl Complexes 21
1.1.5.2.5.3 Variation 3: Nickel–Allyl Complexes Derived from Dimerization of 1,3-Dienes 21
1.1.5.2.5.4 Variation 4: Nickel–Allyl Complexes Derived from Dienes and Carbonyl Compounds 22

Science of Synthesis Knowledge Updates 2013/2
© Georg Thieme Verlag KG

1.1.5.3 Nickel–Alkyne Complexes 23

1.1.5.3.1 Method 1: Coupling of Alkynes with Carbon Dioxide 23
1.1.5.3.2 Method 2: Coupling of Alkynes with Carbonyl Compounds 25
1.1.5.3.2.1 Variation 1: Coupling of Alkynes with Aldehydes and Ketones 25
1.1.5.3.2.2 Variation 2: Coupling of Alkynes with Aldimines 26
1.1.5.3.2.3 Variation 3: Coupling of Alkynes with Unsaturated Carbonyl Compounds 28
1.1.5.3.3 Method 3: Reductive Coupling of Alkynes with Epoxides 30
1.1.5.3.4 Method 4: [2 + 2 + 2] Cycloaddition with Heterocumulene Partners 31
1.1.5.3.5 Method 5: Reactions of Nickel–Alkyne Complexes with Strained Ring Systems 33
1.1.5.3.6 Method 6: Addition of Main Group Elements to Alkynes 35
1.1.5.3.6.1 Variation 1: Hydroelement Additions to Alkynes 35
1.1.5.3.6.2 Variation 2: Carbon–Main Group Element Additions to Alkynes 37
1.1.5.3.6.3 Variation 3: Direct Carbon–Hydrogen Additions to Alkynes 39
1.1.5.3.6.4 Variation 4: Direct Carbon–Carbon Additions to Alkynes 40
1.1.5.3.7 Method 7: Nickel–Aryne Complexes 41

1.1.5.4 Nickel–Alkene Complexes 43

1.1.5.4.1 Method 1: Alkene Hydrocyanation 43
1.1.5.4.2 Method 2: Alkene Polymerization 43
1.1.5.4.3 Method 3: Alkene Hydroamination 44
1.1.5.4.4 Method 4: Alkene Hydrophosphinylation 45
1.1.5.4.5 Method 5: Alkene Carboxylation 46
1.1.5.4.6 Method 6: Direct Alkene Addition 46
1.1.5.4.6.1 Variation 1: Direct Hydroalkenylation 46
1.1.5.4.6.2 Variation 2: Direct Hydroalkylation 47
1.1.5.4.7 Method 7: Coupling of Alkenes and Aldehydes 48
1.1.5.4.8 Method 8: Alkene Rearrangements 49
1.1.5.4.8.1 Variation 1: Allylic Isomerization 50
1.1.5.4.8.2 Variation 2: Isomerization of Vinylcyclopropanes and Analogous Compounds 50

1.1.5.5 Nickel–Allene Complexes 51

1.1.5.5.1 Method 1: Allene Oligomerization 52
1.1.5.5.2 Method 2: Allene Carboxylation 52
1.1.5.5.3 Method 3: Reductive Coupling of Allenes and Aldehydes 53
1.1.5.5.4 Method 4: Coupling of Allenes and α,β-Unsaturated Carbonyl Compounds 55

1.2 Product Class 2: Organometallic Complexes of Palladium

1.2.6 High-Valent Palladium in Catalysis New

P. Chen, G. Liu, K. M. Engle, and J.-Q. Yu

1.2.6 **High-Valent Palladium in Catalysis** 63

1.2.6.1 C—H Activation/Functionalization of Arenes and Alkanes 66

1.2.6.1.1 Method 1: Functionalization of Aromatic C—H Bonds 67

Science of Synthesis Knowledge Updates 2013/2
© Georg Thieme Verlag KG

1.2.6.1.1.1 Variation 1: C—C Bond Construction 67
1.2.6.1.1.2 Variation 2: C—O Bond Construction 72
1.2.6.1.1.3 Variation 3: C—X Bond Construction (X = Halo) 74
1.2.6.1.1.4 Variation 4: C—N Bond Construction 77
1.2.6.1.2 Method 2: Functionalization of Aliphatic C—H Bonds 78
1.2.6.1.2.1 Variation 1: C—C Bond Construction 78
1.2.6.1.2.2 Variation 2: C—O Bond Construction 80
1.2.6.1.2.3 Variation 3: C—X Bond Construction (X = Halo) 82
1.2.6.1.2.4 Variation 4: C—N Bond Construction 83

1.2.6.2 Difunctionalization of Alkenes 85

1.2.6.2.1 Method 1: C—O Bond Construction from High-Valent Palladium Centers 85
1.2.6.2.1.1 Variation 1: Initiated by Aminopalladation 85
1.2.6.2.1.2 Variation 2: Initiated by Oxypalladation 90
1.2.6.2.2 Method 2: C—N Bond Construction from High-Valent Palladium Centers 91
1.2.6.2.2.1 Variation 1: Initiated by Aminopalladation 91
1.2.6.2.2.2 Variation 2: Initiated by Fluoropalladation 94
1.2.6.2.3 Method 3: C—X Bond Construction (X = Halo) from High-Valent Palladium Centers 95
1.2.6.2.3.1 Variation 1: Initiated by Aminopalladation 95
1.2.6.2.3.2 Variation 2: Initiated by Carbopalladation 97
1.2.6.2.4 Method 4: C—C Bond Construction from High-Valent Palladium Centers · 99
1.2.6.2.4.1 Variation 1: Initiated by Aminopalladation 100
1.2.6.2.4.2 Variation 2: Initiated by Oxypalladation–Insertion 100
1.2.6.2.4.3 Variation 3: Initiated by Arylpalladation 102

Volume 4: Compounds of Group 15 (As, Sb, Bi) and Silicon Compounds

4.4 Product Class 4: Silicon Compounds

4.4.5 Product Subclass 5: Disilanes and Oligosilanes 2013

C. Marschner and J. Baumgartner

4.4.5 **Product Subclass 5: Disilanes and Oligosilanes** 109

4.4.5.1 Disilanes 110

4.4.5.1.1 Method 1: Synthesis by Formation of Si—Si Bonds 114
4.4.5.1.1.1 Variation 1: Reductive Coupling of Triorganosilyl Halides 114
4.4.5.1.1.2 Variation 2: Dehydrogenative Coupling of Hydrosilanes 116
4.4.5.1.1.3 Variation 3: Coupling of Silyl Halides with Silyl Anions 117
4.4.5.1.2 Method 2: Synthesis by Cleavage of Si—C Bonds 118
4.4.5.1.2.1 Variation 1: Demethylating Chlorination 118
4.4.5.1.2.2 Variation 2: Dearylation and Dealkylation with Strong Acids 119
4.4.5.1.3 Method 3: Synthesis by Functionalization of Si—X Bonds 121
4.4.5.1.3.1 Variation 1: Hydrogenation with Lithium Aluminum Hydride 121

Science of Synthesis Knowledge Updates 2013/2
© Georg Thieme Verlag KG

4.4.5.2 Oligosilanes 122

4.4.5.2.1 Method 1: Synthesis by Formation of Si—Si Bonds 124
4.4.5.2.1.1 Variation 1: Wurtz-Type Coupling 125
4.4.5.2.2 Method 2: Synthesis by Cleavage of Si—Si Bonds and Subsequent Derivatization 126
4.4.5.2.2.1 Variation 1: Silyl Anion Formation 126
4.4.5.2.2.2 Variation 2: Anion Hydrolysis to Hydrosilanes 127
4.4.5.2.2.3 Variation 3: Halogenation 127
4.4.5.2.3 Method 3: Synthesis by Alkylation and Arylation 128
4.4.5.2.3.1 Variation 1: Reactions Using Silyl Anions 128
4.4.5.2.3.2 Variation 2: Reactions Using Silyl Halides 130
4.4.5.2.3.3 Variation 3: Cross Coupling 131
4.4.5.2.4 Method 4: Synthesis by Hydrosilylation 132
4.4.5.2.5 Method 5: Synthesis by Silyl Ether Formation 133
4.4.5.2.6 Method 6: Synthesis by Cleavage of Si—C Bonds 134

4.4.9 **Product Subclass 9: Silylzinc Reagents** 2013
A. Durand, I. Hemeon, and R. D. Singer

4.4.9 **Product Subclass 9: Silylzinc Reagents** 141

Synthesis of Product Subclass 9 141

4.4.9.1 Method 1: Synthesis from a Triorganosilyl Anion Source and Zinc(II) Reagents 141
4.4.9.1.1 Variation 1: Dialkyl(triorganosilyl)zincate Reagents from an Alkylmetal, a (Triorganosilyl)metal Reagent, and a Zinc(II) Salt 143
4.4.9.2 Method 2: Synthesis of Dianion-Type Silylzincates 143

Applications of Product Subclass 9 in Organic Synthesis 144

4.4.9.3 Method 3: Addition of Silyl Groups to Alkenes, Alkynes, and Epoxides 144

4.4.21.13 **Silylamines** 2013
A. Kawachi

4.4.21.13 **Silylamines** 151

4.4.21.13.1 Method 1: Reaction of Chlorosilanes with Amines Bearing NH Groups 151
4.4.21.13.1.1 Variation 1: Reaction of Allyltrichlorosilane with Diamines 151
4.4.21.13.1.2 Variation 2: Reaction of Allyltrichlorosilane with Amino Alcohols 152
4.4.21.13.1.3 Variation 3: Reaction of Silicon Tetrachloride with 1-Methyl-1*H*-imidazole-2(3*H*)-thione 152
4.4.21.13.2 Method 2: Reaction of Silicon Tetrachloride with Silylamines 153
4.4.21.13.3 Method 3: Reaction of Halosilanes with Lithium Amides 154
4.4.21.13.3.1 Variation 1: Reaction of Silicon Tetrabromide with Lithium β-Diketiminates 154
4.4.21.13.3.2 Variation 2: Reaction of Silicon Tetrachloride or Trichlorosilane with *N*,*N*′-Dialkylbenzimidamide Lithium Salts To Form Low-Coordinate Silicon Species 155

Science of Synthesis Knowledge Updates 2013/2
© Georg Thieme Verlag KG

4.4.21.13.3.3 Variation 3: Reaction of Trichlorosilane with *N*,*N*′-Dialkylbenzimidamide Lithium Salts To Form High-Coordinate Silicon Species 156
4.4.21.13.3.4 Variation 4: Reaction of Chlorosilanes with Dilithium Tetra-4-tolylporphyrinate 157
4.4.21.13.4 Method 4: Reaction of Halosilanes with Hetarenes or Tertiary Amines 158
4.4.21.13.4.1 Variation 1: Reaction of Dichlorosilane with 2,2′-Bipyridine To Form a High-Coordinate Silicon Species 158
4.4.21.13.4.2 Variation 2: Reaction of Silicon Tetrafluoride with a Triazacyclononane To Form a Cationic Silicon(IV) Species 158
4.4.21.13.5 Method 5: Reaction of Dichlorosilanes with Hydrazonic Acid Esters and Thermal Rearrangement 159
4.4.21.13.6 Method 6: Reaction of Di- and Trihydrosilanes with N-Heterocyclic Carbenes 159
4.4.21.13.7 Method 7: Dehydrogenative Condensation of Hydrosilanes with Amines 160
4.4.21.13.7.1 Variation 1: Ruthenium-Catalyzed Reaction of Hydrosilanes with Indoles and Carbazoles 160
4.4.21.13.7.2 Variation 2: Ytterbium-Catalyzed Reaction of Hydrosilanes with Amines 161
4.4.21.13.7.3 Variation 3: Zinc-Catalyzed Reaction of Hydrosilanes with Indoles 162
4.4.21.13.7.4 Variation 4: Reaction of 1-Boryl-2-(hydrosilyl)benzenes with Amines 163
4.4.21.13.8 Method 8: Preparation of Cyclic Diaminosilylenes 164
4.4.21.13.8.1 Variation 1: Reduction of Dihalosilanes with Alkali Metals 164
4.4.21.13.8.2 Variation 2: Dehydrochlorination Using N-Heterocyclic Carbenes 165
4.4.21.13.9 Method 9: Reactions of (Aminosilyl)lithiums 166
4.4.21.13.9.1 Variation 1: Preparation of an (Aminosilyl)pinacolborane 166
4.4.21.13.9.2 Variation 2: Preparation of 1,3-Diaminotrisilanes 167

4.4.22 **Product Subclass 22: Silyl Phosphines** 2013

M. Hayashi

4.4.22 **Product Subclass 22: Silyl Phosphines** 169
Synthesis of Product Subclass 22 170
4.4.22.1 Method 1: Synthesis from Silyl Hydrides 170
4.4.22.1.1 Variation 1: By Dehydrohalogenation 170
4.4.22.1.2 Variation 2: By Dehydrogenation with Phosphines 170
4.4.22.1.3 Variation 3: By Hydrosilylation of P—P Bonds 171
4.4.22.2 Method 2: Synthesis from Silyl Halides 172
4.4.22.2.1 Variation 1: From Elemental Phosphorus 172
4.4.22.2.2 Variation 2: From Phosphines 173
4.4.22.2.3 Variation 3: From Metal Phosphides 174
4.4.22.3 Method 3: Substitution by Silyllithiums 178
4.4.22.4 Method 4: Synthesis from Other Silyl Phosphines 178
4.4.22.4.1 Variation 1: By Exchange of Silyl Groups 179
4.4.22.4.2 Variation 2: By Conversion of Phosphines 179
4.4.22.4.3 Variation 3: By Transmetalation of Silyl Phosphines 180
4.4.22.5 Method 5: Miscellaneous Methods 180
Applications of Product Subclass 22 in Organic Synthesis 181
4.4.22.6 Method 6: Synthesis of Silicon-Containing Compounds 181

Science of Synthesis Knowledge Updates 2013/2
© Georg Thieme Verlag KG

4.4.22.6.1 Variation 1: Synthesis of Silyl Ethers by Substitution 181
4.4.22.7 Method 7: Synthesis of Organophosphorus Compounds by Substitution · 182
4.4.22.7.1 Variation 1: Of Haloalkanes 182
4.4.22.7.2 Variation 2: Of Haloarenes 183
4.4.22.7.3 Variation 3: Of Halohetarenes 185
4.4.22.7.4 Variation 4: Of Acyl Halides 186
4.4.22.8 Method 8: Synthesis of Organophosphorus Compounds by Addition 186
4.4.22.8.1 Variation 1: To Aldehydes 187
4.4.22.8.2 Variation 2: To Alkenes 187
4.4.22.8.3 Variation 3: To Alkynes 188
4.4.22.8.4 Variation 4: To Epoxides 189
4.4.22.9 Method 9: Synthesis of Organophosphorus Compounds by Addition–Elimination 190
4.4.22.9.1 Variation 1: Synthesis of Phosphaalkenes 190
4.4.22.9.2 Variation 2: Synthesis of Phosphaalkynes 191
4.4.22.9.3 Variation 3: Synthesis of Phosphorus-Containing Heterocycles 192

4.4.41.8 **β-Silyl Carbonyl Compounds** 2013
F. Nahra and O. Riant

4.4.41.8 **β-Silyl Carbonyl Compounds** 197
4.4.41.8.1 Method 1: Silylmetalation of Alkenes 201
4.4.41.8.1.1 Variation 1: Silylmetalation of α,β-Unsaturated Carbonyl Compounds ... 202
4.4.41.8.1.2 Variation 2: Silylmetalation–Aldolization of α,β-Unsaturated Carbonyl Compounds 204
4.4.41.8.1.3 Variation 3: Silaboration–Oxidation of *meso*-Methylenecyclopropanes ... 204
4.4.41.8.2 Method 2: Hydrosilylation of Alkynes 205
4.4.41.8.2.1 Variation 1: Hydrosilylation of Alkynyl Carbonyl Compounds 206
4.4.41.8.2.2 Variation 2: Hydrosilylation–Geminal Alkylation 206
4.4.41.8.3 Method 3: Asymmetric Conversion of α,β-Unsaturated β-Silyl Carbonyl Compounds into Their Saturated Counterparts 207
4.4.41.8.3.1 Variation 1: Asymmetric Hydrosilylation of α,β-Unsaturated β-Silyl Carbonyl Compounds 208
4.4.41.8.3.2 Variation 2: Asymmetric 1,4-Addition of Carbon Nucleophiles to α,β-Unsaturated β-Silyl Carbonyl Compounds 208
4.4.41.8.3.3 Variation 3: 1,4-Addition of Carbon Nucleophiles to Alkynyl β-Silyl Carbonyl Compounds 210
4.4.41.8.4 Method 4: Rearrangements and Silyl Migration 211

Science of Synthesis Knowledge Updates 2013/2
© Georg Thieme Verlag KG

Volume 17:
Six-Membered Hetarenes with Two Unlike or More than Two Heteroatoms and Fully Unsaturated Larger-Ring Heterocycles

---

17.5 Product Class 5: Seven-Membered Hetarenes with Two or More Heteroatoms

---

17.5.4 Seven-Membered Hetarenes with Two or More Heteroatoms 2013

J. Zhang

17.5.4 **Seven-Membered Hetarenes with Two or More Heteroatoms** 215

17.5.4.1 1,2-Diazepines 219

17.5.4.1.1 Synthesis by Ring-Closure Reactions 220

17.5.4.1.1.1 Method 1: Condensation of 1,5-Diketones with Hydrazine 220

17.5.4.1.1.1.1 Variation 1: Condensation of 1,5-Diketones, 1,5-Keto Acids, or 1,5-Keto Esters with Hydrazine 220

17.5.4.1.1.1.2 Variation 2: Condensation of Imidazothiadiazole Aldehydes with Hydrazine 221

17.5.4.1.1.1.3 Variation 3: Cyclization of Indol-2-ylacetates and Indole-2-carboxylates with Hydrazine 222

17.5.4.1.2 Synthesis by Ring Transformation 223

17.5.4.1.2.1 By Ring Enlargement 223

17.5.4.1.2.1.1 Method 1: Reaction of Benzocyclobutenones and Diazomethylene Compounds 223

17.5.4.1.2.1.2 Method 2: Synthesis from Benzoselenopyrylium Salts and Hydrazine ... 226

17.5.4.1.3 Synthesis by Substituent Modification 227

17.5.4.1.3.1 By Replacement of Oxygen or Sulfur 227

17.5.4.1.3.1.1 Method 1: Synthesis of Amidines from Benzodiazepinethiones 227

17.5.4.1.3.1.2 Method 2: Synthesis of Amidines from Benzodiazepinones and Primary or Secondary Amines Catalyzed by Titanium(IV) Chloride 228

17.5.4.2 1,3-Diazepines 229

17.5.4.2.1 Synthesis by Ring-Closure Reactions 230

17.5.4.2.1.1 Method 1: Synthesis from 2-(2-Isocyanophenyl)acetamides and Sulfur via Isothiocyanate Intermediates 230

17.5.4.2.1.2 Method 2: Synthesis from 4-Hydroxy-2*H*-1-benzopyran-2-one, Cyanoguanidine, and Aromatic or Heteroaromatic Aldehydes Using Molecular Iodine as Catalyst 231

17.5.4.2.1.3 Method 3: Synthesis from a Substituted Aminopyridine and Trichloroacetyl Isocyanate 232

17.5.4.2.1.4 Method 4: Synthesis from a Substituted Imidazol-5-amine and Triethyl Orthoformate 234

Science of Synthesis Knowledge Updates 2013/2
© Georg Thieme Verlag KG

17.5.4.2.1.5 Method 5: Synthesis from a Substituted Imidazole-4,5-dicarboxylate and Guanidine 234

17.5.4.3 1,4-Diazepines 235

17.5.4.3.1 Synthesis by Ring-Closure Reactions 235

17.5.4.3.1.1 Method 1: Synthesis from Benzene-1,2-diamines, Meldrum's Acid, and Isocyanides 235

17.5.4.3.1.2 Method 2: Synthesis from Benzene-1,2-diamines and 1,3-Dicarbonyl Compounds 237

17.5.4.3.1.3 Method 3: Synthesis from Pyridine-2,3-diamine and 1,1,1-Trichlorobut-3-en-2-ones 241

17.5.4.3.1.4 Method 4: Synthesis from Benzene-1,2-diamines, Diketene, Dialkyl Acetylenedicarboxylates, and Trialkyl Phosphites 241

17.5.4.3.1.5 Method 5: Synthesis from Benzene-1,2-diamines and 4-Halogenated N-Substituted 2-Oxo-1,2-dihydropyridine-3-carbodithioates 242

17.5.4.3.1.6 Method 6: Reductive Lactamization of Alkyl 2-[(2-Nitrophenyl)amino]benzoates 243

17.5.4.3.1.7 Method 7: Copper-Catalyzed Cyclization of 2-Iodoaniline Compounds 244

17.5.4.3.1.8 Method 8: Palladium-Catalyzed Intramolecular Carbonylation–Lactamization 245

17.5.4.3.1.9 Method 9: Palladium-Catalyzed Intramolecular Amination of *N*-Alkyl-2-amino-*N*-(2-iodophenyl)benzamides 246

17.5.4.3.1.10 Method 10: Copper-Catalyzed Cyclization of 2-Halobenzoic Acids with Benzene-1,2-diamine 247

17.5.4.3.1.11 Method 11: Intramolecular Aza-Wittig Reaction 248

17.5.4.3.1.12 Method 12: Synthesis from 2-Aminobenzophenones and Bromoacetyl Bromide or Chloroacetyl Chloride 250

17.5.4.3.1.13 Method 13: Bischler–Napieralski Cyclocondensation 253

17.5.4.3.1.14 Method 14: Buchwald Amination–Cyclization 256

17.5.4.3.2 Synthesis by Ring Transformation 259

17.5.4.3.2.1 By Ring Enlargement 259

17.5.4.3.2.1.1 Method 1: Synthesis from α-Amino Acids and Isatoic Acid Anhydride or Analogues 259

17.5.4.3.3 Synthesis by Substituent Modification 260

17.5.4.3.3.1 By Replacement of Chlorine 260

17.5.4.3.3.1.1 Method 1: Metal-Catalyzed Coupling of Chloro-5*H*-dibenzo[*b*,*e*][1,4]diazepines with Organozinc or -magnesium Compounds 260

Science of Synthesis Knowledge Updates 2013/2
© Georg Thieme Verlag KG

Volume 18: Four Carbon—Heteroatom Bonds: X—C≡X, X=C=X, X_2C=X, CX_4

18.1 Product Class 1: Cyanogen Halides, Cyanates and Their Sulfur, Selenium, and Tellurium Analogues, Sulfinyl and Sulfonyl Cyanides, Cyanamides, and Phosphaalkynes

18.1.7 Cyanogen Halides, Cyanates and Their Sulfur, Selenium, and Tellurium Analogues, Sulfinyl and Sulfonyl Cyanides, Cyanamides, and Phosphaalkynes 2013

J. Podlech

18.1.7 **Cyanogen Halides, Cyanates and Their Sulfur, Selenium, and Tellurium Analogues, Sulfinyl and Sulfonyl Cyanides, Cyanamides, and Phosphaalkynes** 265

18.1.7.1 Cyanogen Halides 265

18.1.7.1.1 Applications of Cyanogen Halides in Organic Synthesis 265

18.1.7.1.1.1 Method 1: Electrophilic Cyanation 265
18.1.7.1.1.2 Method 2: Formation of Cyanooxiranes from Ketones 266

18.1.7.2 Cyanates and Their Sulfur, Selenium, and Tellurium Analogues 267

18.1.7.2.1 Synthesis of Thiocyanates 267

18.1.7.2.1.1 Method 1: Nucleophilic Reactions from Thiocyanate Salts 267
18.1.7.2.1.1.1 Variation 1: Thiocyanates from Alcohols and Protected Alcohols 267
18.1.7.2.1.1.2 Variation 2: Ring Opening of Epoxides To Give β-Hydroxy Thiocyanates 268
18.1.7.2.1.1.3 Variation 3: Oxidative α-Thiocyanation of Ketones 269
18.1.7.2.1.1.4 Variation 4: Oxidative Thiocyanation of Aromatic Compounds 270
18.1.7.2.1.2 Method 2: Thiocyanates by Ring Opening of Epoxides and Aziridines with Trimethylsilyl Isothiocyanate 271
18.1.7.2.1.3 Method 3: Thiocyanates from Acyl Isothiocyanates 271
18.1.7.2.1.4 Method 4: Cyanation of Thiols Using *N*-Cyano Heterocycles 272

18.1.7.2.2 Applications of Thiocyanates in Organic Synthesis 272

18.1.7.2.2.1 Method 1: 1,3-Oxathiolan-2-imines from Phenacyl Thiocyanates 273

18.1.7.3 Sulfonyl Cyanides 273

18.1.7.3.1 Applications of Sulfonyl Cyanides in Organic Synthesis 273

18.1.7.3.1.1 Method 1: Diaryl Sulfides from Sulfonyl Cyanides 273
18.1.7.3.1.2 Method 2: Allyl Sulfones from Sulfonyl Cyanides and Allylic Alcohols 274
18.1.7.3.1.3 Method 3: Synthesis of Aryl 4-Hydroxypyridin-2-yl Sulfones 275

18.1.7.4 Cyanamides and Their Derivatives 275

18.1.7.4.1 Synthesis of Cyanamides and Their Derivatives 275

18.1.7.4.1.1 Method 1: Substitution of Cyanamides 275
18.1.7.4.1.1.1 Variation 1: Acylation and Arylation of Cyanamides 275

Science of Synthesis Knowledge Updates 2013/2
© Georg Thieme Verlag KG

18.1.7.4.1.1.2 Variation 2: Reaction of Cyanamides with Isocyanates, Isothiocyanates, Thioamides, or Nitriles Yielding Cyanoureas or Cyanoimidamides 276

18.1.7.4.1.2 Method 2: Cyanation of Amides Using Cyanogen Halides 278

18.1.7.4.1.3 Method 3: Oxidative Elimination from Dithiocarbamates and Thioureas . 279

18.1.7.4.1.4 Method 4: Reaction of Isocyanates and Isothiocyanates with Hexamethyldisilazanide 279

18.1.7.4.1.5 Method 5: Synthesis from Dialkylamino-Substituted Acetamides by a Hofmann-Like Rearrangement 280

18.1.7.4.2 Applications of Cyanamides and Their Derivatives in Organic Synthesis 281

18.1.7.4.2.1 Method 1: Cyanation of Amines, Thiols, and CH-Acidic Compounds 281

18.1.7.4.2.2 Method 2: Synthesis of *N*,*N*-Dialkyl-4,5-dihydro-1*H*-imidazol-2-amines and *N*,*N*-Dialkyl-1*H*-imidazol-2-amines 282

18.1.7.4.2.3 Method 3: Chlorination with *N*-*tert*-Butyl-*N*-chlorocyanamide 283

18.1.7.4.2.4 Method 4: Cyclotrimerization of Alkynes or Diynes with Cyanamides To Give Pyridin-2-amines 284

18.11 Product Class 11: Seleno- and Tellurocarbonic Acids and Derivatives

---

18.11.10 Seleno- and Tellurocarbonic Acids and Derivatives 2013

K. Shimada

18.11.10 **Seleno- and Tellurocarbonic Acids and Derivatives** 289

18.11.10.1 Selenocarbamates 289

18.11.10.1.1 Method 1: Reaction of *N*,*N*-Dimethylselenocarbamoyl Chloride with Lithium Alkaneselenolates, Areneselenolates, Alkanethiolates, or Arenethiolates 289

18.11.10.1.2 Method 2: Reaction of Isoselenocyanates with Nucleophiles 290

18.11.10.1.2.1 Variation 1: Reaction of Alkyl or Aryl Isoselenocyanates with Sodium Hydroselenide 290

18.11.10.1.2.2 Variation 2: Reaction of Acyl Isoselenocyanates with Alcohols, Thiols, or Selenols 291

18.11.10.1.2.3 Variation 3: Reaction of Acryloyl Isoselenocyanates with Sodium Hydroselenide 292

18.11.10.1.2.4 Variation 4: Reaction of Isoselenocyanates with Sodium Alkoxides 292

18.11.10.1.2.5 Variation 5: Reaction of Isoselenocyanates with Sodium Hydroselenide and Acryloyl Chlorides 293

18.11.10.1.2.6 Variation 6: Reaction of Isocyanates with Bis(dimethylaluminum) Selenide and Sodium Alkoxides 295

18.11.10.1.2.7 Variation 7: Nucleophilic Addition of N-Protected Amino Thiols to Isoselenocyanates 296

18.11.10.2 Selenosemicarbazides and Selenosemicarbazones 297

18.11.10.2.1 Method 1: Reaction of Isoselenocyanates with Hydrazine Derivatives ... 297

18.11.10.2.1.1 Variation 1: Reaction of Acyl Isoselenocyanates with Phenylhydrazine ... 297

18.11.10.2.1.2 Variation 2: Reaction of Trityl Isoselenocyanate with Hydrazine 298

18.11.10.2.2 Method 2: Reaction of Carbonyl Compounds with Selenosemicarbazides 299

Science of Synthesis Knowledge Updates 2013/2
© Georg Thieme Verlag KG

18.11.10.2.2.1 Variation 1: Reaction of Aldehydes with Selenosemicarbazides 299
18.11.10.2.2.2 Variation 2: Reaction of Cyclohexanone with Hydrazine Hydrate and Potassium Selenocyanate 300

18.11.10.3 Selenoureas 302

18.11.10.3.1 Method 1: Reaction of *N*,*N*-Dimethylselenocarbamoyl Chloride with Amines 302
18.11.10.3.2 Method 2: Reaction of Viehe's Salt with an Amine and Tetraethylammonium Tetraselenotungstate 303
18.11.10.3.3 Method 3: Reaction of Triethyl Orthoformate with Elemental Selenium and a Primary or Secondary Amine 303
18.11.10.3.4 Method 4: Reaction of N,N-Disubstituted Cyanamides with Sodium Selenide 305
18.11.10.3.5 Method 5: Reaction of Isoselenocyanates with an Amine 306
18.11.10.3.5.1 Variation 1: Reaction of Isoselenocyanates with Protected and Unprotected Glycosylamines 306
18.11.10.3.5.2 Variation 2: Reaction of Phenyl Isoselenocyanate with 2-Aminobenzonitriles 311
18.11.10.3.5.3 Variation 3: Reaction of Isoselenocyanates with Azetidinones under Basic Conditions 312
18.11.10.3.5.4 Variation 4: Reaction of 4-Isoselenocyanato-2,2,6,6-tetramethylpiperidin-1-oxyl with Amines 314
18.11.10.3.5.5 Variation 5: Reaction of Aryl Isoselenocyanates with Dimethylamine 316
18.11.10.3.5.6 Variation 6: Reaction of D-Glucosamine Hydrochloride or D-Mannosamine Hydrochloride with Aryl Isoselenocyanates 317
18.11.10.3.5.7 Variation 7: Reaction of Trityl Isoselenocyanate with a Primary Amine 319
18.11.10.3.5.8 Variation 8: Reaction of Isoselenocyanates Bearing Protected Amino Groups with Amines 319
18.11.10.3.6 Method 6: Reaction of Acyl Isoselenocyanates with Amines 321
18.11.10.3.6.1 Variation 1: Reaction of In Situ Generated Acyl Isoselenocyanates with Arylamines 321
18.11.10.3.6.2 Variation 2: Reaction of In Situ Generated Acyl Isoselenocyanates with Alkylamines 322
18.11.10.3.6.3 Variation 3: One-Pot Reaction of Aroyl Chlorides with Potassium Selenocyanate and Secondary Arylamines 322
18.11.10.3.7 Method 7: Selenation of Isocyanates with In Situ Generated Bis(dimethylaluminum) Selenide and Subsequent Treatment with Amines 323
18.11.10.3.8 Method 8: Reaction of Imidoyl Isoselenocyanates with Aromatic 2-Amino N-Heterocycles 325
18.11.10.3.9 Method 9: Reaction of 1-Methylimidazolium Salts with Selenium Powder and Potassium Carbonate 326

Science of Synthesis Knowledge Updates 2013/2
© Georg Thieme Verlag KG

Volume 31:
Arene—X (X = Hal, O, S, Se, Te, N, P)

31.42 **Product Class 42: Arylphosphines and Derivatives** 2013

M. Stankevič and K. M. Pietrusiewicz

31.42 **Product Class 42: Arylphosphines and Derivatives** 329

31.42.1 Synthesis of Product Class 42 329

31.42.1.1 Method 1: Synthesis by Nucleophilic Substitution at an Electrophilic Phosphorus Atom 329
31.42.1.1.1 Variation 1: Using Organometallic Reagents Prepared from Organic Halides 329
31.42.1.1.2 Variation 2: Using Carbanions Prepared by Reduction of Aryl—O Bonds 332
31.42.1.1.3 Variation 3: Using Carbanions Prepared by Halogen–Metal Exchange 332
31.42.1.1.4 Variation 4: Using Carbanions Prepared by Deprotonation of Acidic C—H Groups 334
31.42.1.1.5 Variation 5: Using Carbanions Prepared by Directed *ortho*-Metalation 336
31.42.1.1.6 Variation 6: Using Activated Silanes 338
31.42.1.1.7 Variation 7: By Miscellaneous Methods 338
31.42.1.2 Method 2: Synthesis by Nucleophilic Substitution with Phosphorus Nucleophiles 339
31.42.1.2.1 Variation 1: Using Phosphorus Nucleophiles Generated by Deprotonation of P—H Bonds 339
31.42.1.2.2 Variation 2: Using Phosphorus Nucleophiles Generated by Reduction of P—X Bonds (X = Halogen) 341
31.42.1.2.3 Variation 3: Using Phosphorus Nucleophiles Generated by Reduction of Aryl—P Bonds 342
31.42.1.2.4 Variation 4: Using Neutral Phosphorus Nucleophiles in the Absence of Base 343
31.42.1.2.5 Variation 5: Using Silylphosphines 344
31.42.1.3 Method 3: Synthesis by Transition-Metal-Catalyzed Coupling Reactions 344
31.42.1.3.1 Variation 1: Reactions Catalyzed by Palladium Complexes 345
31.42.1.3.2 Variation 2: Reactions Catalyzed by Nickel Complexes 347
31.42.1.3.3 Variation 3: Reactions Catalyzed by Copper Complexes 349
31.42.1.3.4 Variation 4: Reactions Catalyzed by Other Transition-Metal Complexes 349
31.42.1.4 Method 4: Synthesis by Addition to Multiple Bonds 349
31.42.1.4.1 Variation 1: Reactions Involving Uncatalyzed Addition 350
31.42.1.4.2 Variation 2: Addition Reactions Mediated by Radical Initiators 351
31.42.1.4.3 Variation 3: Addition Reactions Catalyzed by Transition-Metal Complexes 352
31.42.1.4.4 Variation 4: Addition to Conjugated Alkenes 353
31.42.1.4.5 Variation 5: Addition to Carbonyl or Imino Groups 355
31.42.1.5 Method 5: Synthesis by Decomplexation of Metal–Phosphine Complexes 357
31.42.1.6 Method 6: Synthesis by Deprotection of Arylphosphine–Borane Complexes 359
31.42.1.7 Method 7: Synthesis by Reduction of Arylphosphine Sulfides 360
31.42.1.7.1 Variation 1: Using Raney Nickel 361

Science of Synthesis Knowledge Updates 2013/2
© Georg Thieme Verlag KG

31.42.1.7.2 Variation 2: Using Radical Reagents 362
31.42.1.7.3 Variation 3: Using Phosphorus(III) Compounds 362
31.42.1.8 Method 8: Synthesis by Reduction of Arylphosphine Oxides 363
31.42.1.8.1 Variation 1: Using Silanes 364
31.42.1.8.2 Variation 2: Using Aluminum Hydrides 366
31.42.1.8.3 Variation 3: Using Titanium Complexes as Catalysts 369
31.42.1.8.4 Variation 4: Using Boranes 370
31.42.1.9 Method 9: Synthesis by Modification of a Parent Arylphosphine 371
31.42.1.9.1 Variation 1: Modification of a Functional Group 371
31.42.1.9.2 Variation 2: Modification of the Carbon Skeleton 374

31.42.2 Applications of Product Class 42 in Organic Synthesis 375

Volume 39:
Sulfur, Selenium, and Tellurium

39.18 **Product Class 18: Alkaneselenols**

39.18.2 **Alkaneselenols** 2013

C. Santi

39.18.2 **Alkaneselenols** 391

39.18.2.1 Synthesis of Alkaneselenols 391

39.18.2.1.1 Method 1: Reaction of Alkylating Agents with Alkali Metal Selenides 391
39.18.2.1.2 Method 2: Reduction of Dialkyl Diselenides and Alkyl Selenocyanates 392
39.18.2.1.2.1 Variation 1: Reduction of Dialkyl Diselenides Mediated by Trialkyltin Hydrides: A Radical Route 393
39.18.2.1.2.2 Variation 2: Reduction of Dialkyl Diselenides with Hydrides 394
39.18.2.1.2.3 Variation 3: Reduction of Dialkyl Diselenides with Zinc under Biphasic Conditions 394
39.18.2.1.2.4 Variation 4: Reduction of Selenocyanates 395
39.18.2.1.3 Method 3: Reduction of Elemental Selenium with Alkyl Grignard or Alkyllithium Compounds Followed by Protonation 397

39.18.2.2 Applications of Alkaneselenols in Organic Synthesis 397

39.18.2.2.1 Method 1: Oxidation: Synthesis of Diselenides 397
39.18.2.2.2 Method 2: Reaction with Alkyl and Aryl Halides 398
39.18.2.2.3 Method 3: Nucleophilic Substitution of Alcohols and Enol Ethers 399
39.18.2.2.4 Method 4: Synthesis of Diselenoacetals 401
39.18.2.2.4.1 Variation 1: Diselenoacetal Formation Using Selenols and Protic Acids 401
39.18.2.2.4.2 Variation 2: Diselenoacetal Formation Using Selenols and Lewis Acids 402
39.18.2.2.5 Method 5: Michael-Type Addition Reactions 403

Science of Synthesis Knowledge Updates 2013/2
© Georg Thieme Verlag KG

39.19 Product Class 19: Acyclic Alkaneselenolates

39.19.1.2 Alkaneselenolates of Group 1, 2, and 13–15 Metals 2013

C. Santi

39.19.1.2 **Alkaneselenolates of Group 1, 2, and 13–15 Metals** 407
39.19.1.2.1 Arsenic Alkaneselenolates 407
39.19.1.2.1.1 Method 1: Reaction of a 2-Arsapropene with Methaneselenol 407
39.19.1.2.2 Silicon Alkaneselenolates 407
39.19.1.2.2.1 Method 1: Reaction of a Lithium Silaneselenolate with an Alkyl Halide 408
39.19.1.2.3 Germanium Alkaneselenolates 409
39.19.1.2.3.1 Method 1: Reaction of Selenols with Halogermanes 409
39.19.1.2.4 Tin Alkaneselenolates 410
39.19.1.2.4.1 Method 1: Reaction of Alkaneselenolates Generated In Situ with Chlorostannanes 410
39.19.1.2.5 Lead Alkaneselenolates 410
39.19.1.2.5.1 Method 1: Reaction of Sodium Selenolates with Lead(II) Acetate 411
39.19.1.2.6 Boron Alkaneselenolates 411
39.19.1.2.6.1 Method 1: Reaction of a Lithium Trihydroborate with Titanocene Pentaselenide 411
39.19.1.2.7 Aluminum Alkaneselenolates 412
39.19.1.2.8 Indium Alkaneselenolates 412
39.19.1.2.8.1 Method 1: Reaction of Indium(I) Iodide with Diselenides 413
39.19.1.2.9 Magnesium Alkaneselenolates 413
39.19.1.2.9.1 Method 1: Reaction of Grignard Reagents with Elemental Selenium 413
39.19.1.2.10 Lithium Alkaneselenolates 414
39.19.1.2.10.1 Synthesis of Lithium Alkaneselenolates 414
39.19.1.2.10.1.1 Method 1: Reduction of Dialkyl Diselenides 414
39.19.1.2.10.1.2 Method 2: Insertion of Elemental Selenium into a C—Li Bond 415
39.19.1.2.10.1.3 Method 3: Reaction of Lithium Enolates with Elemental Selenium 416
39.19.1.2.10.2 Applications of Lithium Alkaneselenolates in Organic Synthesis 416
39.19.1.2.10.2.1 Method 1: Nucleophilic Substitution of Leaving Groups 416
39.19.1.2.10.2.2 Method 2: Hydroselenation of Alkynes 418
39.19.1.2.11 Sodium Alkaneselenolates 419
39.19.1.2.11.1 Synthesis of Sodium Alkaneselenolates 419
39.19.1.2.11.1.1 Method 1: Deprotonation of Selenols 419
39.19.1.2.11.1.2 Method 2: Reduction of Diselenides and Selenocyanates 419
39.19.1.2.11.2 Applications of Sodium Alkaneselenolates in Organic Synthesis 420
39.19.1.2.11.2.1 Method 1: Nucleophilic Substitution of Leaving Groups 420

Science of Synthesis Knowledge Updates 2013/2
© Georg Thieme Verlag KG

39.19.1.2.11.2.2 Method 2: Ring Opening of Cyclopropanes 421
39.19.1.2.12 Potassium Alkaneselenolates 421
39.19.1.2.12.1 Method 1: Reduction of Dialkyl Diselenides Using Hydrazine Hydrate and Potassium Hydroxide 422
39.19.1.2.13 Cesium Alkaneselenolates 422
39.19.1.2.13.1 Method 1: Reaction of Acyl Selenides with Cesium Carbonate and Amines 422

Volume 40: Amines, Ammonium Salts, Amine *N*-Oxides, Haloamines, Hydroxylamines and Sulfur Analogues, and Hydrazines

---

40.1 Product Class 1: Amino Compounds

40.1.1.5.4.5 Substitution on the Amine Nitrogen (2013)

P. J. Scammells

40.1.1.5.4.5 **Substitution on the Amine Nitrogen** 427
40.1.1.5.4.5.1 Dealkylation Reactions of Amines 427
40.1.1.5.4.5.1.1 Method 1: The von Braun Reaction with Cyanogen Bromide 427
40.1.1.5.4.5.1.2 Method 2: Photolytic Dealkylation 429
40.1.1.5.4.5.1.3 Method 3: Reductive Cleavage of the C—N Bond 434
40.1.1.5.4.5.1.4 Method 4: Sequential N-Demethylation–N-Acylation with Palladium(II) Acetate and Acetic Anhydride 436
40.1.1.5.4.5.1.5 Method 5: Cleavage of the C—N Bond Using Solid-Supported Reagents . 438
40.1.1.5.4.5.1.6 Method 6: The Polonovski Reaction 440
40.1.1.5.4.5.1.7 Method 7: Reaction with Dialkyl Azodicarboxylates 444
40.1.1.5.4.5.2 Replacement of Oxygen Functionalities 444
40.1.1.5.4.5.2.1 Method 1: Reactions of Ammonia with Alcoholic Hydroxy Groups 445
40.1.1.5.4.5.2.2 Method 2: Reactions of Primary or Secondary Amines with Alcoholic Hydroxy Groups 448
40.1.1.5.4.5.2.3 Method 3: Direct Amination with Sulfonamides 454
40.1.1.5.4.5.3 Replacement of Nitrogen Functionalities 455
40.1.1.5.4.5.3.1 Method 1: Condensation of Primary Amines 456

Author Index 463

Abbreviations 493

Science of Synthesis Knowledge Updates 2013/2
© Georg Thieme Verlag KG