RESEARCH NEWS

The 1973 Nobel Prize for Chemistry

The 1973 Nobel Prize for Chemistry has been awarded jointly to Ernst Otto Fischer of the Technische Universität in Munich, Germany, and Geoffrey Wilkinson of Imperial College in London for their pioneering research in organometallic chemistry. In particular, their independent and imaginative efforts in the development of the chemistry of "sandwich" complexes of the transition metals are cited. This work revolutionized the field of organometallic chemistry and has had very significant impact on the broader fields of inorganic, organic, and theoretical chemistry.

The entry of both of this year's Nobel laureates in chemistry into the transition metal-organic field was prompted by two reports, in 1951, of serendipitous preparations of a remarkably stable organoiron compound, dicyclopentadienyliron. To Fischer, who was just beginning his academic career at the Technische Hochschule in Munich, and to Wilkerson, who was in his first year as an assistant professor at Harvard University at that time, its formulation as a σ-bonded species stabilized by ionic-covalent resonance seemed insufficient to explain the extraordinary thermal and chemical stability of this compound. Both were intrigued enough to begin independent experimental investigations on this new organometallic compound. Fischer, in collaboration with W. Pfab, published the results of an x-ray crystal structure determination in 1952 which unambigously established the novel π-complexed sandwich structure (Fig. 1a) for this compound. Wilkinson, in collaboration with M. Rosenblum, M. C. Whiting, and R. B. Woodward, arrived at the same structural conclusion on the basis of chemical, physical, and spectroscopic studies also published in 1952. This compound was christened "ferrocene" after its high aromatic reactivity had been established. The field of "metallocene chemistry" and, in succeeding years, the broader area of transition metal–organic chemistry underwent rapid, almost explosive, development after this breakthrough that stirred the interest and imaginations of inorganic, organic, and theoretical chemists alike. It is noteworthy that both Fischer and Wilkinson have continued as pacesetters and creative innovators in this area to this day. They have continued to make important original contributions which have kept transition metal–organic chemistry a fast-moving and exciting field that has continued to attract young chemists in large numbers.

Ernst Otto Fischer was born in Solln, near Munich, on 10 November 1918, the son of Professor Karl T. Fischer of the Physics Institute of the Technische Hochschule in Munich. His education in chemistry at the Technische Hochschule, which was delayed by his military service before and during World War II, was begun during a semester of study leave in 1941–42 and was continued after the war. He became closely acquainted with the field of organometallic chemistry during his Ph.D. thesis research under the supervision of Professor Walter Hieber, the father of modern metal carbonyl chemistry. After obtaining his Ph.D. degree in 1952, Fischer continued his career at the Technische Hochschule as a scientific assistant engaged in independent research. It was during this time that Fischer, together with his first research students, began work in the metallocene area. The determination of the structure of ferrocene was followed in rapid succession by the preparation of similar sandwich derivatives of cyclopentadienyl and indenyl ligands with other transition metals, thus establishing the general occurrence of such structures. After his *Habilitation* at the Technische Hochschule, Fischer was appointed a dozent and continued his research on organic compounds of transition metals in a series of studies that confirmed him as one of the front-runners in this area, a position which he still maintains today, 20 years later. In a brilliant extrapolation of his views concerning structure and bonding of the π-cyclopentadienyl complexes, Fischer predicted that dibenzenechromium(0), a π-complex in which a *neutral* chromium atom is sandwiched between two *neutral* benzene molecules, should be capable of existence, a view considered rather heretical at the time. However, aided by the outstanding abilities in synthetic chemistry of his co-worker Walter Hafner, Fischer was able to develop a high-yield synthesis of this molecule (Fig. 1b).

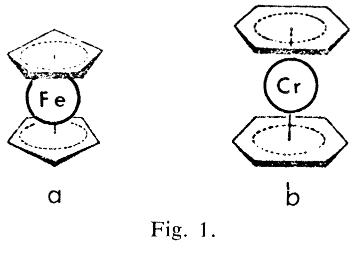

Fig. 1.

This important breakthrough was followed by a rapid development of the chemistry of arene-metal complexes of the transition metals in Fischer's laboratories. In 1957 he became a professor in the Institute of Inorganic Chemistry at the University of Munich, and in 1964 returned to the Inorganic Chemistry Laboratory of the Technische Hochschule of Munich as successor of its retiring director, Professor Hieber. In these years his scientific work was concerned with further development of π-complexed carbocyclic-transition metal complexes and with investigations of transition metal complexes of mono-, di-, and oligoolefins.

A notable new contribution to the development of transition metal organic chemistry was the preparation in 1964 by Fischer and Maasböl of $(OC)_5WC(OCH_3)CH_3$, the first carbene complex of a transition metal to be recognized as such. The development of this new class of compounds has proceeded at a rapid rate through efforts in many laboratories throughout the world, but the Munich group has continued in the forefront.

Under Professor Fischer's direction, the Inorganic Chemistry Laboratory of the Technische Hochschule (now Technische Universität) of Munich has become one of the leading centers in the world for research in organometallic chemistry. The outstanding tradition in synthetic chemistry has been continued in full vigor, but expertise in all modern aspects of spectroscopy and structural chemistry has been carefully developed and nourished. The laboratory has been excellently equipped for all the various spectroscopies, as well as for x-ray structural studies. Well-trained junior staff members active in these areas are able to work independently, but they also provide the vital support that the synthetic programs require. An excellent example of the successful collaboration within this

Ernst O. Fischer

Geoffrey Wilkinson

laboratory is provided by the recent publication describing Fischer's latest exciting contribution, the synthesis of the first carbyne complexes of a transition metal, $X(OC)_4W{\equiv}CPh$ (X, halogen) in which the carbon atom is triply bonded to the metal atom. Full characterization of these novel compounds was provided by ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy and infrared spectroscopy (C. G. Kreiter), mass spectroscopy (J. Müller), and x-ray crystallography (G. Huttner). It may be anticipated that this discovery of a completely new class of organo–transition metal complexes has opened an important new and fertile field of organometallic chemistry.

Professor Fischer's achievements have been recognized with many honors over the years. Notable among these were the award of the Alfred Stock Memorial Prize of the Society of German Chemists (1959), election to membership in the Bavarian Academy of Sciences and the German Academy of Scientists Leopoldina, and the award of an honorary Ph.D. by the University of Munich in 1972, on the occasion of the 500th anniversary of that institution.

His invited lectureships have led him to almost all continents, and Professor Fischer is no stranger to the United States. He traveled here for several months in 1956 and, in fact, made his first public disclosure of the preparation of dibenzenechromium at the Gordon Research Conference on inorganic chemistry in that year. Most recently, in 1973, he was Arthur D. Little Visiting Professor at the Massachusetts Institute of Technology.

A report on Ernst Otto Fischer would be incomplete without mention of his warm human qualities, which have gained him innumerable and lasting friends throughout the world and which have inspired his students to give the best of themselves. His contributions as an inspiring teacher and as a superb lecturer also merit mention, as does the enthusiasm and dedication with which he undertakes all tasks. His imaginative and original approach to chemistry, his uncompromising insistence on high quality and standards and his own personal integrity have gained him the respect and admiration of all who know him.

Geoffrey Wilkinson was born on 14 July 1921 in Todmorden, England. He obtained his B.Sc. degree in 1941 and his Ph.D. degree in 1946 at the Imperial College of Science and Technology in London. During World War II he served as a junior scientific officer in the United Kingdom–United States–Canadian atomic energy project in Canada. During this time he studied neutron-capture cross sections and fission yields. Subsequently, he spent several years with Professor Glenn T. Seaborg's group at the Lawrence Radiation Laboratory at the University of California in Berkeley where he performed studies on the radioisotopes of lanthanides and heavier elements. A move to the Massachusetts Institute of Technology as a research associate in chemistry in 1950 provided Wilkinson with an opportunity to change from nuclear chemistry to inorganic chemistry. The latter area, he felt, was full of new promise, and he believed that the main thrust of its development would focus on the chemistry of the transition elements. At MIT, Wilkinson worked with Professor J. W. Irvine, Jr., on phosphorus trihalide complexes of zerovalent nickel, such as $Ni(PCl_3)_4$ and $Ni(PF_3)_4$, and also reported on an intriguing PF_3 complex of hemoglobin.

An appointment as assistant professor at Harvard University followed in 1951. Here Wilkinson continued some studies in nuclear chemistry. However, the possibility of novel organic π-complexes of transition metals already claimed his attention. Indeed, one of the authors of this article recalls Wilkinson's suggestion to him of the possible existence of $Ni(C_2H_4)_4$ in 1951, before ferrocene was reported. Wilkinson thus was in a receptive frame of mind when the two reports describing $(C_5H_5)_2Fe$ were published. His initial work on this compound was followed by studies devoted to better routes to ferrocene and the preparation of similar complexes of other metals and of cyclopentadienyl metal carbonyls and nitrosyls, in collaboration with his students, especially J. M. Birmingham, F. A. Cotton, and the late T. S. Piper.

Wilkinson was quick to exploit new physical techniques such as NMR spectroscopy, then in its infancy, for structural determinations. He discovered the characteristic high-field NMR absorption of hydrogen bonded to transition metals (for example, in dicyclopentadienylrhenium hydride) and provided the correct explanation for the rapid intramolecular rearrangement occurring in the first recognized fluxional molecule, a σ-bonded cyclopentadienyliron compound.

In 1956 Wilkinson accepted his present position as professor of inorganic chemistry at Imperial College. His return to the British Isles contributed enormously to the establishment of modern inorganic chemistry as a strong discipline in British universities.

Wilkinson's research at Imperial College continued with studies of transition metal complexes of cyclic polyolefins, metal nitrosyls, and metal hydrido complexes. Work in the latter area led to his important work on the activation of molecular hydrogen by rhodium complexes. The discovery that $(Ph_3P)_3RhCl$ (now called Wilkinson's catalyst) was a versatile homogeneous catalyst for the hydrogenation of olefins and acetylenes at 25°C and 1 atmosphere pressure was followed by active and successful pursuit of other transition metal–based homogeneous catalyst systems effective in promoting olefin isomerization, hydroformylation, hydrogenation, and hydrosilylation reactions.

However, with all the intense activity in transition metal–organic chemistry during the last two decades, the view that the simple σ-bonded alkyl derivatives of type R_nM (R, alkyl; M, metal) were inherently unstable still persisted. In 1972 Wilkinson proved this belief fallacious by his isolating and characterizing hexamethyltungsten as a stable molecule, and other simple transition metal alkyls with β-branched alkyl substituents were found to be quite stable.

Wilkinson's name is well known throughout the world to chemistry students in inorganic courses as the coauthor (with his former student, F. A. Cotton) of *Advanced Inorganic Chemistry*. This book has influenced greatly the content and teaching of inorganic chemistry courses.

Professor Wilkinson has received many awards honoring his distinguished research accomplishments. He was elected a Fellow of the Royal Society (1965) and a foreign member of the Royal Danish Academy of Sciences (1968) and of the American Academy of Arts and Sciences (1970). The American Chemical Society Award in Inorganic Chemistry (1965), the Lavoisier Medal of the French Chemical Society (1968), and the Chemical Society Award in Transition Metal Chemistry (1971) are among the awards that he has received. He has held many invited lectureships in Europe and in the United States.

All who know Geoffrey Wilkinson have been impressed by his warmth, quick wit, and optimistic enthusiasm, as well as by his creative, intuitive approach to chemistry. It is these qualities, together with the confidence he has instilled into his students, which have made his research group an exciting and enjoyable one to be associated with.

Most chemists will applaud this recognition of creative basic research in synthetic chemistry: research that does not necessarily have direct applications in terms of products useful to society, but which stimulates the efforts of many other chemists in new directions and by doing so inevitably leads to useful and practical results. This has been an award to two "chemist's chemists" whose originality and creativity have over the past 22 years repeatedly resulted in major and important "quantum jumps" in organometallic, inorganic, and organic chemistry.

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The 1973 Nobel Prize for Physics

The 1973 Nobel Prize for Physics has been awarded to Brian D. Josephson of the Cavendish Laboratory, University of Cambridge, Ivar Giaever of the General Electric Research and Development Center, and Leo Esaki of IBM's Thomas J. Watson Research Center. Josephson, a theorist, will receive half the prize money, and Giaever and Esaki, both experimentalists, will share the other half. The three discoveries for which they have been honored were made independently in Japan, the United States, and England between 1958 and 1962, but all are linked to a single quantum mechanical phenomenon called tunneling. All three have had a profound influence on the development of physics during the last decade, and all three have important technological consequences in being and in prospect.

The phenomenon of tunneling is a direct consequence of the wave nature of material particles and was recognized very early in the development of quantum or wave mechanics. It is at once familiar and bizarre. In the field of optics it has long been known (under the name "frustrated internal reflection") that under certain circumstances a light beam propagating in a transparent medium like glass will be totally reflected at a glass-air boundary, but if a second piece of glass is brought into close proximity to the first, part of the beam will pass through the gap between the two. With quantum mechanics came the realization that a particle can be expected to display similar behavior. That is, a particle can pass into a region which classically would be forbidden to it and, if the region is not infinitely thick, can pass (tunnel) through it. A macroscopic example would be a baseball which, when thrown at a concrete wall, does not bounce back, but appears on the other side of the wall without making a hole and continues on its way. The probability of this occurring, while not identically zero, is so astronomically small that it is not surprising that the official rules of baseball do not recognize the possibility. The probability of an analogous event in the microscopic world, involving an electron or other fundamental particle and a wall formed by an atomic or nuclear potential barrier of some sort, is still small (1 in 10^9 is not unusual) but nevertheless large enough to lead to important and readily observable effects. Tunneling was first invoked to explain such effects as early as 1928, when J. R. Oppenheimer developed a theory of field ionization of atoms and R. H. Fowler and L. Nordheim produced a theory of electric field induced emission of electrons from metals. In the same year, G. Gamow and R. W. Gurney and E. U. Condon applied similar ideas to the radioactive decay of nuclei with emission of alpha particles.

The invention of the transistor in 1948 led to an explosive increase in research on semiconductors and particularly on the properties of *p-n* junctions in semiconductors. If one portion of a semiconductor crystal (for example, silicon) is doped with impurities in such a way that the majority carriers of electric current are negatively charged electrons (*n*-type) and the remainder is doped to create positively charged carriers (holes, *p*-type), the interface between the two regions is a *p-n* junction. The functioning of most transistors and other semiconductor devices depends on one or more