## Contents

1  Oxidative Coupling – Bonding between Two Nucleophiles  1
  1.1  Introduction/General  1
  1.1.1  What is Oxidative Cross-Coupling?  1
  1.1.2  Why Oxidative Cross-Coupling?  1
  1.1.3  How Does Oxidative Cross-Coupling Work?  3
  1.1.4  Development and Outlook  4
  References  4

2  Organometals as Nucleophiles  7
  2.1  Classification and Applications of Organometallic Reagents  7
  2.2  Csp-M and Csp-M as Nucleophiles  8
  2.2.1  Alkyne–Alkyne Oxidative Coupling  9
  2.2.1.1  Alkynyl-Si  11
  2.2.1.2  Alkynyl-Sn  12
  2.2.1.3  Alkynyl-B  14
  2.2.1.4  Alkynyl-Mg  17
  2.2.1.5  Alkynyl-Te  19
  2.2.2  Alkyne–Cyano Oxidative Coupling  22
  2.3  Csp–M and Csp²–M as Nucleophiles  22
  2.4  Csp–M and Csp³–M as Nucleophiles  28
  2.5  Csp²–M and Csp²–M as Nucleophiles  30
  2.5.1  Homocoupling of Csp²–M  30
  2.5.2  Cross-Coupling between Different Species of Csp²–M  32
  2.6  Csp³–M and Csp³–M as Nucleophiles  34
  2.7  Csp³–M and Csp³–M as Nucleophiles  37
  2.8  Conclusions  40
  Acknowledgments  41
  References  42
3 Oxidative Couplings Involving the Cleavage of C–H Bonds 45

3.1 Theoretical Understandings and Methods in C–H Bond Functionalization 45

3.1.1 Introduction 45

3.1.2 Mechanisms of C–H Cleavage by Transition Metals 47

3.1.2.1 Oxidative Addition 49

3.1.2.2 Electrophilic Substitution 49

3.1.2.3 σ-Bond Metathesis 52

3.1.2.4 Concerted Metalation Deprotonation (CMD) 52

3.1.2.5 1,2-Addition 55

3.1.2.6 Biomimetic C–H Oxidation 55

3.1.2.7 Carbenoid/Nitrenoid C–H Insertion 56

3.1.3 Methods for Selective C–H Bond Functionalization 58

3.1.3.1 Directed C–H Functionalization 58

3.1.3.2 Sterically Controlled C–H Functionalization 63

3.1.3.3 C–H Functionalization via Ionic Intermediates 63

3.1.3.4 C–H Functionalization via Radical Intermediates 67

3.2 Oxidative Couplings between Organometals and Hydrocarbons 71

3.2.1 C(sp)–H and Organometals as Nucleophiles 71

3.2.2 C(sp²)–H and Organometals as Nucleophiles 73

3.2.3 C(sp³)–H and Organometals as Nucleophiles 93

3.3 Oxidative Couplings between Two Hydrocarbons 95

3.3.1 C(sp)–H and C(sp)–H as Nucleophiles 95

3.3.2 C(sp)–H and C(sp²)–H as Nucleophiles 99

3.3.3 C(sp)–H and C(sp³)–H as Nucleophiles 105

3.3.4 C(sp²)–H and C(sp³)–H as Nucleophiles 106

3.3.4.1 Oxidative Coupling between Directing-Group-Containing Arenes and Unactivated Arenes 107

3.3.4.2 Oxidative Coupling of Arenes without Directing Groups 109

3.3.4.3 Intramolecular Oxidative Coupling of Unactivated Arenes 110

3.3.4.4 Oxidative Heck-Type Cross-Coupling 114

3.3.5 C(sp²)–H and C(sp³)–H as Nucleophiles 123

3.3.5.1 Intramolecular Oxidative Coupling between Aromatic C(sp²)–H and C(sp³)–H 123

3.3.5.2 Intramolecular Oxidative Coupling between Alkene C(sp²)–H and C(sp³)–H 125

3.3.5.3 Intermolecular Oxidative Coupling between C(sp²)–H and C(sp³)–H 127

3.3.6 C(sp³)–H and C(sp³)–H as Nucleophiles 128

3.4 Conclusions 130

4 Bonding Including Heteroatoms via Oxidative Coupling 139

4.1 Introduction 139

4.2 Oxidative C–O Bond Formation 140
4.2.1 C–H and O–M as Nucleophiles 140
4.2.2 C–H and O–H as Nucleophiles 140
4.2.2.1 C(sp², Aryl)–O Bond Formation 140
4.2.2.2 C(sp², Heteroaryl, Alkenyl)–O Bond Formation 144
4.2.2.3 C(sp³, Benzyl)–O Bond Formation 145
4.2.2.4 C(sp³, Alkanes with Directing Group)–O Bond Formation 145
4.2.2.5 C(sp³, Ethers, Amines, Amides, Alkanes)–O Bond Formation 148
4.2.2.6 C(sp³, allyl)–O Bond Formation 148
4.3 Oxidative C–N Bond Formation 152
4.3.1 C(sp)–N Bond Formation 152
4.3.2 C(sp², Arenes with Directing Group)–N Bond Formation 153
4.3.3 C(sp², Simple Arenes)–N Bond Formation 156
4.3.4 C(sp², Heteroaryl)–N Bond Formation 156
4.3.5 C(sp², Alkenyl)–N Bond Formation 159
4.3.6 C(sp³, Alkyl)–N Bond Formation 163
4.3.7 C(sp³, Allyl)–N Bond Formation 164
4.4 Oxidative C–Halo Bond Formation 166
4.4.1 C–H and Halo–H as Nucleophiles 167
4.4.2 C–H and Halo–M as Nucleophiles 168
4.5 Oxidative C–S Bond Formation 170
4.5.1 C(sp²)–S Bond Formation 170
4.5.2 C(sp)–S Bond Formation 171
4.6 Oxidative C–P Bond Formation 172
4.6.1 C(sp², Aryl)–P Bond Formation 172
4.6.2 C(sp², Heteroaryl)–P Bond Formation 173
4.6.3 C(sp², Alkenyl)–P Bond Formation 176
4.6.4 C(sp)–P Bond Formation 176
4.6.5 C(sp³)–P Bond Formation 176
4.7 Oxidative C–B Bond Formation 177

References 178

5 Oxidative Radical Couplings 185
5.1 Introduction 185
5.2 Oxidative Radical C–C Couplings 185
5.2.1 Coupling of Csp³–H with Csp–H Bonds 185
5.2.2 Coupling of Csp³–H with Csp²–H Bonds 187
5.2.3 Coupling of Csp³–H with Csp³–H Bonds 200
5.2.4 Coupling of Csp²–H with Csp²–H Bonds 204
5.3 Oxidative Radical C–C Couplings through Cascade Process 208
5.4 Oxidative Radical C–C Couplings via C–C(N) Bond Cleavage 217
References 222

Index 225