

POSTGRADUATE CHEMISTRY SERIES

**Organic
Synthesis
using
Transition
Metals**

Rod Bates

Contents

1	Introduction	1
1.1	Structures and mechanisms	2
1.2	The eighteen electron rule and oxidation state	4
1.3	The reactions	5
1.4	Handling	8
	References	8
2	Coupling reactions	9
2.1	Introduction	9
2.2	Lithium and magnesium	12
2.3	Zinc: the Negishi reaction	12
2.4	Aluminium and zirconium	14
2.5	Tin: the Stille reaction	14
	2.5.1 Macrocyclization using the Stille reaction	17
	2.5.2 Stille reaction troubleshooting	18
2.6	Boron: the Suzuki reaction	19
2.7	Copper	24
	2.7.1 The Sonogashira reaction	24
2.8	Choosing the right coupling reaction	26
2.9	Coupling of enolates	28
2.10	Coupling with aromatic hydrocarbons	29
2.11	Homocoupling	30
2.12	Heteroatom coupling reactions	32
	References	34
3	Carbonylation	38
3.1	Carbonylative coupling reactions	38
3.2	Carbonylation of alkenes	42
3.3	Carbonylation using iron and cobalt acyl complexes	43
3.4	η^3 -Allyl carbonyl complexes	46
3.5	Decarbonylation reactions	49
	References	50
4	Alkene and alkyne insertion reactions	53
4.1	The Heck reaction	53
	4.1.1 Catalysts	54
	4.1.2 Leaving groups	56
	4.1.3 The organic halide	58
	4.1.4 The alkene	59

4.1.5	The intramolecular Heck reaction	61
4.1.6	Domino reactions	63
4.1.7	Synthesis of alkanes	67
4.2	Insertion reactions involving zirconium and titanium	67
4.2.1	Zirconium hydrides	67
4.2.2	Alkene and alkyne complexes	68
	References	72
5	Electrophilic alkene complexes	75
5.1	Electrophilic palladium alkene complexes	75
5.1.1	Oxygen nucleophiles	75
5.1.2	Nitrogen nucleophiles	79
5.1.3	Carbon nucleophiles	80
5.1.4	Electrophilic alkyne and allene complexes	82
5.2	Electrophilic iron complexes	86
5.2.1	Fp complexes of alkynes	91
5.2.2	Alkylation of allyl Fp complexes and formal cycloadditions	91
5.3	Cobaloxime π -cations	92
	References	93
6	Reactions of alkyne complexes	96
6.1	Alkyne cobalt complexes	96
6.1.1	Propargyl cations: the Nicholas reaction	98
6.1.2	The Pauson–Khand reaction	100
6.1.3	Syntheses using multiple cobalt reactions	102
	References	103
7	Carbene complex chemistry	105
7.1	Chromium carbenes	105
7.1.1	The Dötz Reaction	107
7.1.2	Chromium carbene photochemistry	110
7.2	Vinylidene and carbyne complexes	112
7.3	Tebbe's reagent	116
7.4	Alkene metathesis	118
7.5	Rhodium catalysed carbene reactions	125
	References	128
8	π-Allyl complexes	131
8.1	η^3 -Allyl palladium complexes	131
8.1.1	Regioselectivity	133
8.1.2	Internal versus terminal attack	135
8.1.3	Stereoselectivity	136
8.1.4	Syntheses using palladium catalysed allylation	139
8.1.5	Other routes to π -allyl palladium complexes	141
8.1.6	Propargyl compounds	143
8.2	Electrophilic π -allyl complexes of other metals	143
	References	146

9 Diene, dienyl and arene complexes	148
9.1 η^4 -Diene complexes	149
9.2 η^3 -Dienyl complexes	153
9.3 η^6 -Arene complexes of chromium and other metals	156
9.4 η^2 -Arene complexes	160
References	162
10 Cycloisomerization and formal cycloaddition reactions	164
10.1 Formal six electron, six atom cycloadditions	164
10.2 Cycloadditions involving fewer than six atoms	167
10.3 Cycloadditions involving more than six atoms	170
10.3.1 The [5 + 2] cycloaddition	170
10.3.2 The [4 + 4] cycloaddition	171
10.3.3 The [6 + 2] and [6 + 4] cycloadditions	172
10.4 Cycloisomerization and related reactions	174
10.4.1 Diene-ene cycloisomerizations	178
References	179
Abbreviations	182
Index of transition metal catalysts and reagents	183
Index	185