

At Least 60 Years of Ferrocene: The Discovery and Rediscovery of the Sandwich Complexes

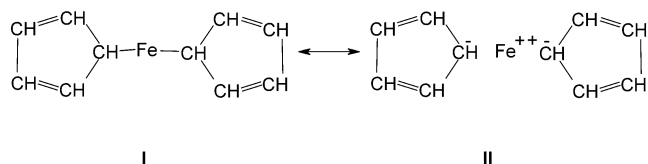
Helmut Werner*

history of chemistry · Nobel Prizes ·
polyphenylchromium compounds ·
sandwich complexes

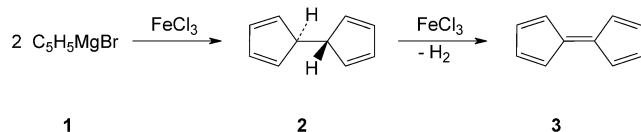
Dedicated to Peter L. Pauson

In December 1951 and February 1952 two papers appeared—a communication in *Nature*^[1] and a short article in the *Journal of the Chemical Society*^[2]—which presumably only a minority of the readers of those journals noticed.^[3] Peter L. Pauson, a young assistant professor at the Duquesne University in Pittsburgh, and his co-worker Thomas J. Kealy had tried to prepare the compound $C_{10}H_8$, named fulvalene, which they assumed would possess aromatic properties, similar to the isomeric naphthalene. Their idea was to convert the anionic cyclopentadienyl ligand of the Grignard reagent **1** to the cyclopentadienyl radical $C_5H_5\cdot$ by oxidation, and convert the dihydrofulvalene **2**, formed by the coupling of two $C_5H_5\cdot$ radicals, to the desired product **3** after dihydrogenation (Scheme 1). Pauson assumed that $FeCl_3$ might be a useful

prepare compounds FeR_2 containing two covalently bonded dialkyl or diaryl groups from $RMgBr$ and $FeCl_3$. Therefore, Pauson and Kealy attributed the unusual stability of $[Fe(C_5H_5)_2]$ “to the tendency of the cyclopentadienyl group to become ‘aromatic’ by acquisition of a negative charge, resulting in important contributions from the resonance form (II) and intermediate forms” (Scheme 2).^[1]



Scheme 2.



Scheme 1.

reagent for the generation of the cyclopentadienyl radical from the Grignard compound as well as for the abstraction of H_2 from intermediate **2** to give **3**, because it was available in its non-hydrated form and as such soluble in ether.^[4] After addition of $FeCl_3$ to a solution of **1** in diethyl ether and standard workup of the reaction mixture, Kealy obtained yellow crystals, the microanalysis of which, however, did not fit the composition $C_{10}H_8$ but was consistent with $FeC_{10}H_{10}$. Apparently bis(cyclopentadienyl) iron $Fe(C_5H_5)_2$ had formed.

“What was this remarkable substance we had made?” asked Pauson and hesitated at first to propose a structure for the new stuff.^[4] The crystals dissolved in concentrated sulfuric acid without decomposition, were stable in water and bases, and decomposed above $300^\circ C$. This was inconsistent with the experience of other authors who had previously attempted to

Almost at the same time as Pauson and Kealy, Samuel A. Miller, in those days Director of Research with British Oxygen, with his co-workers John A. Tebbboth and John F. Tremaine isolated, again unexpectedly, $[Fe(C_5H_5)_2]$.^[2] They had attempted to prepare amines from saturated or unsaturated hydrocarbons and nitrogen by using the “doubly-promoted synthetic ammonia catalyst” developed in the context of Haber’s pioneering work on the synthesis of NH_3 . When they reacted cyclopentadiene and N_2 at $300^\circ C$ and atmospheric pressure, they obtained $[Fe(C_5H_5)_2]$. Like Pauson and Kealy, Miller and his team were also surprised that the compound melted at $173^\circ C$ without decomposition and easily sublimed. With regard to the structure, they made only a short comment: “by analogy with the well-known cyclopentadienyl potassium it is believed that substitution has occurred in the methylene group, and that the compound has the structure inset” (meaning a structure corresponding to $R-Fe-R$ with two covalent $Fe-C$ σ bonds). Their limited interest in this problem can be explained by their disappointment that $[Fe(C_5H_5)_2]$ did not catalyze the synthesis of ammonia from the elements.^[2]

Though Miller had, as he reported to Pauson soon after,^[4] unknowingly isolated bis(cyclopentadienyl)iron for the first time three years prior to the publication of their results, he and his group were not the first to have obtained this “remarkable substance”. After reading the communication by Kealy and Pauson, Eugene O. Brimm from Linde Air

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Products, who reported the first synthesis of $[\text{Mn}_2(\text{CO})_{10}]$ in 1954,^[5] wanted to prepare a sample of $[\text{Fe}(\text{C}_5\text{H}_5)_2]$ and asked a colleague at Union Carbide (at that time Linde's parent company) whether he or somebody in his lab had any cyclopentadiene (or its more stable dimer). The reply, that they no longer had any, was accompanied by the statement that, some years previously, they had obtained upon cracking of dicyclopentadiene and passing the vapor stream through an iron pipe a "yellow sludge", which did clog the pipe. They had kept a sample and sent it to Brimm, who immediately proved that it was $[\text{Fe}(\text{C}_5\text{H}_5)_2]$. Obviously, the yellow sludge was generated similarly to the substance isolated by Miller.

However, what was the structure of the obscure compound $[\text{Fe}(\text{C}_5\text{H}_5)_2]$, which, as Sir Ron Nyholm remarked in his Inaugural Lecture 1956 at University College London,^[6] initiated a "Renaissance of Inorganic Chemistry"? There were three people, who after having read the communication from Kealy and Pauson in *Nature* focussed on solving the structural problem: Ernst Otto Fischer at the Technische Hochschule (now Technische Universität) in Munich and Robert B. Woodward and Geoffrey Wilkinson at Harvard University in Cambridge (USA). They were convinced that the structure proposed by Pauson und Kealy was wrong. Fischer, who had just finished his doctoral thesis under the supervision of Walter Hieber, was familiar with the state of the art of coordination chemistry. He assumed that, owing to the high stability, $[\text{Fe}(\text{C}_5\text{H}_5)_2]$ should be a *Durchdringungskomplex*^[7] and that the iron(II) center should possess an 18-electron configuration. The main reason for his suspicion was that the orange crystals, prepared by his student Reinhard Jira following the procedure used by Pauson and Kealy, did not react in an autoclave with CO at about 150 °C and 200 bar and were recovered unchanged.^[8] Thus Fischer concluded that the whole set of the six π -electrons of each cyclopentadienyl anion participate in the bonding to iron(II), and that each five-membered ring formally acts as a tridentate ligand. In the paper, which he and Jira submitted on June 20, 1952 to the *Zeitschrift für Naturforschung* and which appeared one month later with the title "Cyclopentadien-Metallkomplexe, ein neuer Typ metallorganischer Verbindungen", they wrote: "With three π -electron pairs from each of the parallel aromatic cyclopentadiene anions, the central Fe^{II} ion achieves six octahedrally arranged, coordinative covalencies and thus

obtains the krypton configuration".^[9] In support of this conclusion it was mentioned that $[\text{Fe}(\text{C}_5\text{H}_5)]$ is diamagnetic, that based on preliminary X-ray data (collected by Wolfgang Pfab, also a PhD student of Walter Hieber) the molecule possesses a centrosymmetric and not a "stretched" structure, and that similar to $[\text{Fe}(\text{C}_5\text{H}_5)_2]$ a highly stable bis(cyclopentadienyl)cobalt(III) cation (precipitated as the reineckate) could be prepared. In a second paper with the theoretical chemist Ernst Ruch from Munich, Fischer then coined the name "Doppelkegel" (double cone) to characterize the structure of $[\text{Fe}(\text{C}_5\text{H}_5)_2]$ and $[\text{Co}(\text{C}_5\text{H}_5)_2]^+$ (Figure 1).^[10]

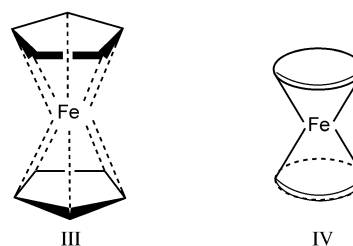


Figure 1. Structural proposals for $[\text{Fe}(\text{C}_5\text{H}_5)_2]$ by Woodward and Wilkinson (III) and by Fischer (IV).

Three months prior to Fischer and Pfab's report, Woodward and Wilkinson (together with Woodward's co-workers Myron Rosenblum and Mark C. Whiting) submitted a preliminary communication entitled "The Structure of Iron Biscyclopentadienyl" to the *Journal of the American Society*, in which they confirmed the diamagnetism of $[\text{Fe}(\text{C}_5\text{H}_5)_2]$.^[11] Moreover, they announced that the IR spectrum of the compound shows only one C–H stretching mode, indicating that all C–H bonds are of the same type and that the dipole moment is zero. They carefully wrote that despite these results "detailed proposals with respect to the electronic structure of iron biscyclopentadienyl would be premature", but proposed, without having crystallographic data, a molecular structure which was quite similar to that of Fischer and Pfab (see Figure 1). In a second paper, submitted on June 2, 1952, Woodward, Rosenblum, and Whiting backed up their proposal by indicating that, in spite of the unsaturated character of the ring ligands, $[\text{Fe}(\text{C}_5\text{H}_5)_2]$ does not behave as a polyolefin but rather as an aromatic molecule and, for example, can be easily acetylated with acetyl chloride in the presence of AlCl_3 .^[12] Therefore, in analogy to benzene Woodward suggested the name ferrocene for $[\text{Fe}(\text{C}_5\text{H}_5)_2]$.^[13] This name was quickly accepted worldwide by the chemical community and soon afterwards transferred to compounds of the general composition $[\text{M}(\text{C}_5\text{H}_5)_2]$, termed metallocenes.

In retrospect the results obtained by Fischer and by Woodward and Wilkinson appeared quite convincing, yet the structural proposals shown in Figure 1 were at first not generally accepted. Jack D. Dunitz, one of the leading crystallographers in the last decades, later confessed that after reading the first paper by Woodward and Wilkinson his spontaneous reaction was "of skepticism, if not plain disbelief", and Leslie E. Orgel, one of the "popes" in theoretical chemistry at that time agreed.^[14] In this sense, also Marshall



Helmut Werner studied chemistry in Jena and Munich and received his PhD with E. O. Fischer in 1961. After postdoctoral work with J. H. Richards at Caltech he became Professor of Inorganic Chemistry at the University of Zürich and was appointed Professor and Head of the Institute of Inorganic Chemistry at the University of Würzburg in 1975. He has been Professor Emeritus since 2002. Apart from numerous international awards he received the prestigious Alfred Stock Prize of the German Chemical Society in 1988 and was elected as a member of the Academy Leopoldina (now: National Academy of Sciences) in the same year. He received honorary doctorates from the University of Zaragoza (2001) and from the University of Jena (2006).

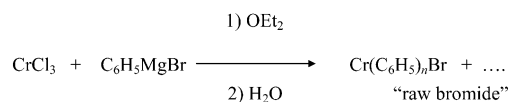
Gates, the assistant editor of the *Journal of the American Chemical Society*, who had to referee the manuscript of Woodward and Wilkinson, wrote in a letter to Woodward on March 28, 1952: “We have dispatched your communication to the printers but I cannot help feeling that you have been at the hashish again.”^[15] However, the early skepticism disappeared after Dunitz and, independently, Philip F. Eiland and Ray Pepinski proved by X-ray crystallography that the structure proposed by Woodward/Wilkinson and Fischer was correct, and after Orgel explained the extraordinary stability of ferrocene on the basis of molecular orbital theory.^[16,17] Also independently, Dunitz and Orgel^[16] as well as Wilkinson^[18] coined the term *molecular sandwich* or *sandwich structure*, which like ferrocene was accepted almost immediately.^[19,20]

Between December 1952 and December 1954 the chemistry of the metallocenes developed at an unprecedented pace.^[21] In those two years the fierce competition between Fischer and Wilkinson, not always conducted fairly,^[22] resulted in the synthesis of the compounds of types $[M(C_5H_5)_2]$, $[M(C_5H_5)_2X_2]$, and $[M(C_5H_5)_2X_3]$ ($X = Cl, Br$) for nearly all the transition metals as well as compounds of the general composition $[M(C_5H_5)_3]$ where M is a lanthanide.^[23] Moreover, also analogous bis(indenyl) metal complexes $[M-(C_9H_7)_2]$ and the first cyclopentadienyl metal carbonyls, such as $[(C_5H_5)Mn(CO)_3]$, $[(C_5H_5)V(CO)_4]$, and $[(C_5H_5)Mo(CO)_3]_2$, were isolated.^[24] Pauson did not participate in the race between Fischer and Wilkinson (which he described as follows: “...they were in constant competition as to who would be first with the next, fairly obvious target”),^[4] because after his return from the United States he took a position as lecturer at the University of Sheffield and initially concentrated his research on topics in organic chemistry.^[25] In his work he reawakened the interest for the chemistry of diolefin and oligoolefin metal carbonyls by demonstrating that butadiene iron tricarbonyl $[(C_4H_6)Fe(CO)_3]$, described already in 1930 by Hans Reihlen as highly unstable,^[26] can be isolated, and that the related compound having 1,3-cyclohexadiene instead of butadiene is also accessible.^[27]

A completely new gateway to the chemistry of the sandwich complexes was opened in 1955. As Dietmar Seyferth recalled, soon after the verification of the structure and bonding of ferrocene, Fischer already reasoned, whether apart from the cyclopentadienyl anion also other aromatic systems could coordinate to transition metals.^[28] In January 1954 Walter Hafner, Fischer's third PhD student,^[29] carried out the first experiment to achieve this goal and reacted $CrCl_3$ with *m*-xylene in the presence of aluminum and $AlCl_3$ under reflux. He isolated an orange solid which, however, did not sublime and was almost insoluble in organic solvents. An analogous experiment with benzene instead of *m*-xylene led to a similar result. For this reason, he concluded that the isolated orange substances were not the desired products $[Cr(C_6H_4Me_2)_2]$ and $[Cr(C_6H_6)]$. On Fischer's advice, Hafner repeated the reaction of $CrCl_3$ with *m*-xylene, Al, and $AlCl_3$ in an autoclave under CO pressure and obtained $[Cr(CO)_6]$ in excellent yield.^[30]

Fischer's and Hafner's search for bis(arene) chromium(0) complexes received new impetus after Harold H. Zeiss (at the

time an assistant professor at Yale University) disclosed in a seminar at the University of Munich in July 1954 the results of his PhD student Minoru Tsutsui. In laborious work, Tsutsui had been able to repeat the preparation of the so-called polyphenylchromium compounds, first reported by Franz Hein at around 1920 (Scheme 3),^[31] and—while previously



From the “raw bromide”, orange solids of the following composition were isolated:

$Cr(C_6H_5)_5OH$	$Cr(C_6H_5)_5OC_6H_5$	$[Cr^{VI} ?]$
$Cr(C_6H_5)_4OH$	$Cr(C_6H_5)_4I$	$[Cr^V ?]$
$Cr(C_6H_5)_3OH$	$Cr(C_6H_5)_3I$	$[Cr^{IV} ?]$

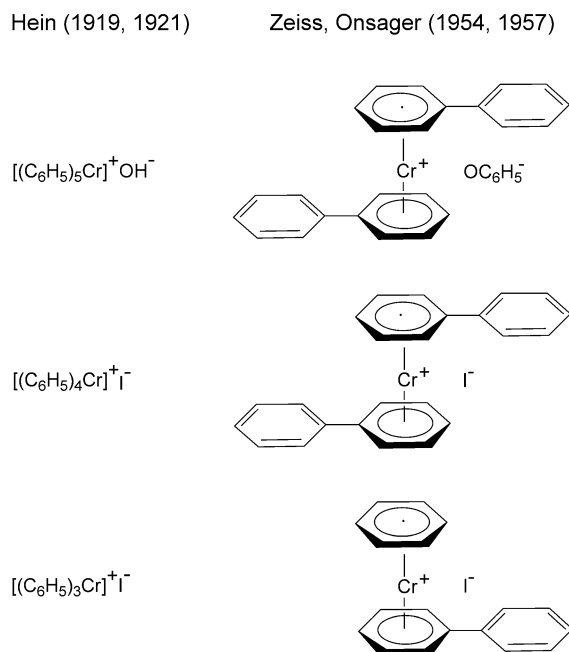
Scheme 3.

several authors had questioned Hein's results—confirmed that these compounds really exist. However, Tsutsui had severe doubts as to whether they possess $Cr-C_6H_5$ σ bonds. Since single crystals were not available and thus no X-ray crystal structure analysis could be carried out, he based his doubts mainly on the results of degradation reactions. After he had shown that $[Hg(C_6H_5)_2]$ reacted with $LiAlH_4$ to give benzene, he also treated Hein's “ $[(C_6H_5)_3Cr]I$ ” with $LiAlH_4$ and obtained diphenyl and benzene in a 1:1 ratio. The analogous reaction of “ $[(C_6H_5)_4Cr]I$ ” with $LiAlH_4$ furnished two equivalents of diphenyl, but no benzene. Treatment of “ $(C_6H_5)_5OH$ ” with $LiAlH_4$ resulted in a mixture of diphenyl and phenol. Though the outcome of these experiments seemed to be clear, Zeiss and Tsutsui hesitated to offer an unambiguous structural proposal for Hein's polyphenylchromium compounds.^[32]

An important step toward solving this problem was made by Lars Onsager, a colleague of Zeiss at Yale, who received the Nobel Prize in Chemistry in 1968. Already in 1954, he became interested in Tsutsui's work and assumed a structural relationship between the ferricinium cation $[Fe(C_5H_5)_2]^+$, described by Fischer^[9] as well as by Wilkinson,^[33] and the tetraphenyl chromium cation $[Cr(C_6H_5)_4]^+$, postulated as part of the “tetraphenylchromium salts” by Hein.^[31] Onsager assumed that instead of $[Cr(C_6H_5)_4]^+$ the cation should have the composition $[Cr(C_6H_5C_6H_5)_2]^+$ and proposed a “*biconoidal structure*” for it. He supported this idea by indicating that $[Fe(C_5H_5)_2]^+$ as well as $[Cr(C_6H_5)_4]^+$ displays a magnetic moment of 1.73 Bohr magnetons, which corresponds to one unpaired electron and thus to the oxidation state Fe^{III} and Cr^I for the metal in the two cations.^[34]

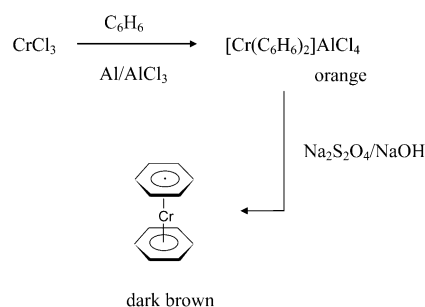
In 1954, this was undoubtedly—as Seyferth wrote later—a “*rather revolutionary proposal*”,^[35] and one can understand that Zeiss and Tsutsui had trouble getting their results published. At the 126th meeting of the American Chemical Society in September 1954, Zeiss presented a paper describing Tsutsui's experimental work as well as Onsager's struc-

tural proposal for Hein's polyphenylchromium compounds. At the same time, he also submitted a preliminary communication to the *Journal of the American Chemical Society*. However, this was rejected by the referees "for lack of conclusive evidence",^[36] in particular because an X-ray crystal structure analysis was missing. Thus, in early 1955 just a small portion of the results was published in abbreviated form.^[37] It was only after Fischer's paper with Dietlinde Seus on the synthesis of $[\text{Cr}(\text{C}_6\text{H}_5\text{C}_6\text{H}_5)]$ and $[\text{Cr}(\text{C}_6\text{H}_5\text{C}_6\text{H}_5)_2]\text{I}$ appeared in 1956^[38] that the complete manuscript of Zeiss and Tsutsui was accepted (Scheme 4).^[39]



Scheme 4.

Prior to this, Fischer and Hafner had already disclosed the preparation of bis(benzene) chromium using the so-called reducing Friedel–Crafts synthesis.^[40] The deciding point was that Hafner had attended Zeiss' seminar at the University of Munich and instantly remembered the outcome of his own previous experiments. A few days later, he repeated the reaction of CrCl_3 , Al, AlCl_3 and benzene in the absence of CO. He reduced the orange solid, which he had initially isolated, with sodium dithionite in aqueous NaOH and obtained dark brown, moderately air-sensitive crystals (Scheme 5). They sublimed in vacuo, were diamagnetic, and had the composition $[\text{Cr}(\text{C}_6\text{H}_6)_2]$. The X-ray crystal structure analysis, carried out by Erwin Weiss (in those days a PhD student of Walter Hieber, later professor of inorganic chemistry at the University of Hamburg) revealed that the molecule, similar to ferrocene, was centrosymmetric and consistent with the configuration of a sandwich complex.^[41] Hafner also prepared a series of salts of the bis(benzene) chromium cation by oxidation of $[\text{Cr}(\text{C}_6\text{H}_6)_2]$, which were light-sensitive but stable in neutral or basic solution.^[30] Somewhat later, also the molybdenum analogue $[\text{Mo}(\text{C}_6\text{H}_6)_2]$



Scheme 5.

was prepared in Fischer's group,^[42] followed by a number of neutral and cationic bis(arene) transition-metal complexes.^[43]

In light of the shared opinion which Fischer and Wilkinson had about the structure and bonding of the metallocenes, it was discussed among the organometallic community, why Wilkinson did not also try to prepare bis(benzene) chromium. The idea might have been in his head,^[21] and as he recalled,^[44] in autumn 1952 he had already asked the young theoretician William Moffit, who had just started at Harvard: "What is the chance of benzene binding to a transition metal?" A few days later, Moffit came back stating that such an arrangement should not be stable since a molecule such as $[\text{M}(\text{C}_6\text{H}_6)_2]$ would readily decompose. As Wilkinson had, in his own words, "implicit faith in theoretical chemists at that time", he forgot all about it and thus let Fischer go first. It was, as he ironically commented in 1975, "the first of more than one interesting experience with theoretical chemists".^[44]

What were Hein's feelings after Fischer's and Zeiss' work became known to him? At first, he was understandably shocked to realize that for more than three decades he had proposed an erroneous structure for his "polyphenylchromium compounds". At the same time, however, he felt also relieved that the lasting problem had now been solved. He was—as one would have said in the past—a "Grandseigneur" (Figure 2). Certainly, he was pleased that Fischer informed him instantly after the manuscript reporting the synthesis of bis(benzene) chromium and analogous bis(arene) chromium complexes was accepted for publication by the *Zeitschrift für Naturforschung*.^[40] Moreover, Hein did not hesitate to follow up on Fischer's idea and carry out degradation reactions in his own laboratory with samples of $[\text{Cr}(\text{C}_6\text{H}_5\text{C}_6\text{H}_5)_2]$ and $[\text{Cr}(\text{C}_6\text{H}_5\text{C}_6\text{H}_5)_2]\text{I}$ prepared in Munich, and the so-called "Cr-(C_6H_5)₄" and "Cr(C_6H_5)₄I" from his own group.^[31,45] In those days, I worked as a student in Hein's institute in Jena and attended the course in preparative inorganic chemistry under the supervision of Karl Eisfeld. On Hein's advice, Eisfeld carried out degradation reactions with samples of Fischer's $[\text{Cr}(\text{C}_6\text{H}_5\text{C}_6\text{H}_5)_2]\text{I}$ and Hein's "Cr(C_6H_5)₄I" (e.g., with $[\text{Hg}(\text{CH}_3\text{CO}_2)_2]$, LiAlH_4 , I_2). Later he told me that Hein only slightly twitched his eyelids when he saw that the degradation products of both compounds were identical and thus the structure proposed by Fischer and Zeiss was correct. Hein's commented the result as follows: "It should be mentioned, and briefly explained, why I considered the organochromium compounds, at the time of their discovery, to be 'tetraphenylchromium' salts, and not formulations of the type now



Figure 2. Ernst Otto Fischer and Franz Hein talking to each other at Hein's farewell symposium in Jena in September 1969 (shown in the background is Professor Rudolf Taube).

suggested by H. Zeiss and E. O. Fischer. The main reason was that at that time, there were no precedents for such a view, and I firmly believe that if I had brought such a formulation of this type into consideration, I would not have been taken seriously in the context of the state of knowledge at the time.”^[46] In the end, Hein was very satisfied that his co-worker Richard Weiss^[47] and independently Zeiss and Herwig^[48] succeeded to prepare oligophenylchromium compounds with Cr–C₆H₅ σ bonds and confirmed that they do in fact exist. Finally, Hein and his co-workers also showed that σ -phenyl chromium compounds rearrange intramolecularly to π -arene chromium complexes, which illustrates a direct relationship between the two types of substances.^[49]

Fischer and Wilkinson continued their pioneering work on sandwich and half-sandwich complexes until the mid-1960s, but then directed their interest to other important aspects in organometallic chemistry at almost the same time. Fischer reported in 1964 the synthesis of the first carbene metal complex, followed by the synthesis of the first carbyne metal complex in 1973, and Wilkinson (in competition with Lappert) dedicated most of his research efforts to the preparation of homoleptic alkyl and aryl transition-metal compounds, previously assumed to be highly labile. The disinterest in the chemistry of the sandwich complexes was so profound that even in their Nobel Prize Lectures both Fischer and Wilkinson reported about their current research projects.^[50]

The decision of the Nobel Prize Committee to award the Nobel Prize in Chemistry in 1973 to Fischer and Wilkinson for their work on the chemistry of the sandwich complexes was applauded unanimously, not only in Germany and Great Britain but worldwide.^[51] In the laudation the Nobel Prize

Committee stated that the work of the laureates not only revolutionized the field of organometallic chemistry but also had a great impact on the development of inorganic, organic, and theoretical chemistry in general. To counteract the critics that neither Fischer nor Wilkinson were the first to prepare a sandwich complex, the Nobel Prize Committee emphasized that “a very essential part of a scientific discipline is its structure and its concepts. Fischer and Wilkinson widened the basic concepts of chemistry by their work and therefore also changed the structure of chemistry.” And it was added that the Prize should be seen as “an award for ‘chemistry for chemists’”.^[52]

However, the cheers about the decision of the Nobel Prize Committee were also accompanied by a note of discord sounded by Woodward. Two days after the decision had been announced, he wrote to the Chairman of the Committee: “The notice in The Times of London (October 24, p. 5) of the award of this year’s Nobel Prize in Chemistry leaves me no choice but to let you know, most respectfully, that you have—inadvertently, I am sure—committed a grave injustice”.^[53] And by quoting several newspaper articles, describing Fischer’s and Wilkinson’s work without mentioning his contributions, he continued: “The problem is that there were two seminal ideas in this field—first the proposal of the unusual and hitherto unknown sandwich structure, and second, the prediction that such structures would display unusual ‘aromatic’ characteristics. Both of these concepts were simply, completely, and entirely mine, and mine alone.” He added that “as a gesture to a friend and junior colleague” he had invited Wilkinson to join him in the experiments to verify his structural proposal for ferrocene. He also claimed that Wilkinson’s initial reaction to his view has been “close to derision”, and he continued: “But in the event he had second thoughts about his initial scoffing view of my structural proposal and its consequences, and all together we published the initial seminal communication that was written by me. The decision to place my name last in the roster of authors was made, by me alone, again as a courtesy to a junior staff colleague of independent status”.^[53]

Wilkinson provided a vastly different view and claimed that, when he saw the proposed linear structure for [Fe-(C₅H₅)₂] soon after Kealy’s and Pauson’s paper had appeared,^[1] he was saying to himself “Jesus Christ it can’t be that”.^[45] He recalled that because he had no cyclopentadiene at his disposal, he had contacted Woodward, who had also seen the communication by Kealy and Pauson. However, according to Wilkinson, Woodward was mainly interested in the assumed aromatic characteristics than in the structure of ferrocene, while he was keen himself to find out whether other transition metals were also able to produce sandwich-type complexes.^[44] Rosenblum, who on Woodward’s advice carried out the reaction of ferrocene with acetylchloride in the presence of AlCl₃ and prepared acetylferrocene,^[12] offered a somewhat different perspective, but this was described in Rosenblum’s personal recollections^[54] and in the essay by Laszlo and Hoffmann entitled “Ferrocene: Ironclad History or Rashomon Tale?” in more detail.^[13] Rosenblum conceded, that after the aromatic characteristics of ferrocene were confirmed, Woodward did not pursue the

work “since his principal interest lay elsewhere, in the intellectual drama and art of organic synthesis”.^[54] For this he was awarded the Nobel Prize in Chemistry in 1965.

The Nobel Prize Committee reacted with composure to Woodward’s objection. Since he had said in his letter^[53] that he had not been able to find “a complete account of the ancillary material released to the press” and continued “that quite possibly this material may well make a clear acknowledgment—ignored by the press—of my definite contributions in those respects”, Arne Fredga, the Chairman of the Nobel Prize Committee for Chemistry replied, “that the committee does not make available to the press information about a newly elected Nobel Laureate... and it is customary not to mention co-workers and co-authors who are not sharing the prize, and this rule has been followed also in the present case”.^[53]

Nevertheless, the majority of the chemical community approved the decision of the Nobel Prize Committee, particularly because even without the participation of Fischer and Wilkinson the chemistry of the sandwich complexes further developed at high speed. Even most recently, this has not slowed down, as illustrated by studies of Carmona,^[55] Ellis,^[56] and Lammertsma.^[57] Therefore, one can agree with a remark by Cotton—one of the heroes of inorganic chemistry in the 20th century—that the award of the Nobel Prize in Chemistry in 1973 to Fischer und Wilkinson was “one of the best choices the Nobel Committee ever made”.^[58] For the attending organometallic chemists, the pleasure of Fischer and Wilkinson about the Prize found expression in 1974 at a conference, organized by Wolfgang Beck in honor of Walter Hieber, when after the final reception the former rivals let themselves be persuaded to a dance (Figure 3). The story of the discovery and re-discovery of the sandwich complexes, which covered almost four decades, could thus be entitled “Elusions, Confusions”, in agreement with the title of Theodor Fontane’s famous novel, “*Irrungen, Wirrungen*”.^[59]



Figure 3. Geoffrey Wilkinson and Ernst Otto Fischer dancing at the final reception of the Conference on Organometallic Chemistry in July 1974 in Ettal (photo courtesy of Professor Wolfgang Beck).

Undoubtedly, we are all quite human, including the giants in science, and this is evident also in this story.^[60]

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- [1] T. J. Kealy, P. L. Pauson, *Nature* **1951**, 168, 1039–1040.
- [2] S. A. Miller, J. A. Tebbboth, J. F. Tremaine, *J. Chem. Soc.* **1952**, 632–635.
- [3] L. M. Venanzi, *Chimia* **1994**, 48, 16–22.
- [4] P. L. Pauson, *J. Organomet. Chem.* **2001**, 637–639, 3–6.
- [5] E. O. Brimm, M. A. Lynch, W. J. Sesny, *J. Am. Chem. Soc.* **1954**, 76, 2125–2126.
- [6] R. S. Nyholm, *Inaugural Lecture at University College London, 1 March 1956*, H. K. Lewis, London.
- [7] At that time the nomenclature for transition-metal complexes introduced by Alfred Werner and his school was generally used, particularly in German-speaking countries; see: F. Hein, *Chemische Koordinationslehre*, Hirzel, Leipzig, **1950**.
- [8] E. O. Fischer, R. Jira, *J. Organomet. Chem.* **2001**, 637, 7–12.
- [9] E. O. Fischer, W. Pfab, *Z. Naturforsch. B* **1952**, 7, 377–379.
- [10] E. Ruch, E. O. Fischer, *Z. Naturforsch. B* **1952**, 7, 676.
- [11] G. Wilkinson, M. Rosenblum, M. C. Whiting, R. B. Woodward, *J. Am. Chem. Soc.* **1952**, 74, 2125–2126.
- [12] R. B. Woodward, M. Rosenblum, M. C. Whiting, *J. Am. Chem. Soc.* **1952**, 74, 3458–3459.
- [13] Roald Hoffmann reported that while Woodward originally favored the name “ferrozene”, Mark Whiting proposed “ferrocene”, which finally was chosen; see: P. Laszlo, R. Hoffmann, *Angew. Chem.* **2000**, 112, 127–128; *Angew. Chem. Int. Ed.* **2000**, 39, 123–124.
- [14] J. D. Dunitz in *Organic Chemistry: Its Language and Its State of the Art* (Ed.: M. V. Kisakurek), Helvetica Chimica Acta, Basel, **1993**, pp. 9–23.
- [15] T. M. Zydowsky, *Chem. Intell.* **2000**, 29–34.
- [16] P. F. Eiland, R. Pepinsky, *J. Am. Chem. Soc.* **1952**, 74, 4971.
- [17] J. D. Dunitz, L. E. Orgel, *Nature* **1953**, 171, 121–122.
- [18] G. Wilkinson, *J. Am. Chem. Soc.* **1952**, 74, 6148–6149.
- [19] Peter Pauson mentioned that when he visited William von E. Doering at Columbia University in New York in September 1951, Doering already proposed a sandwich-type structure for ferrocene.^[4,20]
- [20] P. L. Pauson, *Q. Rev.* **1955**, 9, 391–414.
- [21] In looking back on his time with Wilkinson at Harvard, F. Albert (Al) Cotton wrote: “Geoff (Wilkinson) very soon recognized that molecules similar to ferrocene with other metals might well exist and set about trying to make them. I think that Geoff clearly decided at a very early date, that his goal would be to make cyclopentadienylmetal compounds of as many transition metals as possible, and he never lost sight of that goal”; see: F. A. Cotton, *J. Organomet. Chem.* **2001**, 637, 18–26.
- [22] In an essay with E. O. Fischer,^[8] Reinhard Jira mentioned: “In the spring of 1954... Wilkinson visited Munich at Fischer’s invitation. He showed us a sample of MnCp₂ 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.”^[8]
- [23] a) G. Wilkinson, F. A. Cotton, *Progr. Inorg. Chem.* **1959**, 1, 1–124; b) E. O. Fischer, H. P. Fritz, *Adv. Inorg. Chem. Radiochem.* **1959**, 1, 55–115.
- [24] Wilkinson published some preliminary communications also in the journal *Zeitschrift für Naturforschung* and commented this with the remark “taking the war to the enemy”; see Ref. [21].

- [25] In this context, it is worth mentioning that in organic synthesis Pauson's name became well-known later through the Pauson–Khand reaction, which is one of the most useful methods to prepare cyclopentenones; see: P. L. Pauson, *Tetrahedron* **1985**, *41*, 5855–5860.
- [26] a) H. Reihlen, A. Gruhl, G. von Hessling, O. Pfrenge, *Liebigs Ann. Chem.* **1930**, *482*, 161–182; b) At that time, Hans Reihlen was Associate Professor of Inorganic Chemistry at the University of Tübingen.
- [27] B. F. Hallam, P. L. Pauson, *J. Chem. Soc.* **1958**, 642–645.
- [28] Dietmar Seyferth, Fischer's first postdoc in the 1950s, wrote in an essay: "E. O. Fischer had another idea, a most daring one at the time: that similar transition metal sandwich complexes with two **neutral** benzene molecules π -bonded to a **neutral, zero-valent** metal atom might be capable of existence, specifically **bis-(benzene)chromium**. He reasoned that if each benzene molecule donates 6π electrons into the appropriate vacant chromium atomic orbitals, then a stable 18-electron noble-gas (krypton) configuration (the same as in ferrocene) would be achieved and a stable, sandwich-type molecule might result." See: D. Seyferth, *Organometallics* **2002**, *21*, 2800–2820.
- [29] I am convinced (and I am sure that Fischer would have definitely agreed) that Walter Hafner was one of the best, probably the best, graduate student in Fischer's group during Fischer's entire career (1952–1984). After Hafner finished his PhD thesis, he worked for the "Consortium für Elektrochemische Industrie", a subsidiary company of Wacker-Chemie in Munich, and there laid the foundation for the palladium-catalyzed oxidation of ethene to acetaldehyde, the Wacker process. Hafner retired in 1992 and died in 2004.
- [30] W. Hafner, PhD Thesis, Technische Hochschule München, **1955**.
- [31] a) F. Hein, *Ber. Dtsch. Chem. Ges.* **1919**, *52*, 195–196; b) F. Hein, *Ber. Dtsch. Chem. Ges.* **1921**, *54*, 1905–1938; c) F. Hein, *Ber. Dtsch. Chem. Ges.* **1921**, *54*, 2708–2727.
- [32] H. Zeiss in *Organometallic Chemistry, ACS Monograph Series No. 147* (Ed.: H. Zeiss), Reinhold, New York, **1960**, pp. 380–425.
- [33] J. A. Page, G. Wilkinson, *J. Am. Chem. Soc.* **1952**, *74*, 6149–6150.
- [34] Wilhelm Klemm (at that time Professor of Inorganic Chemistry at the University of Danzig, now Gdansk) and his co-worker Anna Neuber determined already in 1936 the magnetic moment of Hein's polyphenylchromium compounds; see: W. Klemm, A. Neuber, *Z. Anorg. Allg. Chem.* **1936**, *227*, 261–271.
- [35] D. Seyferth, *Organometallics* **2002**, *21*, 1520–1530.
- [36] F. Gordon A. Stone commented on this in his book: "The idea of a metal atom hexahapto-coordinated to a benzene ring... was evidently alien to some referees of that era. Since ferrocene was by then well known they should have had more imagination". See F. Gordon A. Stone, *Leaving No Stone Unturned*, American Chemical Society, Washington, **1993**, p. 24.
- [37] a) H. Zeiss, M. Tsutsui, *Angew. Chem.* **1955**, *67*, 282; b) H. Zeiss, *Yale Sci. Mag.* **1955**, *29*, 14.
- [38] E. O. Fischer, D. Seus, *Chem. Ber.* **1956**, *89*, 1809–1815.
- [39] H. Zeiss, M. Tsutsui, *J. Am. Chem. Soc.* **1957**, *79*, 3062–3066.
- [40] E. O. Fischer, W. Hafner, *Z. Naturforsch. B* **1955**, *10*, 665–668.
- [41] E. Weiss, E. O. Fischer, *Z. Anorg. Allg. Chem.* **1956**, *286*, 142–145.
- [42] E. O. Fischer, H.-O. Stahl, *Chem. Ber.* **1956**, *89*, 1805–1808.
- [43] E. O. Fischer, H. P. Fritz, *Angew. Chem.* **1961**, *73*, 353–364.
- [44] G. Wilkinson, *J. Organomet. Chem.* **1975**, *100*, 273–278.
- [45] F. Hein, W. Eißner, *Ber. Dtsch. Chem. Ges.* **1926**, *59*, 362–366.
- [46] F. Hein, *Chem. Ber.* **1956**, *89*, 1816–1821.
- [47] F. Hein, R. Weiss, *Z. Anorg. Allg. Chem.* **1958**, *295*, 145–152.
- [48] W. Herwig, H. Zeiss, *J. Am. Chem. Soc.* **1957**, *79*, 6561.
- [49] E. Uhlig, *Organometallics* **1993**, *12*, 4751–4756.
- [50] a) E. O. Fischer, *Angew. Chem.* **1974**, *86*, 651–663 (Nobel Lecture); b) G. Wilkinson in *Les Prix Nobel en 1973* (Ed.: W. Odelberg), Nobel Foundation, Stockholm, **1974**.
- [51] D. Seyferth, A. Davison, *Science* **1973**, *182*, 699–701.
- [52] See: http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1973/press.html.
- [53] See Ref. [15], pp. 32–33.
- [54] M. Rosenblum, *J. Organomet. Chem.* **2001**, *637–639*, 13–15.
- [55] I. Resa, E. Carmona, E. Gutierrez-Puebla, A. Monge, *Science* **2004**, *305*, 1136–1138.
- [56] W. W. Brennessel, R. E. Jilek, J. E. Ellis, *Angew. Chem.* **2007**, *119*, 6244–6248; *Angew. Chem. Int. Ed.* **2007**, *46*, 6132–6136.
- [57] R. Wolf, J. C. Slootweg, A. W. Ehlers, F. Hartl, B. de Bruin, M. Lutz, A. L. Spek, K. Lammertsma, *Angew. Chem.* **2009**, *121*, 3150–3153; *Angew. Chem. Int. Ed.* **2009**, *48*, 3104–3107.
- [58] See Ref. [21], p. 25.
- [59] T. Fontane, *Irrungen, Wirrungen*, F. W. Steffens, Leipzig, **1888**.
- [60] H. Zankl, *Nobelpreise—Brisante Affären, umstrittene Entscheidungen*, Wiley-VCH, Weinheim, **2005**.