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Phosphorus Chemistry: Introduction

In 1669, a ruined businessman from Hamburg, Hennig Brandt, searching for gold in concentrated urine, observed a strange luminescence that is now known to result from elemental phosphorus (phosphorus comes from the Greek: which brings light). This spectacular discovery attracted a lot of interest and was reproduced all around Europe.

The first known publication on phosphorus: "De Phosphoris quatuor Observatio" by Johann Elsholz, Physician to the Elector of Brandeburg Berolini, dates from 1676 and was followed by a letter entitled "Phosphoro Mirabili" by Johann Kunckel (1678). Just after this, Robert Boyle in England also succeeded in preparing phosphorus and published the first book dealing with its chemistry, *The Aerial Noctiluca* (1680). In this book, he proposed several possible applications of phosphorus such as the preparation of luminous displays. After the death of Boyle, his assistant A. G. Hanckwitz prepared phosphorus which was sold all around Europe under the name of "phosphorus anglicus". The numerous demonstrations of the miraculous light evolved by phosphorus that proliferated from the end of the 17th century are in themselves evidence of the impact of this discovery. It is noteworthy that none of the scientists of the day realized that this was the first example of an element, isolated by mankind, that exists in nature only in the form of its derivatives. It was not until 1790 that calcium phosphate was recognized as the ideal precursor for phosphorus.

Three centuries after its discovery, at least 5000 scientists are working with phosphorus, numerous applications having been found in all fields of chemistry, from organic chemistry to material science through inorganic chemistry, organometallic chemistry, biochemistry, etc.

This special issue was planned to illustrate most of these fields. Before discussing the reviews collected in this volume, which have been written by an outstanding assembly of experts, I wish to draw the reader's attention to the fact that some of the authors were, unfortunately, not able to complete their contributions on time, but they still hope to finish them in the near future. Therefore, some of the presently missing reviews will appear in the forthcoming issues of *Chemical Reviews*.

The review by Michael Witt and Herbert W. Roesky, "Transition and Main Group Metals in Cyclic Phosphazanes and Phosphazenes", draws attention to the relatively new field of cyclic metal–nitrogen–phosphorus systems. The first representative member of phosphorus heterocycles containing a metal–nitrogen multiple bond was described by the authors of this review in 1986. Here, greater emphasis has been placed upon synthetic, structural, and NMR spectroscopic aspects. The potential applications of these compounds as catalysts for the polymerization of α-olefins, hydrogenation, and hydroformylation reactions, as well as precursors for inorganic polymers, are mentioned, making exciting reading.

Anne-Marie Caminade and Jean-Pierre Majoral have extensively reviewed one century of the "Synthesis of Phosphorus-Containing Macrocycles and Cryptands", emphasizing recent developments. Indeed, most of this work has been accomplished in the last 10 years, and it is now possible to tailor many types of phosphorus macrocycles with well-defined size, shape, properties, and complexation ability, which differs from those of organic macrocycles. The end of the review is devoted to more elaborate structures, such as cryptands.

The first tricoordinate hypervalent phosphorus (10-P-3) compound (ADPO) was reported by Arduengo in 1983. The chemistry of ADPO has led to many other important discoveries in the field of phosphorus and main-group chemistry which are covered by the review by Anthony (Bo) Arduengo and Constantine Stewart, "Low-Coordinate Hypervalent Phosphorus". For example, the electromorphism possible between the 8-P-3 and 10-P-3 geometries for ADPO led to the discovery of the "edge-inversion" process for tricoordinate main-group 5 compounds. The ADPO-related compounds have also led to exciting new transition-metal adducts that add new dimensions to transition metal–phosphorus chemistry.

Keith Dillon's review, "Phosphoranides", deals with these hypervalent anionic phosphorus(IV) species formally having more than four electron pairs in the phosphorus valence shell. (In other words the phosphorus has a 10-P-4 arrangement.) Phosphoranides are of considerable importance as models for the reactive intermediates involved in nucleophilic substitution reactions at phosphorus(III) centers. Since the isolation of the first example by the author in 1969, the chemistry of these species has developed considerably, especially in the area of transition-metal complexes.

After hypervalent species, we come to low-coordinate phosphorus compounds. The review by Jean-Marc Denis and Annie-Claude Gaumont deals with the

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"Preparation, Characterization, and Synthetic Potential of Unstabilized Compounds Containing Phosphorus–Carbon Multiple Bonds". The chemistry of trivalent phosphorus derivatives bearing p_π–p_π bonds has been one of the most studied areas of phosphorus chemistry in the last two decades. Thus, several reviews are available on this topic, most of which focus on kinetically stabilized species. In contrast, the emphasis here is on unstabilized compounds making this review very valuable.

The article by Michał Pietrusiewicz and Maria Zabłocka emphasizes the progress made in recent years in the "Preparation of Scalemic P-Chiral Phosphines and their Derivatives". (The term scalemic refers to unequal mixtures of enantiomers.) It highlights the fact that these compounds are presently accessible in almost any conceivable structural type and functional pattern which could possibly be required for their advantageous use in contemporary asymmetric synthesis and catalysis. The preparative methods include those using principles of asymmetric transformations but also chiral columns.

The coordinating ability of phosphines has been recognized since the middle of the 19th century. The review by Hermann Mayer and William Kaska, entitled "Stereochemical Control of Transition Metal Complexes by Polyphosphine Ligands", specifically covers the chemistry of polydentate tertiary phosphine complexes with the exclusion of bidentate compounds and derivatives which do not have direct phosphorus–metal bonds. The chemistry described in this review portrays polyphosphine ligand complexes as major partners in modern coordination chemical interactions.

Following the discovery of PH_3 in 1785 by Gengembre and P_2H_4 in 1844 by Thénard, more than 100 years passed before additional phosphorus hydrides (phosphanes) were reported. In the past 25 years, further homologues of the general series P_nH_{n+2} (with $n = 3$–9) have been detected and the structures of the members with $n = 3$–7 elucidated, mainly by the Cologne group. The recent progress concerning these open-chain phosphanes, which display close structural relationships with saturated acyclic hydrocarbons, has been reviewed by Marianne Baudler and Klaus Glinka in the paper entitled "Open-Chain Polyphosphorus Hydrides (Phosphanes)". One can note that many interesting unpublished results are included.

"Synthetic Applications of Metalated Phosphonium Ylides" is the title of the review by Henri-Jean Cristau. Metalated ylides have been widely used as polydentate ligands in coordination chemistry, but this review emphasizes the recent developments in the use of lithium phosphonium diylides and yldiides in organic synthesis. Compared to classical Wittig reagents, their higher nucleophilicity, coupled with the presence of the metal, opens the way to numerous new applications.

^{31}P NMR spectroscopy is a wonderful tool for all phosphorus chemists. A fascinating use of this technique is presented in the review by David Gorenstein entitled "Conformation and Dynamics of DNA and Protein–DNA Complexes by ^{31}P NMR". It demonstrates that ^{31}P NMR chemical shifts and ^{31}P–^{1}H coupling constants can serve as probes of the conformation and dynamics of nucleic acids, particularly the deoxyribose phosphate backbone. This review summarizes state of the art techniques and therefore should be of interest for all phosphorus and biological chemists.

The theoretical chemistry paper written by Declan Gilheany has a somewhat provocative title: "No d Orbitals but Walsh Diagrams and Maybe Banana Bonds: Chemical Bonding in Phosphines, Phosphine Oxides, and Phosphonium Ylides". He demonstrates that the concept of d orbital involvement in bonding is not useful in main-group chemistry. The structures of all phosphines can be rationalized in one simple orbital picture, and this can be used to understand the structure of their oxides. It should be noted that the author's perspective is that of a synthetic chemist.

In addition to critically reviewing the current status of the field, most of the authors have suggested new directions for future research. In years to come, I believe that phosphorus chemistry will be as fascinating as was its discovery in the 17th century. To conclude I quote the Nobelist Professor Richard Kuhn from his opening address to an International Conference on Phosphorus Chemistry in Heidelberg: "Without phosphorus, there is no life!"

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Guest Editor