# Introduction to phosphorus chemistry

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HAROLD GOLDWHITE
*Professor of Chemistry, California State University, Los Angeles*

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# Preface

This book presents an introduction to the chemistry of a single element, phosphorus, as an example of a range of topics of interest in the whole of chemistry. The chemistry of phosphorus involves many of the major themes of modern chemistry – for example, bonding; physical techniques; and structure, both static and dynamic. In surveying the chemistry of phosphorus, it is necessary to cross and recross the boundaries of the various subdisciplines of chemistry that are today beginning to erode. There is an "inorganic" chemistry of phosphorus; organophosphorus chemistry is a large and expanding domain; phosphorus is an economically important element, and a vitally important element in the biosphere.

Many books have already been devoted, in whole or in part, to this important and interesting element. There are, however, few recent brief and introductory surveys, of the type this book attempts, of the major points of interest in the chemistry of this element. This book is intended for the chemist at an advanced undergraduate or graduate level who is interested in learning the fundamentals of the chemistry of phosphorus. Because an attempt is made at conciseness, the book cannot claim to be comprehensive or entirely current. The most significant developments in phosphorus chemistry through the end of June 1979 have been included. The critical bibliography and suggestions for further reading list the most useful secondary and tertiary sources in phosphorus chemistry. The primary literature is not included, because that would greatly expand the bibliography with little added utility for the intended reader of this work. Fortunately for those working in phosphorus chemistry, the major developments are rapidly made accessible in reviews and specialist reports, as indicated.

Chemists in the United States are, in the main, reluctant to adopt *Système Internationale* (SI) units. However the SI system's consistency and ease of use will certainly lead to a steady increase in its adoption by chemists. In this book I have given both SI and the more familiar cgs units where appropriate.

I carried out my original investigations in phosphorus chemistry under the direction of Dr. B. C. Saunders at Cambridge University, and later worked

collaboratively in a very different area of phosphorus chemistry with Professor R. N. Haszeldine at the University of Manchester Institute of Science and Technology. I owe much to these chemists, and to my undergraduate, graduate, and postdoctoral collaborators over the years.

The present text had its origin in courses given at California State University, Los Angeles; at the University of Strasbourg; and at the National University of Mexico. I thank my colleagues and students at all three institutions for their valued contributions to the development of this material.

Finally, I thank my parents, my wife, and my children for their continuous strong support and help; their contributions to my work have been of inestimable value.

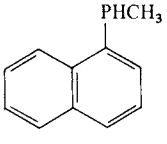
Harold Goldwhite

Los Angeles

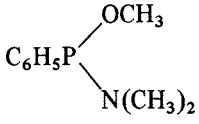
## Notes on nomenclature

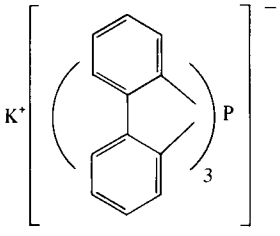
The nomenclature of phosphorus chemistry is in a somewhat confused (and confusing) state. Although an "agreed" system of naming phosphorus compounds was put forward jointly by the Chemical Society of London and the American Chemical Society in 1952, it was not adopted wholeheartedly by authors or editors and in the present literature the same phosphorus compound may be given several different names. This is a fundamentally undesirable situation, but it seems unlikely to change in the near future, in view of the already existing proliferation of names. The International Union of Pure and Applied Chemistry (IUPAC) has, in its latest proposals on the nomenclature of organic compounds containing phosphorus (Tentative Nomenclature of Organic Chemistry, Section D, Bulletin No. 31, August 1973) explicitly endorsed the naming of such compounds in three different ways: (1) as substitution products of parent hydrides, for example, of $PH_3$, phosphine; (2) as derivatives of parent compounds, for example, $H_2POH$, phosphinous acid; (3) by coordination nomenclature as compounds of phosphorus, with an oxidation state affixed, if the author desires.

The proposals for phosphorus nomenclature (and that of analogous arsenic, antimony, and bismuth compounds) occupy 27 text pages in the IUPAC monograph and will not be reproduced here. Instead examples of alternative names for some common structural types will be presented, so that the reader will be able to follow not only the text of this book, but also the current literature of the subject.

| Compound | Acceptable name(s) (and comments) |
|---|---|
| $PH_3$ | Phosphine ( a parent compound) |
|   | Methyl(1-naphthyl)phosphine (alphabetic ordering of radicals) |

| Compound | Acceptable name(s) (and comments) |
|---|---|
| $CH_3—\underset{\displaystyle PH_2}{\underset{\vert}{CH}}—CH_2OH$ | 2-Phosphino-1-propanol (using phosphino as a name for the $—PH_2$ substituent) |
| $HP(CH_2CH_2COOH)_2$ | 3,3′-Phosphinediyldipropionic acid (phosphinediyl is the recommended name for HP< as a substituent) |
| $\overset{11}{CH_3}\overset{10}{CH_2}\overset{9}{\underset{\displaystyle CH_3}{\underset{\vert}{P}}}—\overset{8}{CH_2}\overset{7}{CH_2}\overset{6}{\underset{\displaystyle C_2H_5}{\underset{\vert}{P}}}—\overset{5}{CH_2}\overset{4}{CH_2}\overset{3}{CH_2}\overset{2}{\underset{\displaystyle H}{\underset{\vert}{P}}}\overset{1}{CH_3}$ | 6-Ethyl-9-methyl-2,6,9 triphosphaundecane (using substitution nomenclature with the suffix-*a* for a chain compound with several phosphorus atoms) |
| $CH_3COP(CH_3)_2$ | Acetyldimethylphosphine (acyl compounds are named as phosphine derivatives) |
| $(C_6H_5)_2PLi$ | Lithium diphenylphosphide (the suffix-*ide* indicates the negative character of the phosphorus atom) |
| $(C_2H_5)_2POCH_3$ | Diethylmethoxyphosphine (as a phosphine derivative)<br>Methyl diethylphosphinite [as an ester of diethylphosphinous acid, $(C_2H_5)_2POH$]<br>Diethylmethoxophosphorus (III) (coordination nomenclature) |
| $CH_3PCl_2$ | Dichloro(methyl)phosphine [the (methyl) is in parentheses to avoid confusion with $CHCl_2PH_2$, (dichloromethyl) phosphine]<br>Methylphosphinous dichloride<br>Dichloro(methyl) phosphorus |

| Compound | Acceptable names(s) (and comments) |
|---|---|
|  | Dimethylamino(methoxy)(phenyl)phosphine<br>Phenyl N,N,P-trimethylphosphonamidite [as a derivative of phosphonamidous acid, $HP(OH)NH_2$]<br>Dimethylamido(methoxo)phenylphosphorus |
| $(CH_3)(C_2H_5)(C_6H_5)(C_6H_5CH_2)P^+Cl^-$ | Benzylethylmethylphenylphosphonium chloride (the suffix-*onium* indicates four-coordinate positive character for phosphorus) |
| $(C_6H_5)(CH_3)_2PO$ | Dimethyl(phenyl)phosphine oxide<br>Dimethyl(oxo)phenylphosphorane (phosphorane denotes the five-coordinate state of phosphorus with, in this example, the oxo substituent formally occupying two coordination sites; see below for other examples)<br>Dimethyl(oxo)phenylphosphorus |
| $(C_6H_5)_3PCH_2$ | Methylene(triphenyl)phosphorane<br>Methylene(triphenyl)phosphorus<br>(Triphenylphosphonio)methylide (when the contribution $P^+-C^-$ is to be stressed) |
| $(CH_3)_2PO(OH)$ | Dimethylphosphinic acid<br>Dimethyl(hydroxo)(oxo)phosphorane<br>Dimethyl(hydroxo)(oxo)phosphorus |

| Compound | Acceptable names(s) (and comments) |
|---|---|
| $ClCH_2PO(OH)_2$ | (Chloromethyl)phosphonic acid<br>Chloromethyl(dihydroxo)(oxo)phosphorane<br>Chloromethyl(dihydroxo)(oxo)phosphorus |
| $C_6H_5P(:O)(Cl)(OCH_3)$ | Methyl phenylchlorophosphonate [ester of phenylchlorophosphonic acid, $C_6H_5P(O)(Cl)OH$]<br>Methyl phenylphosphonochloridate [ester of acid chloride of phenylphosphonic acid, $C_6H_5P(O)(OH)_2$]<br>Chloro(methoxo)(oxo)phenylphosphorus |
| $(C_6H_5)_3PBr_2$ | Dibromotriphenylphosphorane<br>Dibromotriphenylphosphorus |
|  | Potassium tris(2,2′-biphenylylene) phosphate(V) (Stock system)<br>Potassium tris(2,2′-biphenylylene)phosphate(I-) (ion-charge system) |
| $H_2P—PH_2$ | Diphosphane (the old name, diphosphine, is strongly discouraged) |