

Main-group-based rings and polymers

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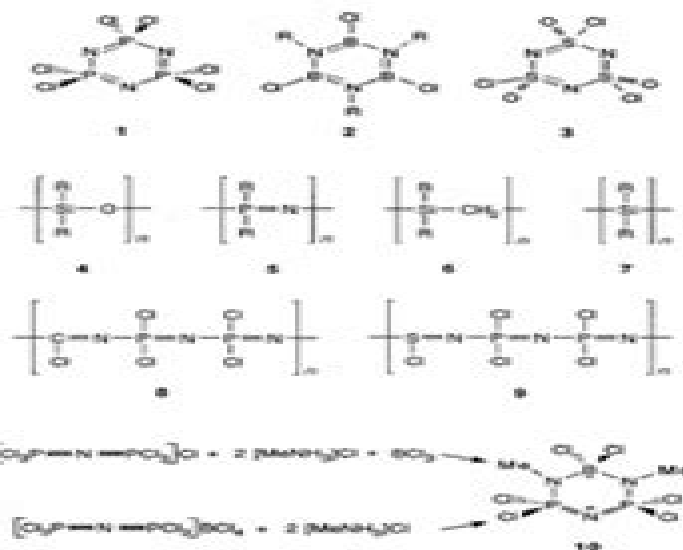
The synthesis and study of heterocycles containing main-group elements have played a pivotal role in the development of inorganic chemistry. Well known 'text-book' classes of inorganic rings include the cyclic phosphazene **1**, which was first prepared by Liebig and Rose¹ in 1834, and borazines such as **2**, the initial example of which was first synthesized by Stock and Pohland² in 1926. A further example is provided by sulfamides **3** which have been known since the 1950s.³ It is noteworthy that the ring skeletons in phosphazenes **1** and borazines **2** have been shown to be very robust and to permit facile halogen atom replacement reactions.⁴ This chemistry has been well studied and has provided much useful information on nucleophilic substitution reactions in inorganic chemistry. The bonding used to describe structures such as **1–3** and the possible application of the label 'inorganic benzene' has been the subject of much debate.

Current research continues to uncover fascinating new ring systems which pose intriguing questions with respect to their bonding or which exhibit unexpected reactivity. Some noteworthy examples include ten-electron gallium-based systems and pseudo aromatic cyclic silylenes,^{5,6} novel cyclic tellurium imides,⁷ and interesting aluminum–nitrogen heterocycles⁸ among others.⁹ In addition to these important fundamental questions, a further reason for studying inorganic rings is their potential use as precursors to polymers and solid-state materials.

The synthesis of long chains of atoms of inorganic elements, inorganic polymers, provides a substantial synthetic challenge but is motivated by the possibility of accessing new materials with interesting and useful properties.¹⁰ The most well known and widely used current routes to high molecular weight polysiloxanes **4**,¹¹ polyphosphazenes **5**,¹² and poly(carbosilanes) **6**,¹³ involve a ring-opening polymerization (ROP) reaction. With this in mind, interest in the polymerization behaviour of other inorganic rings has recently gathered momentum. Polysilanes **7**,¹⁴ poly(carbophosphazenes) **8**,¹⁵ and poly(thiophosphazenes) **9**¹⁶ represent examples of well characterized polymers which have been successfully prepared by ROP in the past decade.

The use of inorganic rings to construct solid-state materials with novel properties has also been successfully developed. For example, materials with interesting electronic, magnetic and conductive properties have been prepared from sulfur–nitrogen or selenium–nitrogen heterocycles.^{17,18} In addition, inorganic rings have attracted considerable attention as precursors to ceramics via thermolysis; examples include the use of aluminum–nitrogen or gallium–arsenic heterocycles to prepare AlN and GaAs, respectively.^{19,20}

In this perspective we describe two areas of research on main group heterocycles which have been pursued in our research group. These involve, first, boron–nitrogen–phosphorus heterocycles and secondly, rings of sulfur(vi), nitrogen and phosphorus atoms. Our focus has been on the discovery of new structures and reactivity and, in particular, on the potential use of these species as precursors to new polymers via ROP reactions.



Boron–Nitrogen–Phosphorus Rings

Early work on B–N–P heterocycles

Cyclic species containing boron, nitrogen, and phosphorus atoms were first described about 30 years ago. The first report of a BP₂N₂ ring was published by Sherif and Schmalbach²¹ in 1966 and described the use of a [5 + 1] cyclocondensation reaction between [H₂NPh₂P=N–PPh₂NH₂]Cl and RBCl₂ (R = Ph or Cl) to yield boron–nitrogen–phosphorus heterocycles. However, by present day standards, the characterization was poor.²² Nevertheless, applications of these rings as pesticides were claimed in a patent.²³

The perchlorinated boron–nitrogen–phosphorus heterocycle **10** was subsequently synthesized by two very similar routes. In 1968 Becke–Goehring and Müller²⁴ reported the reaction of [Cl₂P=N–PCl₂]Cl with BCl₃ and [MeNH₂]Cl in 1,2-dichloroethane and gave a 77% yield of **10**. In 1971 a slight modification of the Becke–Goehring synthesis was reported by Binder.²⁵ This route involved the reaction of [Cl₂P=N–PCl₂]BCl₃ with [MeNH₂]Cl and gave improved yields of 84–90%. Convincing structural characterization of this white crystalline compound was provided by NMR spectroscopy. For example, ¹¹B NMR showed a

Rings Clusters And Polymers Of Main Group And Transition Elements

Alan H. Cowley



Rings Clusters And Polymers Of Main Group And Transition Elements:

Rings, Clusters, and Polymers of Main Group and Transition Elements H. W. Roesky, 1989 The chemistry of rings clusters and polymers is becoming an important branch of inorganic and organometallic chemistry Although inorganic rings have been known for more than 150 years they have only been structurally characterized within the last fifty years Inorganic and organometallic clusters and polymers have recently become the subject of intense interest and study because of their unusual properties and their potential for applications in the areas of catalysis electronics and ceramics Transition metal clusters have been examined as models for heterogeneous catalysts Both rings and clusters might function as potential building blocks for extended solid state systems In comparison with organic polymers however general and versatile methods for the synthesis of inorganic and organometallic polymers are not readily available In particular the preparation of polymers containing transition metal atoms in the polymer backbone is a challenge to inorganic chemistry This book describes the rapid development which has taken place in this field *Inorganic Rings and Polymers of the P-block Elements* Tristram Chivers, Ian Manners, 2009 The focus of the book is monocyclic inorganic ring systems of the p block elements and the polymers that are in many cases derived from them Bicyclic or polycyclic arrangements are considered when they are closely related to those of monocyclic systems *Rings, Clusters, and Polymers of the Main Group Elements* Alan H. Cowley, 1983

Rings, Clusters and Polymers of Main Group and Transition Elements HW Roesky (Ed), 1989 **The Chemistry of Inorganic Ring Systems** R. Steudel, 2013-10-22 The present volume considers the most recent developments in the chemistry of cyclic inorganic and organoelement compounds Nineteen of the 22 chapters are based on invited and other lectures presented at the 6th International Symposium on Inorganic Ring Systems held in Berlin on August 18-22 1991 Main group compounds dominate the content from boron via carbon silicon germanium tin nitrogen phosphorus and arsenic to sulfur and selenium The book is organized by element moving from left to right in the main groups of the Periodic Table followed by one chapter each on bonding and nomenclature of ring molecules The list of contributors comprises distinguished scientists from 8 countries *Physics and Chemistry of Metal Cluster Compounds* L.J. de Jongh, 2013-03-09 On Friday February 20 1980 I had the pleasure to be present at the inaugural lecture of my colleague Jan Reedijk who had just been named at the Chair of Inorganic Chemistry of Leiden University According to tradition the ceremony took place in the impressive Hall of the old University Academy Building In the course of his lecture Jan mentioned a number of recent developments in chemistry which had struck him as particularly important or interesting Among those was the synthesis of large metal cluster compounds and to my luck he showed a slide of the molecular structure of PtI_9C_4 To my luck since at traditional Leiden University it is quite unusual to show slides at such ceremonies This constituted my first acquaintance with this exciting new class of materials I became immediately fascinated by this molecule partly because of the esthetic beauty of its fivefold symmetry partly because as a physicist it struck me that it could be visualized as an embryonically small metal

particle embedded in a shell of CO ligands *Inorganometallic Chemistry* Thomas P. Fehlner, 2013-11-22 There is a certain fascination associated with words The manipulation of strings of symbols according to mutually accepted rules allows a language to express history as well as to formulate challenges for the future But language changes as old words are used in a new context and new words are created to describe changing situations How many words has the computer revolution alone added to languages Inorganometallic is a word you probably have never encountered before It is one created from old words to express a new presence A strange sounding word it is also a term fraught with internal contradiction caused by the accepted meanings of its constituent parts In organic is the name of a discipline of chemistry while metallic refers to a set of elements constituting a subsection of that discipline Why then this Carrollian approach to entitling a set of serious academic papers Organic the acknowledged doyenne of chemistry is distinguished from her brother inorganic by the prefix in i e he gets everything not organic Organometallic refers to compounds with carbon metal bonds It is simple Inorganometallic is everything else i e compounds with noncarbon metal element bonds But why a new term Is not inorganic sufficient By virtue of training limited time resources co workers and so on chemists tend to work on a specific element class on a particular compound type or in a particular phase Thus one finds element oriented chemists e g *Proceedings of the Seventh International Symposium on Inorganic Ring Systems, IRIS VII* Tristan Chivers, 1995-02 *Cyclic Polymers* E.R. Semlyen, 2007-05-08 *Cyclic Polymers* Second Edition reviews the many recent advances in this rapidly expanding subject since the publication of the first edition in 1986 The preparation characterisation properties and applications of a wide range of organic and inorganic cyclic oligomers and polymers are described in detail together with many examples of catenanes and rotaxanes The importance of large cyclics in biological chemistry and molecular biology is emphasised by a wide coverage of circular DNA cyclic peptides and cyclic oligosaccharides and polysaccharides Experimental techniques and theoretical aspects of cyclic polymers are included as well as examples of their uses such as ring opening polymerisation reactions to give commercially important materials This book covers a wide range of topics which should be of interest to many scientific research workers for example in polymer science chemistry and molecular biology as well as providing a reference text for undergraduate and graduate students *Chemistry of the Elements* N. N. Greenwood, A. Earnshaw, 2012-12-02 When this innovative textbook first appeared in 1984 it rapidly became a great success throughout the world and has already been translated into several European and Asian languages Now the authors have completely revised and updated the text including more than 2000 new literature references to work published since the first edition No page has been left unaltered but the novel features which proved so attractive have been retained The book presents a balanced coherent and comprehensive account of the chemistry of the elements for both undergraduate and postgraduate students This crucial central area of chemistry is full of ingenious experiments intriguing compounds and exciting new discoveries The authors specifically avoid the term inorganic chemistry since this evokes an outmoded view of chemistry which is no longer

appropriate in the final decade of the 20th century Accordingly the book covers not only the inorganic chemistry of the elements but also analytical theoretical industrial organometallic bio inorganic and other cognate areas of chemistry The authors have broken with recent tradition in the teaching of their subject and adopted a new and highly successful approach based on descriptive chemistry The chemistry of the elements is still discussed within the context of an underlying theoretical framework giving cohesion and structure to the text but at all times the chemical facts are emphasized Students are invited to enter the exciting world of chemical phenomena with a sound knowledge and understanding of the subject to approach experimentation with an open mind and to assess observations reliably This is a book that students will not only value during their formal education but will keep and refer to throughout their careers as chemists Completely revised and updated Unique approach to the subject More comprehensive than competing titles

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