An Introduction to Organometallic Chemistry

An Introduction to Organometallic Chemistry

A. W. Parkins and R. C. Poller
King's College London

M
MACMILLAN

© A. W. Parkins and R. C. Poller 1986

All rights reserved. No reproduction, copy or transmission of this publication may be made without written permission.

No paragraph of this publication may be reproduced, copied or transmitted save with written permission or in accordance with the provisions of the Copyright Act 1956 (as amended).

Any person who does any unauthorised act in relation to this publication may be liable to criminal prosecution and civil claims for damages.

First published 1986

Published by
Higher and Further Education Division
MACMILLAN PUBLISHERS LTD
Houndmills, Basingstoke, Hampshire RG21 2XS
and London
Companies and representatives
throughout the world

British Library Cataloguing in Publication Data
Parkins, A. W.

An introduction to organometallic chemistry.

1. Organometallic compounds

I. Title II. Poller, R. C.

547'.05 QD411

ISBN 978-0-333-36433-8 ISBN 978-1-349-18198-8 (eBook)

DOI 10.1007/978-1-349-18198-8

CONTENTS

<i>Preface</i>	x
<i>Abbreviations Used</i>	xi
1 Introduction	1
1.1 Scope	1
1.2 History	1
1.3 Nomenclature	3
1.4 Conventions	5
1.4.1 The eighteen electron rule	5
1.4.2 Periodic table	6
1.4.3 Additions to alkenes and Markownikoff's rule	6
1.5 Literature	7
1.5.1 Textbooks	7
1.5.2 Reviews and journals	9
References	10
General reading	10
2 Preparation of Organometallic Compounds	11
2.1 The direct reaction: starting with the metal	12
2.1.1 Mechanistic considerations	14
2.2 Starting with organometallic reagents	18
2.2.1 Reaction of organometallic reagents with metal halides	18
2.2.2 Reaction of organometallic reagents with metal compounds or free metals	21
2.2.3 Reaction of organometallic reagents with organic halides	22
2.2.4 Reaction of organometallic reagents with unsaturated compounds	23
2.3 Metallation: direct replacement of hydrogen by a metal	25
2.4 Starting with alkenes, alkynes or arenes	28
2.4.1 Simple additions	29
2.4.2 Preparation of π -bonded compounds	31
2.5 Electrochemical methods	35
2.5.1 Cathodic processes	35
2.5.2 Anodic processes	36

2.6	Miscellaneous methods	37
	References	39
	General reading	41
3	Structure and Bonding in Organometallic Compounds	42
3.1	σ -bonded compounds	42
3.1.1	Group I derivatives	43
3.1.2	Group II derivatives	45
3.1.3	Group III derivatives	46
3.1.4	Group IV derivatives	48
3.1.5	Group V derivatives	49
3.1.6	Group VI derivatives	50
3.1.7	Group VII derivatives	51
3.1.8	Group VIII derivatives	52
3.2	Carbene and carbyne complexes	52
3.3	π -complexes	54
3.3.1	Mono-alkene (olefin) complexes	56
3.3.2	Alkyne complexes	58
3.3.3	Complexes of conjugated dienes	59
3.3.4	η^3 -Allyl complexes (π -allyl complexes)	61
3.3.5	η^5 -Cyclopentadienyl complexes	63
3.3.6	η^6 -Arene complexes	69
3.3.7	Cyclooctatetraene complexes	71
3.4	Dynamic behaviour of organometallic compounds in solution	72
3.4.1	η^1 -Cyclopentadienyl compounds	72
3.4.2	Mono-alkene complexes	73
3.4.3	Polyene and arene π -complexes	73
3.4.4	Allyl derivatives	74
3.5	Thermochemistry of organometallic compounds	75
	References	76
	General reading	79
4	Organometallic Compounds as Sources of Carbanions	80
4.1	Generation and stability of carbanions	81
4.2	Electrophilic substitution at carbon	84
4.3	Carbanions as nucleophilic reagents	90
4.4	Metallation and determination of acid strengths	94
	References	96
	General reading	97
5	Reactions of Organic Groups Bonded to Metals in Which the Metal-Carbon Bond is Retained	98
5.1	σ -bonded compounds	98
5.1.1	Main group compounds with saturated organic groups	100

CONTENTS

vii

5.1.2	Main group compounds with unsaturated organic groups	101
5.1.3	Main group compounds with aryl groups	103
5.2	π -bonded complexes	104
5.2.1	Ferrocene	104
5.2.2	η^5 -Cyclopentadienyl complexes other than ferrocene	108
5.2.3	η^6 -Arene complexes	111
5.2.4	Tricarbonyl(diene)iron complexes	114
5.2.5	Diene complexes of palladium and platinum	115
5.2.6	Generalisations concerning nucleophilic addition to π -complexes	116
	References	116
	General reading	118
6	The Coordination Chemistry of Organometallic Compounds	119
6.1	General survey	119
6.2	Effects on structure	121
6.2.1	Auto-complexation	122
6.2.2	Adducts of organometallic compounds	123
6.3	Effects on reactivity	124
6.3.1	Oxidative addition and reductive elimination	124
6.3.2	Migratory insertion reactions	127
6.3.3	Effects on electrophilic substitutions	129
6.3.4	Reactions proceeding by charge- and electron-transfer mechanisms	130
6.3.5	Homolytic reactions	133
	References	134
	General reading	135
7	Carbene Chemistry and Organometallic Compounds	136
7.1	Carbene complexes derived from metal carbonyls	137
7.2	Routes to heterocarbene complexes not involving metal carbonyls	139
7.3	Reactions of heterocarbene complexes	142
7.4	Conversion of heterocarbene complexes to carbyne complexes	146
7.5	Carbene complexes formed by α -hydrogen abstraction (alkylidene complexes)	146
7.6	Reactions of high oxidation state alkylidene and alkylidyne complexes	148
7.7	Carbene complexes as intermediates in olefin metathesis	150
7.8	The Fischer-Tropsch synthesis	152
7.9	Mercury derivatives as a source of carbenes	154
	References	155
	General reading	156

8	Stoichiometric Applications of Organometallic Compounds to Organic Chemistry	157
8.1	Main group element compounds	158
8.1.1	Organolithium compounds	158
8.1.2	Organomagnesium compounds	162
8.1.3	Organomercury compounds	167
8.1.4	Organoboranes	172
8.1.5	Organoaluminium compounds	175
8.1.6	Organosilicon compounds	175
8.1.7	Organotin compounds	182
8.2	Transition metal compounds	185
8.2.1	Organocopper compounds	186
8.2.2	Organotitanium compounds	189
8.2.3	Organoiron compounds	191
8.2.4	Organocobalt compounds	196
8.2.5	Organonickel compounds	197
8.2.6	Organozirconium compounds	199
8.2.7	Organorhodium compounds	202
8.2.8	Organopalladium compounds	204
8.2.9	Organochromium compounds	208
	References	210
	General reading	213
9	Catalytic Applications of Organometallic Compounds	214
9.1	Hydrogenation of unsaturated hydrocarbons	216
9.1.1	Hydrogenation using $(\text{Ph}_3\text{P})_3\text{RhCl}$	216
9.1.2	Hydrogenation using other rhodium and iridium catalysts	217
9.1.3	Asymmetric hydrogenation	218
9.1.4	Arene hydrogenation	218
9.2	Reactions involving carbon monoxide	219
9.2.1	Hydroformylation	219
9.2.2	Carboxylation reactions	223
9.2.3	Carbonylation of methanol	225
9.3	Reactions of unsaturated hydrocarbons involving C—C coupling	226
9.3.1	Chain growth of aluminium alkyls and alkene oligomerisation	227
9.3.2	Dimerisation of alkenes	228
9.3.3	Polymerisation of alkenes	229
9.3.4	Polymerisation of butadiene	232
9.3.5	Oligomerisation of butadiene	233
9.3.6	Cyclotrimerisation of alkynes	234
9.3.7	Isomerisation of alkenes	237
9.4	Oxidation of alkenes	238
9.5	Hydrosilation	241

CONTENTS

ix

9.6	Synthesis of substituted alkenes using palladium complexes	243
9.7	Transition metal catalysis with Grignard reagents	243
9.8	Main group catalysis	243
	References	245
	General reading	247

<i>Index</i>	248
--------------	-----

PREFACE

The aim of this book is to provide a concise introduction to organometallic chemistry. The book is intended primarily for senior undergraduate and post-graduate students. Teachers and research workers may also find it useful to consult for specialised information.

We have used an integrated approach to discuss the organometallic chemistry of both transition-metal and main-group elements, making comparisons and contrasts where appropriate. We are aware that organic and inorganic chemists view the subject somewhat differently but have attempted to write a balanced non-partisan account. In writing a relatively short book which gives an overall impression of an immense field, we have had to make some difficult choices. This has led to some chapters being presented in a closely packed style, although we have written the chapters dealing with the principles of the subject in a more discursive explanatory manner. After some thought we decided to give a substantial number of references to key reviews and research papers, so that the book can serve as a guide to the literature of organometallic chemistry.

We are most grateful to Dr D. A. Armitage and Professor A. G. Davies for reading the complete manuscript and making helpful suggestions. We also thank Mrs E. A. Moor for her virtuoso typing of the text and diagrams.

It is unlikely, despite such excellent help, that the book is free from errors. The responsibility for these rests with us, and we welcome comments and criticisms from readers.

London, October, 1984

A. W. P.
R. C. P.

ABBREVIATIONS USED

Ac	acetyl
acac	acetylacetonate anion
ACMP	<i>o</i> -anisylcyclohexylmethylphosphine
AIBN	azobisisobutyronitrile
BASF	Badische Anilin und Soda Fabrik
Bu	<i>n</i> -butyl
CHIRAPHOS	chiral 2,3- <i>bis</i> (diphenylphosphino)butane
COD	cycloocta-1,5-diene
COT	cyclooctatetraene
Cp	cyclopentadienyl
Cy	cyclohexyl
DIOP	chiral 2,3- <i>O</i> -isopropylidene-2,3-dihydroxy-1,4- <i>bis</i> (diphenylphosphino)butane
DMSO	dimethyl sulphoxide
dppe	1,2- <i>bis</i> (diphenylphosphino)ethane
e.s.r.	electron spin resonance
Et	ethyl
HMB	hexamethylbenzene
HMPT	hexamethylphosphoric triamide
HOMO	highest occupied molecular orbital
HSAB	hard and soft acids and bases
ICI	Imperial Chemical Industries
iPr	isopropyl
IUPAC	International Union of Pure and Applied Chemistry
L	unidentate ligand
LUMO	lowest unoccupied molecular orbital
Me	methyl
n.m.r.	nuclear magnetic resonance
Np	neopentyl
Ph	phenyl
phen	1,10-phenanthroline
Pr	<i>n</i> -propyl
py	pyridine
r.t.	room temperature
sBu	<i>s</i> -butyl
solv	solvent

tBu	<i>t</i> -butyl
TCNE	tetracyanoethene
TMED	<i>N,N,N',N'</i> -tetramethylethylenediamine
THF	tetrahydrofuran
Tol	<i>p</i> -tolyl
Ts	<i>p</i> -toluenesulphonyl