



The chemistry of the
metal—carbon bond

Volume 4

The use of
organometallic compounds in
organic synthesis

Edited by

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The chemistry of the
metal—carbon bond
Volume 4

THE CHEMISTRY OF FUNCTIONAL GROUPS

*A series of advanced treatises under the general editorship of
Professor Saul Patai*

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- Supplement F: The chemistry of amino, nitroso and nitro compounds and their derivatives (2 parts)
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- The chemistry of peroxides
- The chemistry of the metal—carbon bond Volume 2
- The chemistry of the metal—carbon bond Volume 3
- The chemistry of organic selenium and tellurium compounds Volume 1
- The chemistry of the metal—carbon bond Volume 4

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Foreword

The Chemistry of the Metal—Carbon Bond is a multi-volume work within the well established series of books covering *The Chemistry of Functional Groups*. It aims to cover the chemistry of the metal—carbon bond as a whole, but lays emphasis on the carbon end. It should therefore be of particular interest to the organic chemist. The general plan of the material is the same as in previous books in the series with the exception that, because of the large amount of material involved, this is a multi-volume work.

The first volume was concerned with:

- (a) Structure and thermochemistry of organometallic compounds.
- (b) The preparation of organometallic compounds.
- (c) The analysis and spectroscopic characterization of organometallic compounds.

The second volume was concerned with cleavage of the metal—carbon bond, insertions into metal—carbon bonds, nucleophilic and electrophilic attack of metal—carbon bonds, oxidative addition, and reductive elimination. It also included a chapter on the structure and bonding of Main Group organometallic compounds. The third volume was concerned with the use of organometallic compounds to create carbon—carbon bonds.

The present volume is concerned with the use of organometallic compounds in organic synthesis. It includes material not available when the third volume 'went to press' concerned with carbon—carbon bond formation, together with chapters concerned with the formation of carbon—hydrogen and other carbon—element bonds. The material is divided into two parts. The first part is concerned with the preparation of Main Group organometallic compounds and their use in organic synthesis. The second part includes the use of transition metal organometallics in organic synthesis and chapters on hydrogenation, saturated carbon—hydrogen bond activation, and the rapidly expanding field of supported metal complex catalysts.

In classifying organometallic compounds we have used Cotton's haptomenclature (η -) to indicate the number of carbon atoms directly linked to a single metal atom.

In common with other volumes in *The Chemistry of the Functional Groups* series, the emphasis is laid on the functional group treated and on the effects which it exerts on the chemical and physical properties, primarily in the immediate vicinity of the group in question, and secondarily on the behaviour of the whole molecule. The coverage is restricted in that material included in easily and generally available secondary or tertiary sources, such as *Chemical Reviews* and various 'Advances' and 'Progress' series, as well as textbooks (i.e. in books which are usually found in the chemical libraries of universities and research institutes) is not, as a rule, repeated in detail, unless it is necessary for the balanced treatment of the subject. Therefore each of the authors has been asked *not* to give an encyclopaedic coverage of his or her subject, but to concentrate on the most important recent developments and mainly on material that has not been adequately covered by

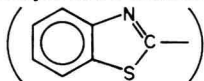
reviews or other secondary sources by the time of writing of the chapter, and to address himself or herself to a reader who is assumed to be at a fairly advanced postgraduate level. With these restrictions, it is realised that no plan can be devised for a volume that would give a *complete* coverage of the subject with *no* overlap between the chapters, while at the same time preserving the readability of the text. The Editors set themselves the goal of attaining *reasonable* coverage with *moderate* overlap, with a minimum of cross-references between the chapters of each volume. In this manner sufficient freedom is given to each author to produce readable quasi-monographic chapters. Such a plan necessarily means that the breadth, depth and thought-provoking nature of each chapter will differ with the views and inclinations of the author.

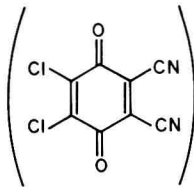
The publication of the Functional Group Series would never have started without the support of many people. Foremost among these is Dr Arnold Weissberger, whose reassurance and trust encouraged the start of the task. This volume would never have reached fruition without Mrs Baylis's help with typing and the efficient and patient cooperation of several staff members of the Publisher, whose code of ethics does not allow us to thank them by name. Many of our colleagues in England, Israel and elsewhere gave help in solving many problems, especially Professor Z. Rappoport. Finally, that the project ever reached completion is due to the essential support and partnership of our wives and families.

Shrivenham, England

FRANK HARTLEY

List of Abbreviations Used

ac	acrylonitrile
Ac	acetyl
acac	acetylacetone
acacen	bis(acetylacetonate)ethylenediamine
aibn	azobisisobutyronitrile
all	allyl
An	actinide metal
ap	antiplanar
appe	$\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{PPh}_2$
Ar	aryl
bae	bis(acetylacetonate)ethylenediamine
9-bbn	9-borabicyclo[3.3.1]nonane
bda	benzylideneacetone
bipy	2, 2'-bipyridyl
bnah	<i>N</i> -benzyl-1,4-dihydronicotinamide
Btz	benzothiazole 
Bu	butyl
Bz	benzyl
cd	circular dichroism
cdt	(<i>E, E, E</i>) cyclododeca-1, 5, 9-triene
cht	cycloheptatriene
CI	chemical ionization
CIDNP	chemically induced dynamic nuclear polarization
CNDO	complete neglect of differential overlap
coct	cyclooctene
cod	cycloocta-1, 5-diene
cot	cyclooctatetraene
Cp	η^5 -cyclopentadienyl
Cp*	η^5 -pentamethylcyclopentadienyl
C.P.	cross-polarization
Cy	cyclohexyl
dabco	1,4-diazobicyclo[2.2.2]octane

dba	dibenzylideneacetone
dbn	1,5-diazabicyclo[5.4.0]non-5-ene
dbp	dibenzophosphole
dbu	1,8-diazabicyclo[5.4.0]undec-7-ene
dccd	dicylohexylcarbodiimide
dcpe	1,2-bis(dicyclohexylphosphino)ethane
ddq	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
	
def	diethyl fumarate
DEPT	distortionless enhancement by polarisation transfer
diars	<i>o</i> -bis(dimethylarsino)benzene
dibah } dibal }	diisobutylaluminium hydride
dien	H ₂ NCH ₂ CH ₂ NHCH ₂ CH ₂ NH ₂
diop	2,3- <i>o</i> -isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane
dma	<i>N,N</i> -dimethylacetamide
dme	1,2-dimethoxyethane
dmfm	dimethyl fumarate
dmg	dimethyl glyoximate
dmm	dimethyl maleate
dmpe	bis(1,2-dimethylphosphino)ethane
dmpf	1,1'-bis(dimethylphosphino)ferrocene
dotnH	bis(diacetylmonoxime)propylene-1,3-diamine
dpm	dipivaloylmethanato
dppb	bis(1,4-diphenylphosphino)butane
dppe	bis(1,2-diphenylphosphino)ethane
dppf	1,1'-bis(diphenylphosphino)ferrocene
dppm	bis(1,1-diphenylphosphino)methane
dppp	bis(1,3-diphenylphosphino)propane
dmsO	dimethyl sulphoxide
ee	enantiomeric excess
EI	electron impact
<i>E</i> _p	peak potential
ESCA	electron spectroscopy for chemical analysis
Et	ethyl
eV	electronvolt
Fc	ferrocene
FD	field desorption
FI	field ionization
fmn	fumaronitrile
FMO	frontier molecular orbital
fod	F ₃ C(CF ₂) ₂ COCH=C(O)C(CH ₃) ₃
Fp	Fe(η^5 -C ₅ H ₅)(CO) ₂
Fp*	Fe(η^5 -C ₅ H ₅)(CO)(PPh ₃)
FT	Fourier transform

Hex	hexyl
c-hex	cyclohexyl
hfac	hexafluoroacetone
hfacac	hexafluoroacetylacetonato
hmdb	hexamethyl(Dewar)benzene
hmpa	hexamethylphosphoramide
hmpt	hexamethylphosphotriamide
HOMO	highest occupied molecular orbital
INDOR	inter-nuclear double resonance
INEPT	inter-sensitive nuclei enhanced by polarisation transfer
LCAO	linear combination of atomic orbitals
lda	lithium diisopropylamide
LiCA	lithium <i>N</i> -isopropylcyclohexylamide
Ln	lanthanide metal
LUMO	lowest unoccupied molecular orbital
M	metal
<i>M</i>	parent molecule
ma	maleic anhydride
map	2-methyl-2-nitrosopropane
<i>m</i> -cpba	<i>m</i> -chloroperbenzoic acid
Me	methyl
Mes	methanesulphonyl
meSal	<i>N</i> -methylsalicylaldiminato
MNDO	modified neglect of diatomic overlap
ms	millisecond
Ms	mesityl
nadh	nicotinamide adenine dinucleotide
nbd	norbornadiene
nbs	<i>N</i> -bromosuccinimide
ncs	<i>N</i> -chlorosuccinimide
nmp	<i>N</i> -methylpyrrolidone
Non	nonyl
Np	naphthyl
oA	<i>o</i> -allylphenyldimethylarsine
Oct	octyl
Pc	Phthalocyanine
Pe	pentenyl
Ph	phenyl
phen	<i>o</i> -phenanthroline
phth	phthalimide
pmdeta	pentamethyldiethylenetriamine
ppm	parts per million
Pr	propyl
PRDDO	partial retention of diatomic differential overlap
psi	pounds per square inch

pvc	poly(vinyl chloride)
py	pyridyl
pz	pyrazolyl
R	any radical
RT	room temperature
salen	bis(salicylaldehyde)ethylenediamine
salophen	bis(salicylaldehyde)- <i>o</i> -phenylenediamine
SCE	saturated calomel electrode
{Si}	silica (used as a support)
sia	sianyl (3-methyl-2-butyl)
S _N i	substitution nucleophilic internal
SOMO	singly occupied molecular orbital
sp	synplanar
SPT	selective population transfer
tba	tribenzylideneacetylacetone
tbdms	<i>tert</i> -butyldimethylsilyl
tcod	tricyclooctadiene
tene	tetracyanoethylene
teta	5, 5, 7, 12, 12, 14-hexamethyl-1, 4, 8, 11-tetraazacyclotetradecane
tfa	trifluoroacetic acid
tfbb	tetrafluorobenzobarrelene
Tfo	triflate
thf	tetrahydrofuran
thp	tetrahydropyranyl
thpo	tetrahydropyranyloxy
Thx	thexyl (—CMe ₂ CHMe ₂)
tmed	tetramethylethylenediamine
tmof	trimethyl orthoformate
tms	trimethylsilyl
tmtu	tetramethylthiourea
Tol	tolyl
tond	1, 3, 5, 7-tetramethyl-2, 6, 9-trioxobicyclo[3.3.1]nona-3, 7-diene
tos	tosyl
tpp	tetraphenylporphyrin
triphos	1, 1, 1-tris(diphenylphosphinomethyl)ethane
tta	thallium(III) acetate
ttfa	thallium(III) trifluoroacetate
ttn	thallium(III) nitrate
tu	thiourea
un	olefin or acetylene
X	halide

Part 1

Preparation and Use of Main Group Organometallics in Organic Synthesis

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CHAPTER 1

Preparation and use in organic synthesis of organolithium and Group IA organometallics

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