

Homogeneous Catalysis

Understanding the Art

by

Piet W.N.M. van Leeuwen

*University of Amsterdam,
Amsterdam, The Netherlands*



KLUWER ACADEMIC PUBLISHERS

DORDRECHT / BOSTON / LONDON

Table of contents

Preface	xi
Acknowledgements	xiii
1. INTRODUCTION	1
1.1 CATALYSIS	1
1.2 HOMOGENEOUS CATALYSIS	6
1.3 HISTORICAL NOTES ON HOMOGENEOUS CATALYSIS	7
1.4 CHARACTERISATION OF THE CATALYST	8
1.5 LIGAND EFFECTS	10
1.5.1 Phosphines and phosphites: electronic effects	10
1.5.2 Phosphines and phosphites: steric effects	12
1.5.3 Linear Free Energy Relationships	14
1.5.4 Phosphines and phosphites: bite angle effects	16
1.6 LIGANDS ACCORDING TO DONOR ATOMS	20
1.6.1 Anionic and neutral hydrocarbyl groups	20
1.6.2 Alkoxy and imido groups as anionic ligands	21
1.6.3 Amines, imines, oxazolines and related ligands	21
1.6.4 Phosphines, phosphites, phosphorus amides, phospholes and related ligands	23
1.6.5 Carbenes, carbon monoxide	24
1.6.6 Common anions	25

2.	ELEMENTARY STEPS	29
2.1	CREATION OF A "VACANT" SITE AND CO-ORDINATION OF THE SUBSTRATE	29
2.2	INSERTION VERSUS MIGRATION	30
2.3	β -ELIMINATION AND DE-INSERTION	35
2.4	OXIDATIVE ADDITION	36
2.5	REDUCTIVE ELIMINATION	39
2.6	α -ELIMINATION REACTIONS	41
2.7	CYCLOADDITION REACTIONS INVOLVING A METAL	42
2.8	ACTIVATION OF A SUBSTRATE TOWARD NUCLEOPHILIC ATTACK	44
2.8.1	Alkenes	44
2.8.2	Alkynes	45
2.8.3	Carbon monoxide	45
2.8.4	Other substrates	46
2.9	σ -BOND METATHESIS	48
2.10	DIHYDROGEN ACTIVATION	48
2.11	ACTIVATION BY LEWIS ACIDS	50
2.11.1	Diels-Alder additions	51
2.11.2	Epoxidation	51
2.11.3	Ester condensation	52
2.12	CARBON-TO-PHOSPHORUS BOND BREAKING	52
2.13	CARBON-TO-SULFUR BOND BREAKING	55
2.14	RADICAL REACTIONS	57
3.	KINETICS	63
3.1	INTRODUCTION	63
3.2	TWO-STEP REACTION SCHEME	63
3.3	SIMPLIFICATIONS OF THE RATE EQUATION AND THE RATE-DETERMINING STEP	64
3.4	DETERMINING THE SELECTIVITY	68
3.5	COLLECTION OF RATE DATA	71
3.6	IRREGULARITIES IN CATALYSIS	72
4.	HYDROGENATION	75
4.1	WILKINSON'S CATALYST	75
4.2	ASYMMETRIC HYDROGENATION	77
4.2.1	Introduction	77
4.2.2	Cinnamic acid derivatives	79
4.2.3	Chloride versus weakly coordinating anions; alkylphosphines versus arylphosphines	86
4.2.4	Incubation times	86

4.3	OVERVIEW OF CHIRAL BIDENTATE LIGANDS	86
4.3.1	DuPHOS	86
4.3.2	BINAP catalysis	87
4.3.3	Chiral ferrocene based ligands	89
4.4	MONODENTATE LIGANDS	90
4.5	NON-LINEAR EFFECTS	93
4.6	HYDROGEN TRANSFER	94
5.	ISOMERISATION	101
5.1	HYDROGEN SHIFTS	101
5.2	ASYMMETRIC ISOMERISATION	103
5.3	OXYGEN SHIFTS	105
6.	CARBONYLATION OF METHANOL AND METHYL ACETATE	109
6.1	ACETIC ACID	109
6.2	PROCESS SCHEME MONSANTO PROCESS	114
6.3	ACETIC ANHYDRIDE	116
6.4	OTHER SYSTEMS	118
6.4.1	Higher alcohols	118
6.4.2	Phosphine-modified rhodium catalysts	119
6.4.3	Other metals	122
7.	COBALT CATALYSED HYDROFORMYLATION	125
7.1	INTRODUCTION	125
7.2	THERMODYNAMICS	126
7.3	COBALT CATALYSED PROCESSES	126
7.4	COBALT CATALYSED PROCESSES FOR HIGHER ALKENES	128
7.5	KUHLMANN COBALT HYDROFORMYLATION PROCESS	130
7.6	PHOSPHINE MODIFIED COBALT CATALYSTS: THE SHELL PROCESS	131
7.7	COBALT CARBONYL PHOSPHINE COMPLEXES	132
7.7.1	Carbonyl species	132
7.7.2	Phosphine derivatives	135
8.	RHODIUM CATALYSED HYDROFORMYLATION	139
8.1	INTRODUCTION	139
8.2	TRIPHENYLPHOSPHINE AS THE LIGAND	141
8.2.1	The mechanism	141
8.2.2	Ligand effects and kinetics	144
8.2.3	Regioselectivity	147
8.2.4	Process description, rhodium-tpp	149
8.2.5	Two-phase process, tppts: Ruhrchemie/Rhône-Poulenc	150
8.2.6	One-phase catalysis, two-phase separation	152

8.3	DIPHOSPHINES AS LIGANDS	153
8.3.1	Xantphos ligands: tuneable bite angles	155
8.4	PHOSPHITES AS LIGANDS	161
8.4.1	Electronic effects	161
8.4.2	Phosphites: steric effects	162
8.5	DIPHOSPHITES	163
8.6	ASYMMETRIC HYDROFORMYLATION	166
8.6.1	Rhodium catalysts: diphosphites	166
8.6.2	Rhodium catalysts: phosphine-phosphite ligands	168
9.	ALKENE OLIGOMERISATION	175
9.1	INTRODUCTION	175
9.2	SHELL-HIGHER-OLEFINS-PROCESS	176
9.2.1	Oligomerisation	176
9.2.2	Separation	180
9.2.3	Purification, isomerisation, and metathesis	180
9.2.4	New catalysts	181
9.3	ETHENE TRIMERISATION	184
9.4	OTHER ALKENE OLIGOMERISATION REACTIONS	187
10.	PROPENE POLYMERISATION	191
10.1	INTRODUCTION TO POLYMER CHEMISTRY	191
10.1.1	Introduction to Ziegler Natta polymerisation	193
10.1.2	History of homogeneous catalysts	196
10.2	MECHANISTIC INVESTIGATIONS	199
10.2.1	Chain-end control: syndiotactic polymers	199
10.2.2	Chain-end control: isotactic polymers	201
10.3	ANALYSIS BY ^{13}C NMR SPECTROSCOPY	202
10.3.1	Introduction	202
10.3.2	Chain-end control	204
10.3.3	Site control mechanism	204
10.4	THE DEVELOPMENT OF METALLOCENE CATALYSTS	206
10.4.1	Site control: isotactic polymers	206
10.4.2	Site control: syndiotactic polymers	209
10.4.3	Double stereoselection: chain-end and site control	211
10.5	AGOSTIC INTERACTIONS	212
10.6	THE EFFECT OF DIHYDROGEN	214
10.7	FURTHER WORK USING PROPENE AND OTHER ALKENES	215
10.8	NON-METALLOCENE ETM CATALYSTS	220
10.9	LATE TRANSITION METAL CATALYSTS	222

11. HYDROCYANATION OF ALKENES	229
11.1 THE ADIPONITRILE PROCESS	229
11.2 LIGAND EFFECTS	233
12. PALLADIUM CATALYSED CARBONYLATIONS OF ALKENES	239
12.1 INTRODUCTION	239
12.2 POLYKETONE	239
12.2.1 Background and history	239
12.2.2 Elementary steps: initiation	241
12.2.3 Elementary steps: migration reactions	244
12.2.4 Elementary steps: chain termination, chain transfer	250
12.2.5 Elementary steps: ester formation as chain termination	252
12.3 LIGAND EFFECTS ON CHAIN LENGTH	256
12.3.1 Polymers	256
12.3.2 Ligand effects on chain length: Propanoate	258
12.3.3 Ligand effects on chain length: Oligomers	261
12.4 ETHENE/PROPENE/CO TERPOLYMERS	262
12.5 STEREOSELECTIVE STYRENE/CO COPOLYMERS	263
13. PALLADIUM CATALYSED CROSS-COUPLING REACTIONS	271
13.1 INTRODUCTION	271
13.2 ALLYLIC ALKYLATION	273
13.3 HECK REACTION	281
13.4 CROSS-COUPLING REACTION	286
13.5 HETEROATOM-CARBON BOND FORMATION	290
13.6 SUZUKI REACTION	294
14. EPOXIDATION	299
14.1 ETHENE AND PROPENE OXIDE	299
14.2 ASYMMETRIC EPOXIDATION	301
14.2.1 Introduction	301
14.2.2 Katsuki-Sharpless asymmetric epoxidation	301
14.2.3 The Jacobsen asymmetric epoxidation	305
14.3 ASYMMETRIC HYDROXYLATION OF ALKENES WITH OSMIUM TETROXIDE	308
14.3.1 Stoichiometric reactions	308
14.3.2 Catalytic reactions	312
14.4 JACOBSEN ASYMMETRIC RING-OPENING OF EPOXIDES	314
14.5 EPOXIDATIONS WITH DIOXYGEN	316

15. OXIDATION WITH DIOXYGEN	319
15.1 INTRODUCTION	319
15.2 THE WACKER REACTION	320
15.3 WACKER TYPE REACTIONS	324
15.4 TEREPHTHALIC ACID	327
15.5 PPO	332
16. ALKENE METATHESIS	337
16.1 INTRODUCTION	337
16.2 THE MECHANISM	339
16.3 REACTION OVERVIEW	343
16.4 WELL-CHARACTERISED TUNGSTEN AND MOLYBDENUM CATALYSTS	344
16.5 RUTHENIUM CATALYSTS	346
16.6 STEREOCHEMISTRY	349
16.7 CATALYST DECOMPOSITION	350
16.8 ALKYNES	352
16.9 INDUSTRIAL APPLICATIONS	354
17. ENANTIOSELECTIVE CYCLOPROPANATION	359
17.1 INTRODUCTION	359
17.2 COPPER CATALYSTS	360
17.3 RHODIUM CATALYSTS	364
17.3.1 Introduction	364
17.3.2 Examples of rhodium catalysts	367
18. HYDROSILYLATION	371
18.1 INTRODUCTION	371
18.2 PLATINUM CATALYSTS	373
18.3 ASYMMETRIC PALLADIUM CATALYSTS	378
18.4 RHODIUM CATALYSTS FOR ASYMMETRIC KETONE REDUCTION	380
19. C-H FUNCTIONALISATION	387
19.1 INTRODUCTION	387
19.2 ELECTRON-RICH METALS	389
19.3 HYDROGEN TRANSFER REACTIONS OF ALKANES	394
19.4 BORYLATION OF ALKANES	395
19.5 THE MURAI REACTION	396
19.6 CATALYTIC σ -BOND METATHESIS	397
19.7 ELECTROPHILIC CATALYSTS	397
SUBJECT INDEX	403