The 1976 Nobel Prize for Chemistry

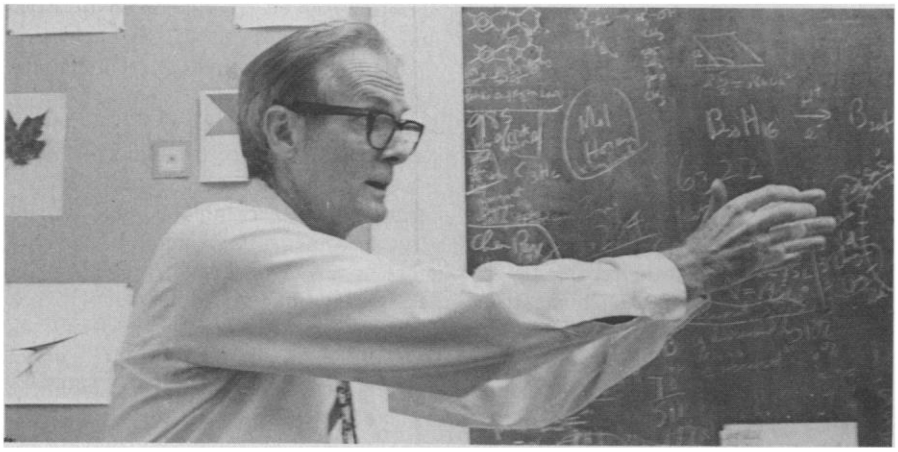
The 1976 Nobel Prize for Chemistry has been awarded to William Nunn Lipscomb, Jr., of Harvard University for his original research on the structure and bonding of boron hydrides and their derivatives. This honor was given in recognition of theoretical and experimental work over a span of more than 25 years, during which the field of boron chemistry has experienced a dramatic metamorphosis from a highly esoteric (some would say obscure) corner of chemistry into a major area having impact on many other fields—especially organic, organometallic, and polymer chemistry. Many individuals and a number of research groups throughout the world have played important roles in this evolution, but in the effort to develop a viable theory of structure and bonding for these remarkable molecules Lipscomb has long been the dominant figure.

The Nobel Prize is the latest in a long series of honors that have come to Lipscomb, and is particularly timely in its recognition of high achievement in the advancement of fundamental understanding of the chemical bond. It is in this sense—in its impact on theoretical and experimental chemists and their perception of what induces stability in molecules—that Lipscomb's work derives its greatest significance. The boranes, although interesting in their own right, have a profound message for the rest of chemistry, which is fundamentally this: the structures and bonding in molecular frameworks are not, after all, limited by the old Lewis concept of an electron pair joining each pair of bonded atoms. Instead, there exists a vast and diverse chemistry in which stable, cage-like molecules hardly imaginable a few years ago are now routinely synthesized. Although this new chemistry is by no means restricted to boron and prominently features carbon, phosphorus, many transition metals, and indeed nearly half the elements in the periodic table, it is fair to say that it all began with the boron hydrides—and it is here that Lipscomb's powerful insight and creative imagination have been so effectively felt.

Lipscomb was born in Cleveland in 1919 and graduated with a B.S. degree from the University of Kentucky in 1941, an association which earned him the nickname "Colonel" among his close associates long before he was officially named a Kentucky Colonel by the governor of that state. He completed his graduate education at the California Institute of Technology, receiving the Ph.D. degree in 1946, and while there was strongly influenced by Professor (later Nobel laureate in Chemistry) Linus Pauling. At the time, the structures of the boron hydrides were a frustrating problem for theoretical chemists, primarily because the "electron deficiency" of the boron atom—its combination of four valence orbitals with only three electrons, as opposed to carbon which has four of each—seemed to rule out hydrocarbon-like chain or ring structures for the boranes. Years before, several hydrides including diborane (B_2H_6) and higher homologs such as B_4H_{10}, B_5H_9, B_5H_{11}, and $B_{10}H_{14}$ had been prepared and characterized in a monumental piece of work by the great German chemist Alfred Stock; the structures, however, were unknown. The shape of B_2H_6 had been the subject of much speculation (the correct structure was predicted by W. Dilthey as far back as 1921) and was eventually established experimentally by W. C. Price in 1947, but the higher boranes were a total mystery which intrigued Lipscomb as a graduate student and as a young assistant professor at the University of Minnesota.

In 1948 came a major development, when J. S. Kasper, C. M. Lucht, and D. Harker published preliminary results on the structure of $B_{10}H_{14}$ and revealed it to have a basket-like arrangement of boron atoms, totally unlike the hydrocarbons and not remotely predicted by anyone. It was clear that the key to experimental elucidation of the boron structures lay in the technique of x-ray diffraction, and Lipscomb began an intensive program of x-ray structural investigations which has continued to the present, eventually revealing the structures of all the remaining Stock boranes as well as numerous others. This was in itself a notable achievement because the majority of the original boranes were highly volatile, pyrophoric, and reactive materials which required vacuum-line handling and the collection of x-ray data at low temperatures—even today a difficult operation experimentally, but especially so two decades ago when x-ray work was a slow and tedious process. The pattern that emerged as the geometries of B_5H_9 (a square pyramid), B_6H_{10} (a pentagonal pyramid), B_5H_{11} (a distorted square pyramid), and other boranes were successively examined was bewildering and seemed to lack a clear guiding principle, in sharp contrast to the chain hydrocarbons, where each member bears a clear and predictable relationship to the next. Lipscomb, determined not only to establish the structures but to understand them as well, considered the concept of three-center bonding which had been invoked by H. C. Longuet-Higgins to account for the hydrogen bridges in diborane. In such a bond, a hydrogen atom is linked to two boron atoms by a single pair of electrons. The crucial extension of this idea, first proposed by Lipscomb in collaboration with Bryce Crawford, Jr., and W. H. Eberhardt in a classic 1954 paper in the *Journal of Chemical Physics*, was that one pair of electrons could also serve to link three boron atoms in a B–B–B three-center bond. With the proper combination of three-center and two-center bonds, so that the numbers of available valence orbitals and valence electrons in the molecule are properly balanced, even the most complex borane cage structures could be described in this language.

This concept was the key to the devel-



William Nunn Lipscomb, Jr.

opment of a topological theory of bonding in the boranes, which not only provided a plausible explanation of the known structures but, more importantly, made possible the prediction of new compounds, thus guiding the efforts of synthetic chemists and paving the way for the profusion of new kinds of borane molecules which was to follow. It was now clear why the boron hydrides and the hydrocarbons differ so drastically in structure: the boranes, lacking sufficient electrons to utilize a pair for each bonding interaction, fold in on themselves to form three-dimensional cage frameworks held together in part by three-center bonds. Moreover, these are stable frameworks; the electron deficiency of boron influences geometry but does not in itself detract from stability, as witness the carboranes, which far outstrip most organic compounds in resistance to chemical and thermal stress.

In a stream of elegant papers over the next quarter-century Lipscomb and his co-workers developed the basic principles of the topological theory in increasingly sophisticated ways, utilizing molecular orbital methods and high-speed computers. Not only geometric structure but charge distribution and chemical reactivity were predicted, and where data were available, correlated with experiment. A measure of the magnitude of this contribution is that, although by the early 1960's the boranes were the largest known family of molecular hydrides other than the hydrocarbons, nearly all the the general theory developed to deal with these compounds had come from Lipscomb and his associates.

In 1959 Lipscomb accepted a professorship at Harvard, later assuming the Abbott and James Lawrence chair in chemistry. With his research group transplanted from Minnesota and the addition of several new students and postdoctoral investigators, the theoretical and x-ray studies of the boranes were extended and a program of synthesis was initiated, eventually producing several new boranes and, of course, their structures. A separate effort in the group was directed toward x-ray studies of complex protein structures, a program which has produced major contributions in that area as well. Meanwhile, Lipscomb's systematization of borane structural chemistry had laid the foundation for major advances, since synthetic chemists were now equipped with a working rationale. Many of the new developments such as carboranes (borane cages containing carbon atoms bound into the framework) and the polyhedral $B_nH_n^{2-}$ ions were anticipated by Lipscomb years before their actual isolation was reported.

The synthesis of polyhedral carboranes by several industrial groups added a new dimension to borane chemistry, and here also Lipscomb and his collaborators played a leading role in its development through x-ray studies of key compounds, molecular orbital treatments leading to predictions of relative stabilities, calculations of charge distribution, and experimental and theoretical investigation of polyhedral cage rearrangements. Meanwhile the carboranes attracted wide interest because of their unusual structure and properties. Compounds such as the icosahedral $C_2B_{10}H_{12}$ isomers, pentagonal bipyramidal $C_2B_5H_7$, and many others proved extremely stable (p-$C_2B_{10}H_{12}$ withstands 700°C over prolonged periods) and have been successfully utilized in the synthesis of polymeric materials having extraordinary resistance to thermal and chemical degradation. Perhaps even more significantly, the carboranes demolished old notions about the structural role of carbon. With carbon frequently assuming a coordination number of five or six, the carboranes constitute an extension of carbon chemistry which has profound (but not yet fully recognized) implications for the future directions of organic synthesis. Thus, the pyramidal molecules $C_4B_2H_6$ and $C_3B_3H_7$ are in fact new kinds of organic heterocycles, albeit ones that have not yet penetrated the sanctums of standard organic textbooks. Sooner or later, it seems clear that organic chemists will have to come to grips with the revolution in our concept of the covalent bond that has been brought about through the medium of boron chemistry, so strongly influenced and guided by Lipscomb.

The insight into electron-deficient borane structures originally provided by Lipscomb carries over not only to the carboranes but also to their organic cousins, the so-called "nonclassical" carbonium ions. The three-center bond descriptions given by Lipscomb to B_5H_9 and B_6H_{10} can as easily be applied to their hydrocarbon analogs, the pyramidal ions $C_5H_5^+$ and $C_6H_6^{2+}$, both presently known as alkyl derivatives. As other new types of electron-deficient cage molecules are discovered, the broad application of Lipscomb's original borane structural theory is becoming more and more apparent. Molecules not normally regarded in this sense, for example, metallocenes, organometallics such as $(C_4H_4)Fe(CO)_3$ or $[(CO)_3Fe]_5C$, metal clusters, and many others, can be viewed as borane analogs. Thus the boranes, once viewed as molecular mavericks, have in fact provided the key to conceptually link a whole vast array of cluster-type molecules for which classical Lewis bond descriptions fail.

Although the main thrust of Lipscomb's research has been in molecular structure and bonding theory, his work in borane chemistry has covered broad areas and there is scarcely any aspect of that field to which he has not made major contributions. His book, *Boron Hydrides*, published in 1963, is a mine of ideas ranging far beyond the confines suggested by its title. In a series of papers and in a later book with Gareth Eaton he dealt with the problem of ^{11}B nuclear magnetic resonance and its correlation with molecular structure. And in one of the more promising areas of application of boron chemistry, the use of boron compounds in radiation therapy of brain tumors, Lipscomb's group has been one of several reporting important synthetic advances in recent years.

Throughout all of this work and over the years, the dominant personal characteristics of Professor Lipscomb have been an unfailing scientific imagination, a refusal to accept the limitations imposed by current dogma, an ability to perceive relationships often missed by others, and, above all, a delight in the intellectual challenge of uncovering scientific truth. An accomplished clarinetist who plays chamber music regularly with professionals (and who once seriously considered a musical career), Lipscomb is a many-sided individual, a member of the Baker Street Irregulars (devotees of Sherlock Holmes), and a man capable of quoting Lewis Carroll in papers on valence bond theory. The atmosphere in his laboratory has always been one of free-wheeeling discussion of new possibilities in synthesis, structure, and chemical bonding, in which free rein is given to the imagination. In his 1954 paper with Eberhardt and Crawford on the valence structure of the boron hydrides, the philosophy stated at the outset is "We have even ventured a few predictions, knowing that if we must join the ranks of boron hydride predictors later proved wrong, we shall be in the best of company." His willingness to risk occasional error as the price to be paid for opening new vistas in chemistry has served science well and has set a superb example for others to follow. In an era when basic science has been on the defensive, this year's Nobel award in chemistry is a reminder of its indispensable role and a fitting recognition of one of the extraordinary scientific innovators of our time.

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