

***The Synthesis
and
Characterization
of
Inorganic Compounds***

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William L. Jolly

Professor of Chemistry

University of California, Berkeley

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The Synthesis
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dedicated to

LUDWIG FREDERICK AUDRIETH (1901–1967)
who taught the importance of analogy

and

WENDELL MITCHELL LATIMER (1893–1955)
who taught the importance of thermodynamics

Preface

Inasmuch as inorganic chemistry encompasses a wide variety of chemical structures and reactions, inorganic synthesis is a difficult and challenging field, in which chemists must be exceptionally versatile. Almost all aspects of chemistry are touched on — the systematization of chemical reactions with thermodynamics and kinetics, the determination and prediction of structure, the correlation and prediction of physical properties, the theory of chemical bonding, chemical analysis, and the design and manipulation of laboratory apparatus. Besides possessing competence in these areas, synthetic chemists must be imaginative and must know how to apply analogies to the solution of problems.

The purpose of this book is to discuss the important principles and techniques applicable to synthetic inorganic chemistry. Because I cannot write authoritatively on all the topics described above, some chapters in this book are necessarily brief and introductory. Nevertheless, I believe that these topics should be discussed in a single book by one author for the following reasons: (1) the level of discussion is consistent throughout the text, (2) relationships between topics can be readily indicated, and (3) the

book is made cohesive by the central theme of chemical synthesis. I hope the book can serve as a useful reference and guide for all experimental chemists. I believe it can be used as a text for several kinds of physical and inorganic chemistry courses.

I wish to thank my colleagues who examined parts of the manuscript and offered constructive criticism: Leo Brewer, Robert E. Connick, Rollie J. Myers, Richard E. Powell, and Kenneth N. Raymond.

WILLIAM L. JOLLY

Berkeley, California

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Introduction

1

THE PREPARATION OF NEW COMPOUNDS

Why do chemists prepare new compounds?¹ This question may seem inappropriate in a book the main purpose of which is to describe *how* chemists prepare new compounds. In fact, devotees of pure research may well consider the question irrelevant and trivial. However, it must be remembered that among the readers of this book are students who have not yet engaged in research and who have not enjoyed the thrill of original discovery. Naturally, such students will seek some sort of justification for a scientific endeavor like inorganic synthesis.

Discovery Through Curiosity

Curiosity led Alfred Stock to the discovery of an entirely new class of compounds: the boron hydrides and their derivatives. Stock has stated² that in

¹ Some of the material in this chapter first appeared in *J. Chem. Educ.*, **36**, 513 (1959).

² A. Stock, *Hydrides of Boron and Silicon*, Cornell University Press, Ithaca, N.Y., 1933.

1912 he chose to study the boron hydrides because he felt that boron, the neighbor of carbon in the periodic system, might be expected to form a much greater variety of interesting compounds than merely boric acid and the borates, which were almost the only ones known at that time. But Stock probably never dreamed that, in the following twenty years, he and his co-workers would prepare such an extensive and fascinating series of compounds as is described in his monograph, "Hydrides of Boron and Silicon."² Some of these compounds are shown in Fig. 1.1. In retrospect, Stock stated,

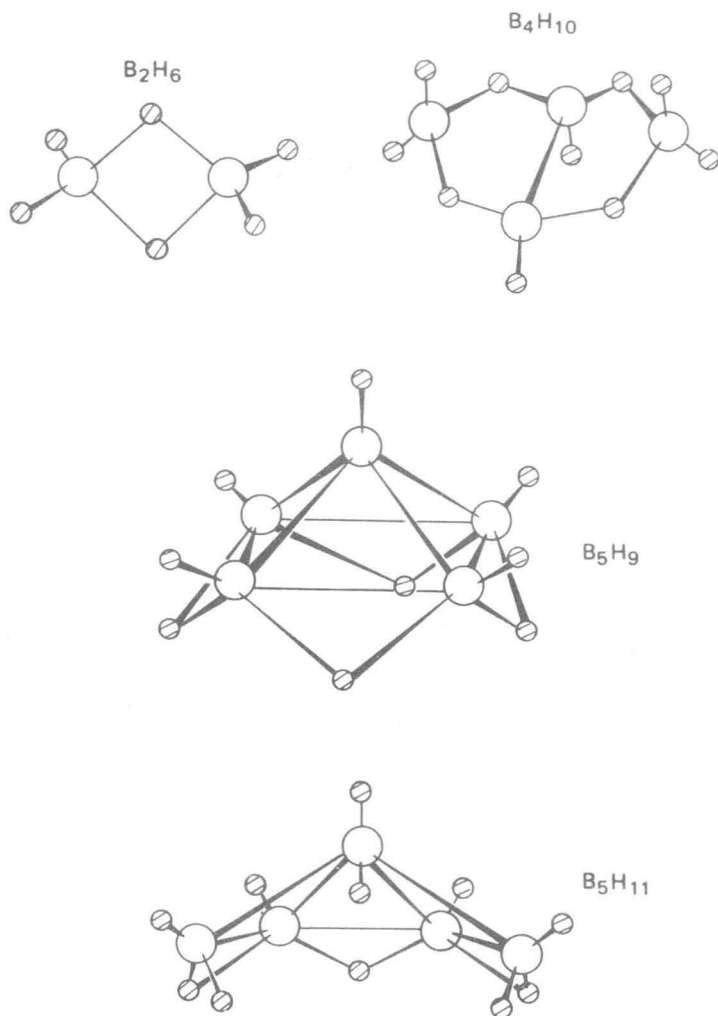
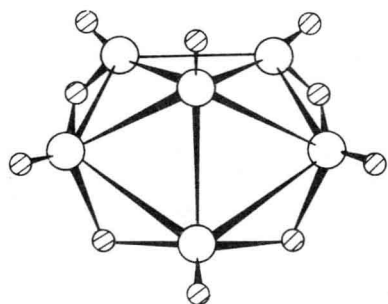
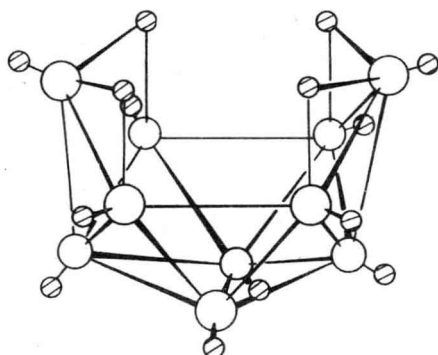
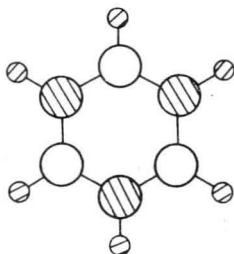


FIG. 1.1. Some compounds discovered by Stock and his co-workers.

 B_6H_{10}  $B_{10}H_{14}$  $B_3N_3H_6$

“The chemistry of boron has proved unexpectedly rich in results and many-sided in character although, just as in the case of silicon, the mobile portion of its chemistry is confined to the laboratory. In nature boron’s dominating affinity for oxygen restricts it to the monotonous role of boric acid and the borates and prevents it from competing with carbon, its neighbor in the periodic system.”² These words were written in 1932. Surely Stock would have been amazed if he could have known of the rapid development of boron chemistry in the 1960’s. Even modern chemists marvel at the synthesis and characterization of polyhedral boranes, such as that shown in Fig. 1.2.³

³ J. N. Francis and M. F. Hawthorne, *J. Am. Chem. Soc.*, **90**, 1663 (1968).

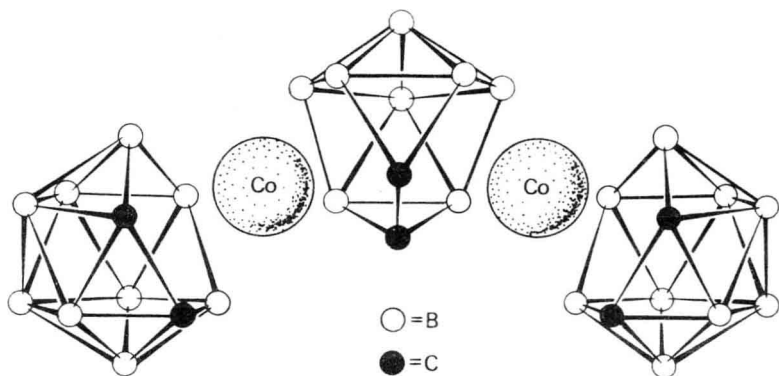


FIG. 1.2. The structure of the red anion³ $B_{26}C_6H_{32}Co_2^{2-}$. All the carbon atoms and boron atoms are bonded to hydrogen atoms (not shown). Structure determined by D. H. Templeton, A. Zalkin, and D. J. St. Clair. Reproduced with permission of the American Chemical Society.

“Accidental” Discovery

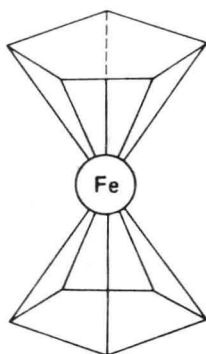
Simple chance, coupled with astute observation, has been responsible for the discovery of many new compounds. Often, in the course of what is thought to be a straightforward synthesis or investigation, something completely unexpected happens. Perhaps a precipitate forms, a gas is evolved, a reaction mixture turns an unusual color, or a yield of expected product is very low. Unfortunately, the average chemist usually ignores such phenomena and goes on to work he can understand. But the curious chemist tries to find out what “went wrong” and in the process usually makes a significant—sometimes a spectacular—discovery.

Let us consider the unsuccessful, yet famous, attempt of Kealy and Pauson⁴ to prepare dihydro-fulvalene (dicyclopentadienyl) by the coupling of cyclopentadienyl radicals. These investigators attempted the synthesis by the oxidation of cyclopentadienylmagnesium bromide by ferric chloride. (The technique of treating a Grignard reagent with ferric chloride is a well-known method for preparing hydrocarbons—for example, diphenyl from phenylmagnesium bromide.) However, they obtained no dihydro-fulvalene. Instead, they isolated a remarkably stable organo-iron compound, which they identified as bis(cyclopentadienyl)iron(II). In their reaction, the ferric chloride presumably was first reduced to ferrous chloride by the Grignard reagent and the following reaction then took place:



Later studies showed the bis(cyclopentadienyl)iron(II) (“ferrocene”) to have the illustrated “sandwich” type of structure.

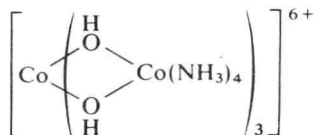
⁴ T. J. Kealy and P. L. Pauson, *Nature*, **168**, 1039 (1951).



Soon after this discovery, better synthetic methods were developed for preparing ferrocene, and analogous compounds of the other transition metals were prepared.⁵

Testing Theories by Synthesis

There are innumerable examples of compounds that were prepared for the first time to test the validity of a theory. In 1893, Alfred Werner proposed his now famous coordination theory to explain the properties of inorganic "complex compounds."⁶ At the time of its proposal it was a revolutionary doctrine, and for many years it met with criticism. Although some of the criticisms were not well founded, others were thoroughly sound and challenged Werner's ingenuity and experimental skill to the utmost. For example, the theory predicted optical isomerism for certain types of hexa-coordinate complexes, and Werner succeeded in resolving the *cis* form of the $\text{Co(en)}_2(\text{NH}_3)\text{Br}^{2+}$ ion into (+) and (-) forms.⁷ But his unyielding critics argued that the optical activity centered in the carbon atoms of the ethylenediamine molecules (even though they are optically inactive themselves). Werner⁸ provided final proof that the optical activity of such compounds lay in the geometrical configuration about the metal ion by effecting the resolution of a complex containing no carbon, the μ -hexahydroxododecaamminetetracobalt(III) ion:



⁵ G. E. Coates, *Organo-Metallic Compounds*, 2nd ed., John Wiley & Sons, Inc., New York, 1960, pp. 233-359.

⁶ A. Werner, *Z. anorg. Chem.*, **3**, 267 (1893).

⁷ A. Werner, *Ber.*, **44**, 1887 (1911). See Chapter 23 for a discussion of optical activity.

⁸ A. Werner, *Ber.*, **47**, 3087 (1914).

Discovery to Fulfill a Need

New compounds are often prepared because they are urgently needed. A problem that arose during the Atomic Bomb Project of World War II was the need to handle the very reactive molten metals uranium and plutonium. In a search for new refractories that could easily be formed and sintered into crucibles, yet would be stable and refractory, it was felt that certain sulfides might be useful. Preliminary thermodynamic calculations and estimations indicated that the most stable sulfides should lie in the periodic table around thorium and the rare earth metals. Accordingly, the sulfides of the most abundant rare earth, cerium, were investigated.⁹ The theretofore unknown CeS was found to be a particularly good refractory that is useful whenever one wishes to avoid contamination of very electropositive metals by oxygen.

It is also interesting that most of the impetus for the renaissance of boron hydride chemistry beginning around 1941 was provided by a need for materials of importance to national defense. From 1941 to 1945 a great deal of effort was expended in an attempt to find a volatile uranium compound that could be used in the separation of the natural uranium isotopes, by either gaseous diffusion, centrifugation, thermal diffusion, or distillation. (Uranium hexafluoride was a known compound at the time and was eventually used, but it was feared that it might prove too difficult to prepare and handle on a large scale.) The fact that the hydroborates of aluminum and of beryllium had proved to be the most volatile compounds of these elements suggested the attempt to prepare a hydroborate of uranium. Uranium(IV) hydroborate, $U(BH_4)_4$, as well as the methyl derivatives, $U(BH_4)_3(BH_3CH_3)$ and $U(BH_3CH_3)_4$, were prepared and proved to be the most volatile uranium compounds other than the hexafluoride.^{10,11} But of more interest than the preparation of these compounds were the results of efforts to improve the methods of preparing the starting materials and the intermediates required for the preparations. **Many new types of reactions were observed, hitherto unknown compounds were discovered, and the chemistry of the boron hydrides was greatly enlarged.**¹²

Immediately after **World War II, a program for the development of boranes as fuels for air-breathing engines was started.**¹³ This effort led to the intensive study of many novel alkylated boranes and to the discovery of the remarkably stable class of compounds known as carboranes. Even after

⁹ E. D. Eastman, L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, *J. Am. Chem. Soc.*, **72**, 2248 (1950).

¹⁰ H. I. Schlesinger and H. C. Brown, *J. Am. Chem. Soc.*, **75**, 219 (1953).

¹¹ H. I. Schlesinger, H. C. Brown, L. Horvitz, A. C. Bond, L. D. Tuck, and A. O. Walker, *J. Am. Chem. Soc.*, **75**, 222 (1953).

¹² H. I. Schlesinger and H. C. Brown, *J. Am. Chem. Soc.*, **75**, 186 (1953).

¹³ R. T. Holzmman, ed., *Production of the Boranes and Related Research*, Academic Press Inc., New York, 1967.