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How metallocene chemistry and research began in Munich

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Reinhard Jira (left) and Ernst Otto Fischer (right) in 2001.

The beginning of the research on bis-cyclopentadienyl metal compounds in Munich was accompanied by a series of coincidental but essential events that culminated with the awarding of the Nobel Prize in chemistry to G. Wilkinson and E.O. Fischer in 1973.

1. Fischer

My father was a Professor of Physics at the Technische Hochschule München. Before World War I, he spent a year at the University of Cambridge in England. From that time until about 1940, when it became impossible to receive foreign journals and books in Germany, he subscribed to the magazine Nature.

After World War II, when my father was already Professor Emeritus and had suffered a stroke, the question arose as to whether the subscription to this journal should be renewed. Although he was by then unable to speak, I believed he would recommend renewal. When I received the third issue, I found the paper by Kealy and Pauson on dicyclopentadienyl iron [1]. Curious about the properties of this new substance, I ordered dicyclopentadiene from BASF, the large chemical company that supported Professor Hieber's Institute of Inorganic Chemistry at the Technische Hochschule München, where I was working on my doctoral thesis. The substance was shipped to Professor Hieber who asked me about its purpose. When I showed him Pauson's paper, he too was curious and encouraged me to proceed.

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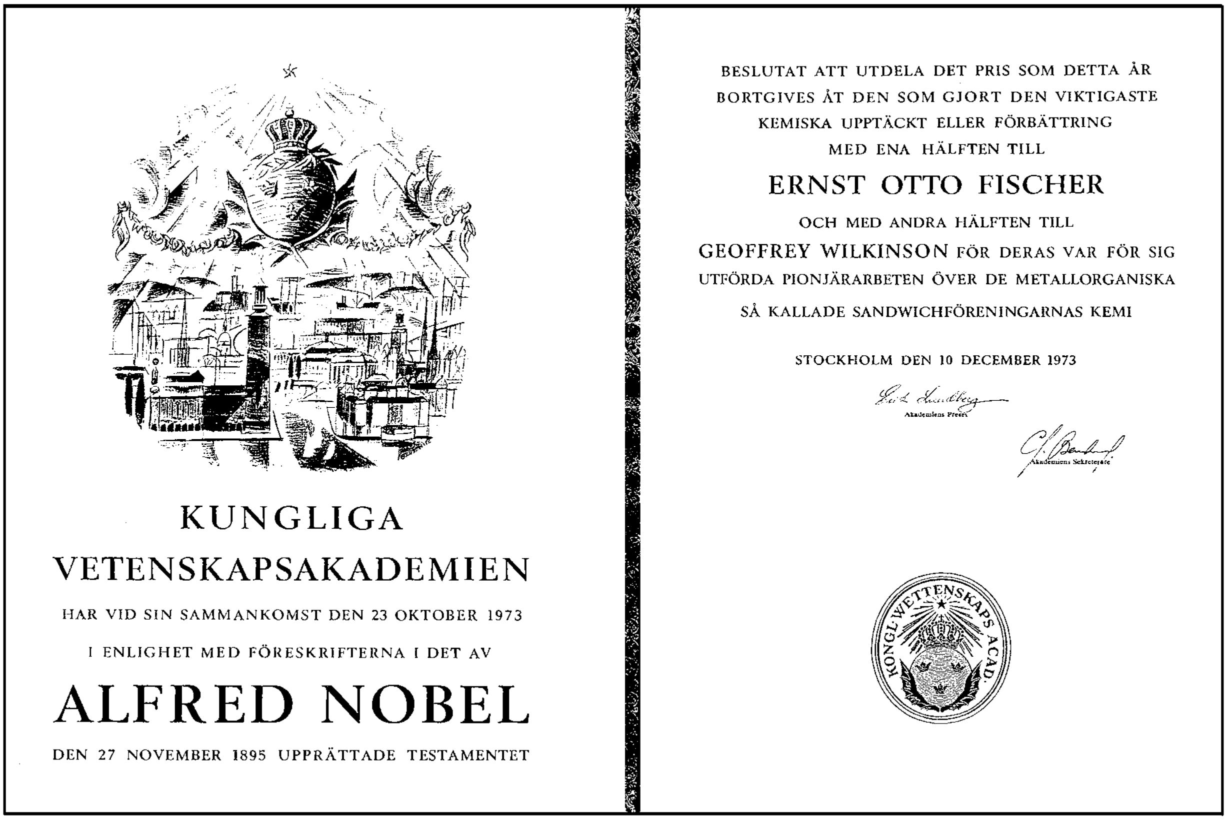


KUNGLIGA
VETENSKAPSAKADEMIEN
HAR VID SIN SAMMANKOMST DEN 23 OKTOBER 1973
I ENLIGHET MED FÖRESKRIFTERNA I DET AV
ALFRED NOBEL
DEN 27 NOVEMBER 1895 UPPRÄTTADE TESTAMENTET

BESLUTAT ATT UTDELA DET PRIS SOM DETTA ÅR
BORTGIVES ÅT DEN SOM GJORT DEN VIKTIGASTE
KEMISKA UPPTÄCKT ELLER FÖRBÄTTRING
MED ENA HÄLFTEN TILL
ERNST OTTO FISCHER
OCH MED ANDRA HÄLFTEN TILL
GEOFFREY WILKINSON FÖR DERAS VAR FÖR SIG
UTFÖRDA PIONJÄRARBETEN ÖVER DE METALLORGANISKA
SÅ KALLADE SANDWICHFÖRENINGARNAS KEMI

STOCKHOLM DEN 10 DECEMBER 1973

Akademiens Preses

Akademiens Sekreterare

2. Jira

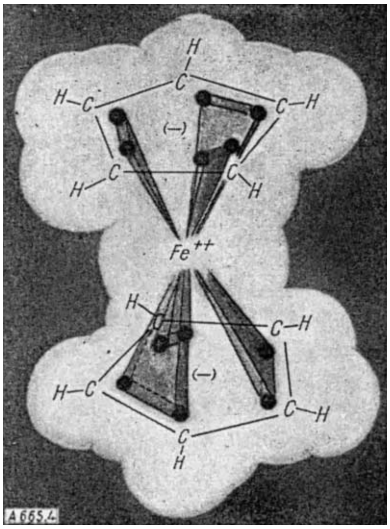
Towards the end of my study of chemistry at the Technische Hochschule München, now Technische Universität München, to take the second examination towards the 'Diplomchemiker' degree I still had to carry out a few practical syntheses drawn from chemical literature and I was assigned to E.O. Fischer. At the time, he was a research assistant in the Institute of Inorganic Chemistry and had just finished the experimental work for his doctoral thesis.

One day he showed me Pauson's paper [1], brought in a bottle of dicyclopentadiene received from BASF, and asked me to reproduce this synthesis. First, the dicyclopentadiene had to be depolymerized; a procedure was available and the corresponding Grignard reagent was allowed to react with $FeCl_3$. The next day he appeared, very inquisitively, and asked about the result. I showed him the orange crystals obtained when the ether solvent was evaporated, and he was very excited. We agreed that the stability toward air and moisture did not agree with the structure proposed by Pauson. Further evidence was obtained after following Fischer's suggestion to treat these crystals with carbon monoxide at high temperature (ca. 150 °C) in an autoclave at 200 bar using equipment available in Hieber's laboratory. The crystals remained unchanged and no iron pentacarbonyl was obtained.

These experiments completed my practical work before the examination.

3. Fischer

The high stability of the compound against atmospheric and chemical conditions led me to the conclusion that probably the six π-electron pairs for the two 'aromatic' rings of the cyclopentadienyl anions would participate in the bonding to the central iron atom, with each cyclopentadienyl ring functioning as a tridentate ligand and filling the iron orbitals up to 18 electrons—the 'krypton-configuration,' if the iron is assumed to be present in oxidation state +II. An octahedral structure similar to $Fe(CN)_6^{4-}$ was assumed, representing a new kind of organometallic compound and a new type of 'Durchdringungskomplex' (at the time, we still used Alfred Werner's term for such compounds). In this case, of course, the compound could not have the linear stretched structure proposed by Pauson. A structure with two parallel cyclopentadienyl planes with the iron midway in between was assumed.



This was later confirmed by an X-ray crystallographic study carried out by Wolfgang Pfab. Pfab had been a friend of mine since our common military service and he was also working on his doctoral thesis in Hieber's institute. He was interested in crystallography and activated some X-ray equipment that had been stored unopened at the institute. Using additional equipment at the Institute of Physical Chemistry (Professor G. Scheibe), Pfab showed that the dimensions of the elemental cell with two molecules were too small to allow inclusion of linear stretched molecules proposed by Pauson.

Further evidence for the assumption of a 'Durchdringungskomplex' was its diamagnetism.

Bromination of dicyclopentadienyl iron in CCl_4 followed by treatment with water gave a dichroic blue–red aqueous solution—the same one obtained in Pauson's synthesis when the Grignard-reaction product was hydrolyzed. Precipitating with 'Reinecke'-salt, $NH_4Cr(SCN)_4(NH_3)_2$, showed that the solution contained a cationic form, dicyclopentadienyliron(III), if the iron atom in the neutral dicyclopentadienyliron is considered to be in the oxidation state + II.

Again using the Grignard method and precipitating the solution with 'Reinecke'-salt, we succeeded in synthesizing a very stable yellow cation, dicyclopentadienylcobalt(III). The high stability was in accord with our theory and supported an octahedral Co(III)-complex having a krypton configuration like the isoelectronic Fe(II) complex.

The idea that the π-electrons of the aromatic cyclopentadienyl rings fill the orbitals of the central metal, similar to other ligands like CO, NO, CN etc., proved to be a very fruitful working hypothesis. The magnetic behavior of di- and mono-cyclopentadienyls, carbonyls, nitrosyls, hydrides, etc. could be predicted or, vice versa, by this new structure and bonding relationship.

We had many productive discussions on the bonding relations of these dicyclopentadienyl compounds as 'Durchdringungs'-complexes with another friend of mine, Ernst Ruch, who was a theoretical physicist working at the Institute of Physical Chemistry of the Technische Hochschule and who became a Professor at the Freie Universität of Berlin. Later, we published a paper together (see below).

We were fortunate in that there was a variety of modern instruments available in Munich at this time, with the technicians to run them. Magnetic susceptibilities could be measured with a magnetic balance at the Physical Institute of the Technische Hochschule (Professor G. Joos) and by the *para*-hydrogen method at the Institute of Physical Chemistry of the University of Munich (Professor G.M. Schwab). X-ray analyses were carried out at our Institute of Inorganic Chemistry; the successor to W. Pfab in this field was Erwin Weiss, later a Professor at the University of Hamburg. IR spectra could also be obtained in our institute. Later I had my own equipment and an NMR spectrometer was available in my group earlier than at the Institute of Organic Chemistry. Several times, I sent coworkers for training, mainly to colleagues in the USA, to learn new measurement techniques.

But back to the early days. During the course of the work mentioned, two more publications appeared. The paper by Miller, Tebboth, and Tremaine [2] described another method for preparing dicyclopentadienyliron. It was sent to the publisher earlier than the Kealy and Pauson paper [1] but was published later—thus Miller et al. actually deserve the first claim. The paper by Wilkinson, Rosenblum, Whiting, and Woodward [3] showed us that there was another group working on this subject. Wilkinson et al. came to the same conclusion on the structure of dicyclopentadienyliron, deducing it from the fact that there is only one kind of hydrogen found in the IR spectrum. So we accelerated our first publication to June 1952; in it, we described the results and conclusions mentioned above [4]. In November 1952, we followed up with the paper by Ernst Ruch and myself [5] in which the octahedral d^2sp^3 hybrid bonding of the 'aromatic' cyclopentadienyl rings to the central iron(II) was again postulated, in contrast to the assumption of Wilkinson et al. [3] of a structure with iron(0) as the central atom. Our structure was described as a 'Doppelkegel' structure. With these publications, a competition developed between Wilkinson's group and mine that continued for several exciting years.

4. Jira

My oral examination took place in the middle of June 1952; the Examiner for Inorganic Chemistry was

Professor Walter Hieber. After the examination, he asked me where I planned to carry out my experimental work and he was pleased to hear that I would like to work at his institute. In fact, he proposed that I work with E.O. Fischer on these new compounds whose structure and bonding relations were being developed at the time.

At first it was not certain that Fischer would stay at the university. He had already signed a preliminary contract with Wacker-Chemie, but Hieber persuaded him to stay in order to work in this promising new field and to receive the venia legendi—the right to teach at the university.

I began working in early July 1952 and I first elaborated a synthesis for the readily water-soluble bis(cyclopentadienyl)cobalt(III) bromide from which other soluble and insoluble salts could be obtained [6].

During this period, a few more papers appeared:

- Woodward, Rosenblum, and Whiting considered bis-cyclopentadienyl iron as 'A New Aromatic System' and created a new common name, 'ferrocene', for this compound. Consequently, the cation obtained by the oxidation of ferrocene is called the "ferricinium" ion [7].
- Wilkinson published the preparation ruthenocene and ruthenicinium salts, the compounds homologous to iron [8].
- Eiland and Pepinsky published an X-ray study with the same result for the structure of bis(cyclopentadienyl)iron previously proposed. They were the first to use the term 'sandwich' for this type of structure.
- Dunitz and Orgel later proved the 'sandwich' structure by Fourier analysis [9].

Evidently, the term 'sandwich' was more appealing than our term 'Doppelkegel', because it has been used extensively in the chemical literature since then, by the term 'ferrocene'.

As we continued our synthetic work, we did not succeed, at first, in obtaining ferrocene-related compounds by using the Grignard method; we used a different method, one in common use at the institute, carrying out reactions in liquid ammonia. This time we were successful. We could synthesize bis-cyclopentadienyl Ni [10] and Co [11] by precipitating as $M(NH_3)_6(C_5H_5)_2$ in liquid ammonia and then decomposing it at atmospheric pressure. An unusual event occurred one time as we admired some freshly obtained beautiful green crystals of $NiCp_2$ (Cp = cyclopentadienyl). Evidently, the crystals were contaminated; they suddenly caught fire and were completely consumed. In our further studies, we took more care and worked under an inert atmosphere. The crystal structure of Cp_2Ni was also determined by W. Pfab [12].

Bis-cyclopentadienyl manganese was more difficult to obtain by the liquid ammonia method. When the first precipitate of $Mn(NH_3)_6(C_5H_5)_2$ was heated for sublimation in high vacuum, an extremely air-sensitive colorless sublimate of $Mn(NH_3)_2(C_5H_5)_2$ was obtained. It was impossible to separate the brown crystals of $Mn(C_5H_5)_2$ from this; however, the Grignard-method was successful [13].

Walter Hafner joined us at this time (1954), and Dietlinde Seus shortly thereafter.

(Walter Hafner)

Walter worked with chromium and vanadium; he synthesized the respective bis-cyclopentadienyl compounds [14,15], while Dietlinde synthesized bis-indenyl compounds of iron [16] and cobalt [17]. After her doctoral examination, Dietlinde joined Hoechst AG for some years; later, she worked as a journalist for a medical journal.

In the spring of 1954, in either May or June, Wilkinson visited Munich at Fischer's invitation. He showed us a sample of $MnCp_2$ that we could confirm as we had already obtained it. In an evening conference, Fischer and Wilkinson agreed to divide up the periodic table between them — that is, to decide which elements should be studied by which group. Actually, the agreement was not worth the paper it was written on. Each group was so fully engaged in its work that no regard was paid to the other.

F.A. Cotton, the first coworker in Wilkinson's group, visited Munich that summer as well. Although in his recollections, Cotton mentioned that the visit had taken place before Wilkinson's, I believe it took place afterward. I remember a discussion with Cotton about $MnCp_2$, probably on its unusual magnetic behavior. Certainly, we had by then obtained mixed crystals with $MgCp_2$, which, to the best of my recollection, was not a subject of discussion with Wilkinson. When I asked Cotton which field of inorganic and coordination chemistry would be the most interesting in the future, he answered, with conviction, 'sandwiches'. This was, in fact, true—at least for the next few years.

When VCp_2 was treated with CO under high pressure, Hafner obtained orange compound $CpV(CO)_4$

[15]. Similarly, I obtained the very stable yellow compound $CpMn(CO)_3$ [13] and dark red, air-sensitive, liquid $CpCo(CO)_2$ [18]. The elements in between, Cr and Fe, form binuclear cyclopentadienyl metal carbonyls. These diamagnetic organometal carbonyls all meet the requirements of the krypton electron configuration.

The working hypothesis that the metal orbitals are filled by the bonding ligand electrons, the cyclopentadienyl anion contributing six electrons, was very successful and readily explained the magnetic behavior of the bis-cyclopentadienyl metal compounds and cyclopentadienyl metal carbonyls. An exception was $MnCp_2$, which macroscopically showed a crystal structure different from the other metallocenes, including $MgCp_2$, and unusual magnetic behavior with temperature-dependent magnetic susceptibility later defined as antiferromagnetism. Above the transition point of 431 K and in mixed crystals with $MgCp_2$, $MnCp_2$ showed a magnetic susceptibility corresponding to five unpaired electrons, which represents an ionic bond between the cyclopentadienyl rings and the central Mn atom.

In January 1955 I took my doctoral examination and left the Institute of Inorganic Chemistry. On 15 March 1955, I joined Consortium für Elektrochemische Industrie, the research organization of Wacker-Chemie.

5. Fischer

After Wolfgang Pfab had left the Institute of Inorganic Chemistry to join BASF, Erwin Weiss continued determining the structures for our compounds by X-ray analyses, although he was officially working with Hieber. The structures of VCp_2 and $MgCp_2$ were published first [19], and followed by the structure of $CrCp_2$ [20]. These compounds showed the same crystal structure as ferrocene and the other metallocenes as could be observed macroscopically from the shape of the crystals. Surprisingly, $MgCp_2$, which crystallizes from an ether solution of the Grignard-compound after standing overnight also has a sandwich-structure, although the bond between the cyclopentadienyl group and the metal is more ionic in character and is easily hydrolyzed. As already mentioned, $MnCp_2$ exhibits a different crystal structure, a rhombic one, in contrast to the monoclinic one of the ferrocene-like compounds. Only in mixed crystals with a $MgCp_2$ content $> 50\%$ and probably above the transition point, does $MnCp_2$ form a ferrocene-like crystal structure [21]. The exact crystal structure of the brown modification of $MnCp_2$ was elucidated by W. Bünder and E. Weiss many years later [22].

Our working hypothesis on the nature of the bonding between the 'aromatic' cyclopentadienyl rings, each contributing three electron pairs to the central metal was so useful in explaining the magnetic behavior of the metallocenes and the composition of the cyclopentadienyl metalcarbonyls that it led us to speculate that coordination of benzene, with its six π-electrons to a central metal might also be possible. As a central metal, chromium seemed to be the most promising element since a krypton configuration as obtained with chromiumhexacarbonyl, would be obtained from chromium with six electrons in the zero valent state and two benzene molecules with six electrons from each. In fact, Walter Hafner succeeded in synthesizing 'dibenzene chromium(0)'—by reacting benzene, aluminum, aluminum chloride, and chromium trichloride in a 'reducing' Friedel–Crafts reaction followed by further reduction of the Cr(I)-intermediate obtained first [23]. X-ray analysis revealed a cubic crystal structure and showed that the molecule dibenzenechromium also contains a ferrocene-like 'sandwich' structure [24].

The first period of my research activities was completed with the synthesis of dibenzene chromium, and a new one began. We showed that we were able to compete with Wilkinson's group and we now had a new field for our research activities, without the fear that another group would intervene. Of course, we also continued research in metallocene chemistry.

In this article about the very beginning of metallocene chemistry in the Munich laboratory, we have described what happened and how we felt. Some of the metallocenes were prepared independently in both groups and were published almost simultaneously. It has not been our task to provide a complete history of the discovery of these compounds by listing all the publications of both groups; this was done in an earlier summary paper [25]. For a more detailed description of the work in Wilkinson's laboratory, see Cotton's recollections in this volume (see Acknowledgements).

6. Jira

When I began my experimental work, I de jure worked with Hieber since Fischer did not yet have the venia legendi and the right to supervise graduate students studying for doctoral degrees. But that was only a formality. The fact that I was elected to assist Hieber at his lectures weighed more heavily; I had to prepare and carry out the experiments during his experimental lectures. There was a lot of work to be done during the academic semesters, which was very time-consuming. Despite this charge, I was very keen to work with E.O. Fischer in this exciting new field for which he was later to be awarded a Nobel Prize.

Later, in my new job with Consortium für Elektrochemische Industrie, I became involved in a similar exciting field of organometallic chemistry. After his doctoral examination, Walter Hafner entered the same laboratory and soon found a new synthesis for the manufacture of acetaldehyde, an important intermediate in industrial chemistry; this synthesis from ethylene is now known as the Wacker process. I consider it a privilege to have worked on the commercialization of this process with Hafner and other colleagues. As is well known, the process has been licensed to many companies all over the world, and the basic Wacker reaction, a regiospecific oxidation of an olefinic double bond to a carbonyl group, initiated a growing area of synthetic organic chemistry catalyzed or promoted by palladium reagents.

I am very grateful that I had the opportunity to work in these two fascinating fields of organometallic chemistry.

Acknowledgements

We gratefully acknowledge the report in this issue by F.A. Cotton, who kindly sent an advanced version of his manuscript to one of us (E.O.F.).

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