

## Introduction

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The literature relating to the chemistry of organophosphorus compounds continues to grow. Our problem as Senior Reporters is to find authors who are willing to undertake the task of reviewing the various areas in a timely manner. The past year has been particularly difficult in this respect, and this volume lacks coverage of some areas that previously have been reviewed continuously over many years. Thus, this year, we are unable to provide a review of the chemistry of quinquivalent phosphorus acids, and the 'Physical Methods' chapter is also missing. The mononucleotide section of the normally extensive chapter on 'Nucleotides and Nucleic Acids' is provided by a new member of the team, Dr Marie Migaud (Queen's, Belfast), but we have not been able to secure the usual coverage of polynucleotide and nucleic acid chemistry. On the credit side, we have a two-year review of the chemistry of trivalent phosphorus acid derivatives, making up for the absence of this topic in the previous Volume 31. We hope to remedy the deficiencies of the present volume in a similar way next year. We would welcome approaches from potential authors, in particular for the 'Physical Methods' chapter, or specific sections thereof, as this topic requires an overview of the application of physical methods of all kinds across the whole of the organophosphorus area, and is a major undertaking.

The synthesis of new chiral phosphines continues to be a major preoccupation, the main focus being applications in metal-catalysed processes. Interest in the synthesis and structural characterisation of metallo-organophosphide systems also continues to grow. In contrast, the volume of new work on low-coordination number  $p_{\pi}$ -bonded phosphorus compounds has declined, as the major features of this area have now become established, although much interesting new work continues to appear. The synthesis of new chiral ligand systems is also now a significant feature in the chemistry of trivalent phosphorus acid esters and amides, applications of such compounds in metal-catalysed processes hitherto having been neglected relative to those involving phosphine ligands. The past year has also seen continued interest in the structure of phosphonium ylides, with particular reference to gaining greater insight into their stability, electronic distributions and conformation, on which the reactivity of these systems depends. In the nucleotide field, the year has been marked by the development of new phosphorylation and chiral thiophosphorylation methods and by improvements in the formation of intramolecular pyrophosphate linkages.

The year has seen yet another diminution in the number of publications dealing with hypervalent phosphorus chemistry but the quality of work

remains high, relying heavily on the latest techniques in NMR spectroscopy and X-ray crystallography. Ample illustration of this is found in a study of cyclic phosphates, phosphonates and phosphonium salts containing sulfuryl groups. The work was designed to compare the coordinating ability of sulfur, reported earlier, with that of sulfuryl oxygen and in fact only one of a series of eight phosphates, phosphonates and phosphonium salts showed evidence of donor action towards phosphorus from phosphoryl oxygen, with a P–O bond distance of 3.007 Å.

The keen interest in phosphazenes continues and many advances and further applications have been reported. There have been further studies of the aza-Wittig reaction, several of which focus on the synthesis of nitrogen heterocycles. Carbophosphazenes have been shown to ring-open tertiary bases, such as quinuclidine, to give amino-substituted derivatives. Several reports concern the preparation of ferrocenyl derivatives and much use has been made of silylated phosphazenes. Complexation with a wide range of metals has produced an interesting array of novel structures. Phosphazenes have been used as phase transfer catalysts and as strong bases, and crystals of a phenylenedioxide cyclotriphosphazene have been used to form inclusion compounds with various aromatics and polymers. Vinyl derivatives have been prepared, leading to fascinating dendritic architectures. A polyphosphazene derived from a chiral amine gave a large optical rotation assigned to the presence of a helical  $P = 3DN$  backbone. Applications as flame retardants abound and a polyphosphazene with pendant cyanate groups was cured to produce a novel cyclo-matrix with improved char yield. There has been much interest in polymers and copolymers, some being amphiphilic and capable of forming micelles. Platinum complexes with greater anticancer activity than Carboplatin have also been reported.

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