

# Main-group-based rings and polymers

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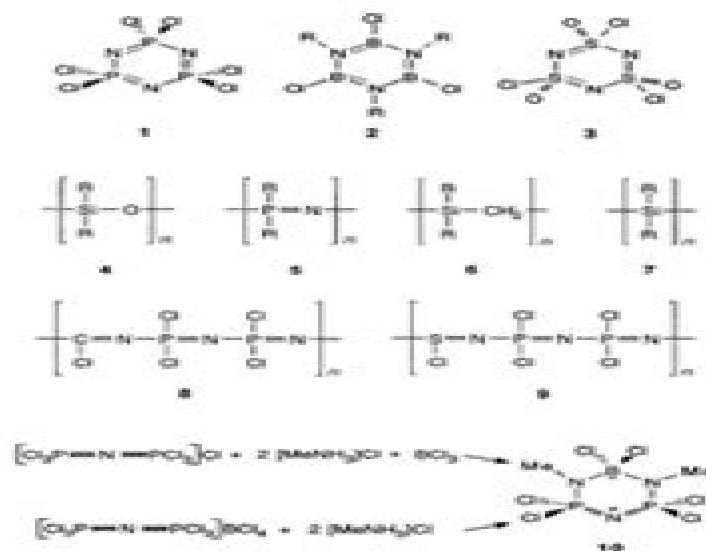
The synthesis and study of heterocycles containing main-group elements have played a pivotal role in the development of inorganic chemistry. Well known 'text-book' classes of inorganic rings include the cyclic phosphazene **1**, which was first prepared by Liebig and Rose<sup>1</sup> in 1834, and borazines such as **2**, the initial example of which was first synthesized by Stock and Pohland<sup>2</sup> in 1926. A further example is provided by sulfamides **3** which have been known since the 1950s.<sup>3</sup> 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.<sup>4</sup> 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,<sup>5,6</sup> novel cyclic tellurium imides,<sup>7</sup> and interesting aluminum–nitrogen heterocycles<sup>8</sup> among others.<sup>9</sup> 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.<sup>10</sup> The most well known and widely used current routes to high molecular weight polysiloxanes **4**,<sup>11</sup> polyphosphazenes **5**,<sup>12</sup> and poly(carbosilanes) **6**,<sup>13</sup> 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**,<sup>14</sup> poly(carbophosphazenes) **8**,<sup>15</sup> and poly(thiophosphazenes) **9**<sup>16</sup> 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.<sup>17,18</sup> 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.<sup>19,20</sup>

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 BP<sub>2</sub>N<sub>2</sub> ring was published by Sherif and Schmalbach<sup>21</sup> in 1966 and described the use of a [5 + 1] cyclocondensation reaction between [H<sub>2</sub>NPh<sub>2</sub>P=N–PPh<sub>2</sub>NH<sub>2</sub>]Cl and RBCl<sub>2</sub> (R = Ph or Cl) to yield boron–nitrogen–phosphorus heterocycles. However, by present day standards, the characterization was poor.<sup>22</sup> Nevertheless, applications of these rings as pesticides were claimed in a patent.<sup>23</sup>

The perchlorinated boron–nitrogen–phosphorus heterocycle **10** was subsequently synthesized by two very similar routes. In 1968 Becke–Goehring and Müller<sup>24</sup> reported the reaction of [Cl<sub>2</sub>P=N–PCl<sub>2</sub>]Cl with BCl<sub>3</sub> and [MeNH<sub>2</sub>]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.<sup>25</sup> This route involved the reaction of [Cl<sub>2</sub>P=N–PCl<sub>2</sub>]BCl<sub>3</sub> with [MeNH<sub>2</sub>]Cl and gave improved yields of 84–90%. Convincing structural characterization of this white crystalline compound was provided by NMR spectroscopy. For example, <sup>11</sup>B NMR showed a

# Rings Clusters And Polymers Of Main Group And Transition Elements

**Ferdinand Rodriguez, Claude  
Cohen, Christopher K. Ober, Lynden  
Archer**

## **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  $\text{Pt}_9\text{C}_4\text{B}_4$  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      **Proceedings of the Seventh International Symposium on Inorganic Ring Systems, IRIS VII** Tristan Chivers, 1995-02      **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      **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      **Principles of Polymer Systems, Sixth Edition** Ferdinand Rodriguez, Claude Cohen, Christopher K. Ober, Lynden Archer, 2014-12-09 Maintaining a balance between depth and breadth the Sixth Edition of Principles of Polymer Systems continues to present an integrated approach to polymer science and engineering A classic text in the field the new edition offers a comprehensive exploration of polymers at a level geared toward upper level undergraduates and beginning graduate students Revisions to the sixth edition include A more detailed discussion of crystallization kinetics strain induced crystallization block copolymers liquid crystal polymers and gels New powerful radical polymerization methods Additional polymerization process flow sheets and discussion of the polymerization of polystyrene and poly vinyl chloride New discussions on the elongational viscosity of polymers and coarse grained bead

spring molecular and tube models Updated information on models and experimental results of rubber elasticity Expanded sections on fracture of glassy and semicrystalline polymers New sections on fracture of elastomers diffusion in polymers and membrane formation New coverage of polymers from renewable resources New section on X ray methods and dielectric relaxation All chapters have been updated and out of date material removed The text contains more theoretical background for some of the fundamental concepts pertaining to polymer structure and behavior while also providing an up to date discussion of the latest developments in polymerization systems Example problems in the text help students through step by step solutions and nearly 300 end of chapter problems many new to this edition reinforce the concepts presented

*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

*Cluster Chemistry* Guillermo Gonzalez-Moraga, 2013-11-09 Cluster chemistry is one of the recent exciting areas of Inorganic Chemistry The occurrence of molecular clusters like fullerene C<sub>60</sub> constitutes a fundamental feature midway between the chemistry of isolated chemical compounds and that of the elements Main features of the Cluster Chemistry of both main group and transition metal elements are treated in this book The author highlights aspects related to the synthesis the structure the special bonding and the reactivity of these species The book is written as a textbook for senior undergraduate and postgraduate students References in tables and illustrations permit the reader to reach relevant original information Professor Gonzalez Moraga fills a demand for a publication appropriate for dissemination

and specially for teaching this exciting subject From the Contents Current Concepts in Modern Chemistry Transition Metal Cluster Chemistry Main Group Transition Metal Mixed Clusters Cluster Compounds of the Main Group Elements Synthetic Analogues of the Active Sites of Iron Sulfur Proteins      Introduction to Modern Inorganic Chemistry, 6th edition R.A. Mackay, 2017-12-21 This popular and comprehensive textbook provides all the basic information on inorganic chemistry that undergraduates need to know For this sixth edition the contents have undergone a complete revision to reflect progress in areas of research new and modified techniques and their applications and use of software packages Introduction to Modern Inorganic Chemistry begins by explaining the electronic structure and properties of atoms then describes the principles of bonding in diatomic and polyatomic covalent molecules the solid state and solution chemistry Further on in the book the general properties of the periodic table are studied along with specific elements and groups such as hydrogen the s elements the lanthanides the actinides the transition metals and the p block Simple and advanced examples are mixed throughout to increase the depth of students understanding This edition has a completely new layout including revised artwork case study boxes technical notes and examples All of the problems have been revised and extended and include notes to assist with approaches and solutions It is an excellent tool to help students see how inorganic chemistry applies to medicine the environment and biological topics      **Inorganic Reactions and Methods, The Formation of Bonds to C, Si, Ge, Sn, Pb (Part 1)** A. P. Hagen, 2009-09-17 For the first time the discipline of modern inorganic chemistry has been systematized according to a plan constructed by a council of editorial advisors and consultants among them three Nobel laureates E O Fischer H Taube and G Wilkinson Rather than producing a collection of unrelated review articles the series creates a framework which reflects the creative potential of this scientific discipline Thus it stimulates future development by identifying areas which are fruitful for further research The work is indexed in a unique way by a structured system which maximizes its usefulness to the reader It augments the organization of the work by providing additional routes of access for specific compounds reactions and other topics      **Polymer Yearbook** Richard A. Pethrick, 1991 This volume contains reviews on state of the art Japanese research presented in the annual Spring and Autumn meetings of the Japanese Polymer Science Society The aim of this section is to make information on the progress of Japanese Polymer Science and on topics of current interest to polymer scientists in Japan more easily available worldwide      *Inorganic Reactions and Methods, Oligomerization and Polymerization Formation of Intercalation Compounds* A. P. Hagen, 2009-09-17 For the first time the discipline of modern inorganic chemistry has been systematized according to a plan constructed by a council of editorial advisors and consultants among them three Nobel laureates E O Fischer H Taube and G Wilkinson Rather than producing a collection of unrelated review articles the series creates a framework which reflects the creative potential of this scientific discipline Thus it stimulates future development by identifying areas which are fruitful for further research The work is indexed in a unique way by a structured system which maximizes its usefulness to the reader It augments the organization of

the work by providing additional routes of access for specific compounds reactions and other topics      Chemistry of the Non-Metals Ralf Steudel, 2020-02-24 The current textbook is an excellent introduction to the chemistry of the non metallic elements The book begins by reviewing the key theoretical concepts of chemical bonding and the properties of different bonding types Subsequent chapters are focused on reactions structures and applications of the non metallic compounds Combining careful pedagogy and clear writing style the textbook is a must have for students studying inorganic chemistry

Metal Clusters in Chemistry Pierre Braunstein, Luis A. Oro, Paul R. Raithby, 2000-01-11 Metal cluster chemistry is at the cutting edge between molecular and solid state chemistry and has therefore had a great impact on the researchers working on organic coordination and solid state chemistry catalysis physics and materials science The development of new sophisticated synthetic techniques has led to enormous progress in the synthesis of this diverse class of compounds The number of clusters is growing rapidly since the possible variations in the metal and ligand sphere are numerous Modern bonding theories such as the isolobal principle have allowed a better understanding of the structures and properties of metal clusters and thus paved the way for the usage of these versatile materials Catalysis and nanomaterials are just two of the very promising application oriented fields Seventy six contributions written by world experts in this research field provide extensive coverage of different aspects of cluster chemistry ranging from synthesis structure determination and dynamics to applications Up to date information including an impressive collection of structural data and illustrations extensive coverage of the most important publications of the last decade and many more features make this three volume set a complete single source guide for all researchers working in the area of cluster chemistry      Chemistry of Arsenic, Antimony and Bismuth

N.C. Norman, 1997-12-31 This book provides a detailed wide ranging and up to date review of all aspects of the chemistry of the elements arsenic antimony and bismuth The chapters are written by an international team of authors each of whom is both active and expert in their particular field The coverage includes chapters on general properties and periodicity the elements themselves inorganic derivatives of the elements coordination and solution chemistry organocompounds organotransition metal compounds environmental and medicinal aspects and analytical methods This volume will be of particular value to graduate and postgraduate chemists and materials scientists in both industry and academia who are concerned with any aspect of the chemistry of these three elements and will also be an essential addition to the reference section of any chemistry library      **Phosphazenes** Mario Gleria, R. De Jaeger, 2004 The main aim of this book is to provide a complete picture of current research on phosphazene compounds carried out around the world The book opens with a general introduction then moves on to cover synthetic aspects of phosphazene polymers their characterization in solution and from the theoretical thermal and mechanical points of view application aspects of poly organophosphazenes and the synthesis characterization and practical utilization of cyclophosphazenes There is particular focus on the use of cyclophosphazenes as hydraulic fluids and additives as cores for star polymers or dendrimers and as starting substrates for

supramolecular chemistry and nanostructured materials The spectroscopic characterization of these compounds by NMR and Raman techniques is also discussed Annotation 2004 Book News Inc Portland OR booknews com

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