



Review

Synthesis and serendipity in boron chemistry: A 50 year perspective[☆]

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ABSTRACT

Chance discovery is ubiquitous in the history of science, especially in areas where theory has tended to lag behind experimental findings. In fields such as organometallic and boron cluster chemistry, serendipity has been particularly important in opening new directions and shaping the evolution of these fields. In this article selected examples from the author's half century of research in borane, carborane, and metallaborane chemistry are used to illustrate the often intricate interplay between unexpected findings and targeted synthesis.

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1. Introduction

The role of chance in science has a long history, from the accidental discoveries of the planets Uranus and Pluto and the elements helium and iodine, to Fleming's fortuitous encounter with the penicillin mold, Penzias and Wilson's observation of cosmic background

[☆] Serendipity (ser-ən-dip-i-tē), *noun*. The faculty or phenomenon of finding valuable or agreeable things not sought for.

From the Persian fairy tale *The Three Princes of Serendip*.

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radiation supporting the Big Bang theory, and countless other well-known examples. While this topic can be discomfiting (perhaps because it tends to undercut our image of science as an orderly progression in man's understanding of the Universe), important turning points have often come about through accident. In chemistry, serendipity has made its appearance many times and in many areas of study, especially in inorganic and organometallic chemistry. The discovery of ferrocene (FeCp_2 , $\text{Cp} = \text{C}_5\text{H}_5$) is a well-known example. Neither of the two groups that first prepared this compound independently by different routes in 1951 [1,2] realized that they had on their hands a new type of metal complex with an almost unimaginable (at that time) molecular structure, but the "iron sandwich" geometry was soon recognized by Robert B. Woodward and Geoffrey Wilkinson [3] and by Ernst Otto Fischer [4].

On some occasions, the confluence of serendipity and planned synthesis has had far-reaching consequences. The original preparation of metallocarboranes by Hawthorne, Young and Wegner in 1965 [5] was "designed" in that the open face of the $\text{C}_2\text{B}_9\text{H}_{11}^{2-}$ (dicarbollide) ion was assumed to be electronically analogous to the cyclopentadienide ion, C_5H_5^- , and hence its reaction with FeCl_2 to yield the sandwich $\text{Fe}^{\text{II}}(\text{C}_2\text{B}_9\text{H}_{11})_2^{2-}$ and its oxidation product $\text{Fe}^{\text{III}}(\text{C}_2\text{B}_9\text{H}_{11})_2^-$ was in line with expectation by these workers. However, the dicarbollide ion itself, and its protonated version ($\text{C}_2\text{B}_9\text{H}_{12}^-$), had been rather surprising products of the treatment of *o*-carborane ($1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$) with bases [6]. Given the extraordinary stability of this carborane towards strong acids and oxidants, it was remarkable to find that attack by hydroxide ion, alkoxides, or other nucleophiles cleanly removes one BH^{2+} unit to create a C_2B_3 open face while leaving the remainder of the cage intact. Taking this finding a step further by introducing metal ions, effectively merging boron and transition metal chemistry in a single experiment, was a pivotal moment in the history of inorganic and organometallic chemistry.

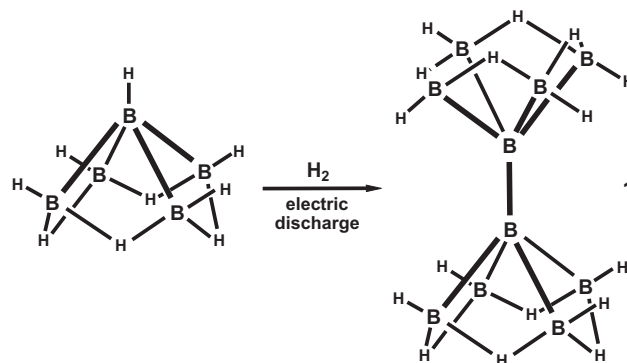
My purpose in this article is not to recount the history of serendipity in chemistry, but rather to discuss its interaction with designed synthesis via a few selected examples in the area of polyhedral boron clusters. Chance discovery may seem less important today than in years past, owing to tremendous advances in computational theory and computer power, synthetic methods, and laboratory instrumentation. Moreover, in research supported by U.S. Government agencies such as the National Science Foundation, the strong current emphasis on development of practical applications discourages projects of a primarily exploratory nature, at least for chemists; in astronomy and high-energy physics, exploration is still the main focus. But nature is still cleverer than we are, and will continue to confound us with unexpected findings for years to come, especially in still-evolving fields such as polyhedral boron chemistry. In this article I will describe a few personal encounters with the role of serendipity in boron chemistry and its interaction with designed synthesis over several decades.

2. Some accidental discoveries

2.1. Decaborane-16

As a graduate student of W. N. Lipscomb at Harvard in the early 1960s in his transplanted group from Minnesota, I was asked by the Colonel to explore the possibility of synthesizing carboranes (polyboron hydrides containing carbon in the skeletal framework, at that time unreported in the journal literature) by subjecting mixtures of volatile boranes and alkynes, e.g., B_5H_9 and acetylene, to an electric discharge in an air-free glass vacuum line. Before starting to work with borane–hydrocarbon mixtures, I elected first to explore the behaviour of B_5H_9 alone in a discharge, a topic on which in 1961 I could find almost no information in the literature. The products I

obtained at first were unexciting, mainly nonvolatile amorphous solids and decaborane-14 ($\text{B}_{10}\text{H}_{14}$). Dilution of the pentaborane with helium gave much the same result. However, when a mixture of B_5H_9 and H_2 gas was exposed to the discharge a new product appeared, with curious properties. A solid at room temperature, it was far more volatile than the well-known $\text{B}_{10}\text{H}_{14}$; unlike the latter hydride, crystals of the new compound on the inside walls of the evacuated room-temperature glass vacuum line easily sublimed away on merely touching the outside of the glass with one's finger. Intriguingly, the infrared spectrum of this material was closely similar to that of B_5H_9 itself, and when elemental analysis confirmed the formula $\text{B}_{10}\text{H}_{16}$, structure **1** with two pyramidal B_5H_8 units connected apex-to-apex seemed likely. Such a molecule would exhibit most of the vibrational modes of B_5H_9 itself, accounting for the similarity of the IR spectra. An X-ray diffraction study confirmed the $1,1'-(\text{B}_5\text{H}_8)_2$ geometry shown [7].



The serendipitous preparation more than 50 years ago of this molecule, the first example of a linked-cage boron hydride (and the first having boron atoms with no attached hydrogens) [8], is curious in that it has been obtained only in a discharge in the presence of H_2 ; to my knowledge no other route affording isolable amounts of this compound has ever been reported. All attempts to develop alternative syntheses, such as Wurtz-type coupling of $1\text{-BrB}_5\text{H}_8$ (bromopentaborane) via reaction with alkali metals, have been unsuccessful, although both of the other two possible linked-cage isomers, $1,2'$ - and $2,2'$ - $(\text{B}_5\text{H}_8)_2$, have been prepared in other laboratories [9,10]. Since H_2 is known to generate atomic H under electric discharge conditions, we have conjectured that the apex hydrogen on B_5H_9 is attacked by H^\bullet to generate H_2 and $\bullet\text{B}_5\text{H}_8$ radicals with the latter combining to generate $1,1'-(\text{B}_5\text{H}_8)_2$, but this has not been established. The chance discovery of $1,1'-(\text{B}_5\text{H}_8)_2$ contrasts with the synthesis of another new boron hydride, $\text{B}_{12}\text{H}_{16}$, in our laboratory a quarter-century later, this time by design (see Section 3.1 below).

2.2. Polyhedral metallaboranes and metal–boron hybrid clusters

The discovery of metallocarboranes by the Hawthorne group in 1965, noted earlier, suggested that closed polyhedral metal–boron clusters lacking carbon in the skeletal framework might also be stable, but as late as 1973 none had been structurally characterized although a few open-cage metallaboranes such as $\text{Zn}(\text{B}_{10}\text{H}_{12})_2^{2-}$ were known [11,12]. At that time our group at Virginia began to explore reactions of transition metal ions with borane anions in nonaqueous media. In what could be described as "semi-serendipitous" chemistry, in the sense that we were looking for metallaboranes but could not predict what species might be produced, we found that the *nido*- B_5H_8^- ion, generated from B_5H_9 by deprotonation with NaH , interacts with CoCl_2 and $\text{Na}^+(\text{C}_5\text{H}_5)^-$ in cold THF to yield a series of cobaltaboranes [13]. Among the

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