

CATALYSIS BY METAL COMPLEXES

37

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**Volume Editors** M. Peruzzini · L. Gonsalvi

# Phosphorus Compounds

Advanced Tools in Catalysis  
and Material Sciences

 Springer

Maurizio Peruzzini · Luca Gonsalvi  
Editors

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Advanced Tools in Catalysis and Material  
Sciences



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ISSN 0920-4652

ISBN 978-90-481-3816-6

e-ISBN 978-90-481-3817-3

DOI 10.1007/978-90-481-3817-3

Springer Dordrecht Heidelberg London New York

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*Cover design:* eStudio Calamar, Berlin/Figueres

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# Catalysis by Metal Complexes

Volume 37

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# Catalysis by Metal Complexes

This book series covers topics of interest to a wide range of academic and industrial chemists, and biochemists. Catalysis by metal complexes plays a prominent role in many processes. Developments in analytical and synthetic techniques and instrumentation, particularly over the last 30 years, have resulted in an increasingly sophisticated understanding of catalytic processes.

Industrial applications include the production of petrochemicals, fine chemicals and pharmaceuticals (particularly through asymmetric catalysis), hydrometallurgy, and waste-treatment processes. Many life processes are based on metallo-enzyme systems that catalyse redox and acid-base reactions.

Catalysis by metal complexes is an exciting, fast developing and challenging interdisciplinary topic which spans and embraces the three areas of catalysis: heterogeneous, homogeneous, and metallo-enzyme.

*Catalysis by Metal Complexes* deals with all aspects of catalysis which involve metal complexes and seeks to publish authoritative, state-of-the-art volumes which serve to document the progress being made in this interdisciplinary area of science.

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## **VOLUME 37: PHOSPHORUS COMPOUNDS: ADVANCED TOOLS IN CATALYSIS AND MATERIAL SCIENCES**

### *Volume Editors*

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# Preface

More than any other element in the periodic table, phosphorus represents a bridge between the living and non-living worlds. It takes part in the DNA–RNA biological cycle, but is also of importance in several inorganic cycles i.e. when used in fertilizers. This unique role makes phosphorus chemistry also valuable for applications in innovative areas at the forefront of molecular sciences, such as materials and polymer sciences, nanotechnology, catalysis, and life sciences, including medicinal applications. The linear relationship of phosphorus with its neighbouring elements (nitrogen, arsenic, silicon, and sulphur) and diagonal relationship with carbon (e.g., P is isolobal with C–H), endows an incredible, but still undervalued potential in many contemporary topics of basic and applied research.

This book aims at collecting state-of-the-art research highlights from world renowned experts in various fields of application of phosphorus, either in the form of review or own research account style articles. The topics covered by the authors fit well with the general objectives of this Book Series, and catalytic applications of phosphorus based compounds are thoroughly described in their multifaceted aspects.

Phosphorus is a key element in catalysis, and the last two Nobel prizes in molecular chemistry were awarded to Noyori, Sharpless and Knowles (2001) for their work on enantioselective catalysis and to Grubbs, Schrock and Chauvin (2005) for their work on the chemistry of transition metal carbene complexes and their applications in metathesis. In both cases the development of highly efficient, specifically tailored phosphorus based ligands are of paramount importance. The book opens with an account of the recent studies on a new family of air-stable chiral primary phosphines based on the binaphthyl backbone and their applications in asymmetric hydrosilylations (Chap. 1). The concept of applying phosphorus ligands to enantioselective catalysis is also the main subject of Chaps. 5 and 10, dealing with P-based planar chiral ferrocenes and chiral phosphorus ligands for enantioselective enyne cycloisomerizations, respectively.

Selected classes of compounds which have found interesting use as ligands for catalytic applications are represented by phosphinines (Chap. 6) and the water soluble 7-phospha-1,3,5-triazaadamantane ligand PTA and its derivatives (Chap. 7). The effect of phosphorus-based ligands in catalysis has also been reviewed for cross-coupling reactions under the mechanistic point of view in Chap. 3.

Some of the chapters of this book are more focused on the synthetic developments in phosphorus containing materials. This is the case of Chap. 2, which reviews the aspects concerning phosphine acetylenic macrocycles and cages, and Chap. 12, which deals with the important field of P-based cryptands, cyclophanes, and corands. Chapter 4 addresses the potential applications of metal complexes containing anionic phosphorus chains for the synthesis of metal phosphides, whereas the synthesis of P-compounds via the metal catalysed addition of P-H bonds to unsaturated organic molecules is thoroughly reviewed in Chap. 8.

The design of advanced phosphorus-containing materials through supramolecular assembly of phosphole-based conjugated ligands is another important field of application which is reviewed in Chap. 12.

Nanotechnology is a multidisciplinary field of applied science and technology covering a broad range of topics from materials science, colloidal science, applied physics, supramolecular chemistry, and even mechanical and electrical engineering. Chapter 9 describes the synthesis and applications of phosphorus-containing dendrimers in catalysis, materials science, and the biological fields.

Phosphorus is also a key element in all known forms of life from bacteria to humans. Phosphate,  $\text{PO}_4^{3-}$ , plays a major role in key biological molecules, such as DNA and RNA, phospholipids or as calcium phosphate which is central in the metabolism of teeth and bone tissues. Emerging research areas are the application of organophosphorus and bioorganometallic compounds in medicine for the understanding of specific biological functions and processes, diagnosis and treatment of a number of different diseases, with applications ranging from antitumour agents, to treatment of malaria, AIDS, tuberculosis, Parkinson's disease, bone tissue diseases and dismetabolism, etc. Some of these aspects are covered in the final Chap. 13.

The scientists who agreed to join their knowledge and expertise in this Book are not only part of the international community working in the field of phosphorus chemistry, but also members of the *European Phosphorus Sciences Network (PhoSciNet)*, part of the European cooperation in science and technology (COST) action ([www.phoscinet.org](http://www.phoscinet.org)), teaming-up to advance phosphorus based sciences by an integrated and targeted research approach in high-impact fields by organising interactions (workshops), by exchange of young researchers, and by fostering the participation of industrial partners.

We are grateful to COST and to all authors to have accepted with enthusiasm the invitation to write this book. We are certain it will be of interest to scientists skilled-in-the-art, by providing a generous and up-to-date source of inspiration, and for those academics and advanced level students who want to enter the

multifaceted field of phosphorus chemistry. It should also enable industry-based researchers to engage with state-of-the-art science at the top level.

Finally, we want to thank the team at Springer London and our coworkers at ICCOM (Drs. M. Caporali, B. Di Credico, L. Zani and Mr. V. Mirabello) for their help in editing this book.

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# Abbreviations

1-Ad	1-Adamantyl
Acac	Acetylacetone
AFM	Atomic force microscopy
AIBN	Azobisisobutyronitrile
B3LYP	Becke's three-parameter, Lee-Yang-Parr exchange-correlation functional
B3PW91	Becke's three parameter, Perdew-Wang 91 exchange-correlation functional
BET	Brunauer, Emmett and Teller
BICP	2,2'-Bis(diphenylphosphino)-1,1'-dicyclopentane
BINAP	2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl
Binepine	4,5-Dihydro-3H-dinaphtho[2,1-c;1',2'-e]phosphepine
BINOL	1,1'-Binaphthalene-2,2'-diol
BIPHEP	2,2'-Bis(diphenylphosphino)-1,1'-biphenyl
BSE	Bovine spongiform encephalopathy
C3-Tunaphos	1,13-Bis(diphenylphosphino)-7,8-dihydro-6H-dibenzo[f,h][1,5]dioxonin
Cod	1,5-Bis(cyclooctadiene)-1,4-cyclooctadiene
CP MAS	Cross polarization magic angle spinning
CTAB	Cetyltrimethylammonium bromide
Cy	Cyclohexyl
Cya	Cyanine
Cyp	Cyclopentyl
DBA	Dibenzylideneacetone
DDQ	2,3-Dichloro-5,6-dicyanobenzoquinone
DFT	Density Functional Theory
DIOP	4,5-Bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane
DMA	<i>N,N</i> -Dimethylacetamide

DME	1,2-Dimethoxyethane
DMF	Dimethylformamide
Dmpe	1,2-Bis(dimethylphosphino)ethane
DMSO	Dimethyl sulfoxide
DNA	Deoxyribonucleic acid
Dppb	1,4-Bis(diphenylphosphino)butane
Dppben	1,2-Bis(diphenylphosphino)benzene
Dppe	Bis(diphenylphosphino)ethane
Dppf	1,1'-Bis(diphenylphosphino)ferrocene
EDTA	Ethylenediaminetetraacetic acid
EGFP	Enhanced green fluorescent protein
FAB-MS	Fast atom bombardment mass spectrometry
FITC	Fluorescein isothiocyanate
FRET	Förster resonance energy transfer
H8-BINAP	2,2'-Bis(diphenylphosphino)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthalene
HAS	Human serum albumin
HeLa	Human epithelioid cervical carcinoma
HEK 293	Human transformed primary embryonal kidney
HIV	Human immunodeficiency virus
HMPA	Hexamethylphosphoramide
HUVEC	Human umbilical vein endothelial cell
LAH	Lithium aluminium hydride
LBL or LbL	Layer-by-layer
LDA	Lithium diisopropylamide
LP	Lone pair
LSPR	Localized surface plasmon resonance
MCM	Mobil composition of matter
Me-DUPHOS	1,2-Bis(2,5-dimethylphospholano)benzene
MeO-BIPHEP	2,2'-Bis(diphenylphosphino)-6,6'-dimethoxy-1,1'-biphenyl
Mes	mesityl (2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub> )
MONOPHOS	(3,5-Dioxa-4-phosphacyclohepta[2,1-a;3,4-a']dinaphthalen-4-yl)dimethylamine
Nbd	2,5-Norbornadiene
NHC	<i>N</i> -Heterocyclic carbene
NK	Natural killer
NMR	Nuclear magnetic resonance
NPs	Nanoparticles
OLEDs	Organic light emitting diodes
PAH	Poly(allylamine hydrochloride)
PAMAM	Poly(AMidoAMine)
PBEPBE	Perdew–Burke–Ernzerhof exchange-correlation functional

PBMCs	Peripheral blood mononuclear cells
PEI	Poly(ethyleneimine)
PL	Photoluminescence
PMDETA	<i>N,N,N',N'',N''</i> -Pentamethyldiethylenetriamine ( $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMeCH}_2\text{CH}_2\text{NMe}_2$ )
PrP <sup>Sc</sup>	Scrapie isoform of the prion protein
PSS	Poly(styrenesulfonate)
PTA	1,3,5-Triaza-7-phosphaadamantane
PVK	Poly(vinylcarbazole)
QDs	Quantum dots
QM	Quantum Mechanics
QM/MM	Quantum Mechanics/Molecular Mechanics
ROMP	Ring-Opening Metathesis Polymerization
SDP	7,7'-Bis(diphenylphosphino)-2,2',3,3'-tetrahydro- 1,1'-spirobiindane
SegPHOS	5,5'-Bis(diphenylphosphino)-4,4'-bi-1,3-benzodioxole
Skewphos	2,4-Bis(diphenylphosphino)pentane
SN2	Bimolecular nucleophilic substitution
Sphos	2-(2',6'-Dimethoxybiphenyl)-dicyclohexylphosphine
SPR	Surface plasmon resonance
TEOS	Tetraethoxysilane
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TMEDA	<i>N,N,N',N'</i> -Tetramethylethylenediamine ( $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$ )
TPA	Two-photon absorption
TPEF	Two-photon excited fluorescence
TTF	Tetrathiafulvalene
UV	Ultra-violet
Xantphos	4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene

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