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Ferrocene—how it all began

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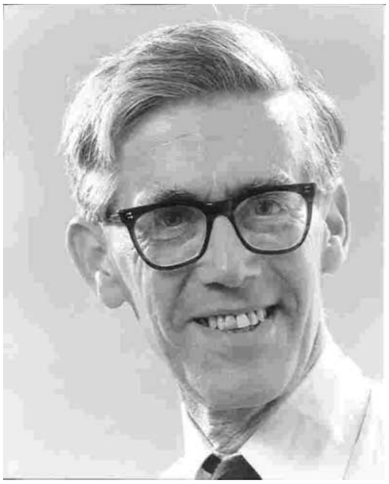
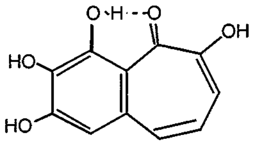


(Peter L. Pauson)

With the rest of my family, I had come to the UK in 1939 as a refugee from Nazi persecution of the Jews. After completing my secondary education, I entered Glasgow University in 1942 to study Chemistry. My inclination towards the organic side was greatly enhanced and my approach to research was moulded by the inspiring teachings of T.S. Stevens.[1] The offer of a research studentship led me to Sheffield University in 1946 to do my PhD under the direction of Professor R.D. Haworth.[2] My task was to study the chemistry of 'purpurogallin'—the brilliant red compound obtained by oxidation of pyrogallol. We succeeded in establishing its structure as the benzotropolone (**1**) and showed that further oxidation followed by decarboxylation led to □-methyltropolone (**2**), the first synthetic and fully characterised simple tropolone.

The concept of 'non-benzenoid aromatics' was still rather new and, although the question as to whether tropolones truly fit into this category has remained controversial, they were certainly topical and of much interest in this context at the time. My obvious interests for my first independent researches were therefore directed towards further work on either tropolones or other non-benzenoid systems.



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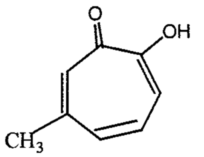

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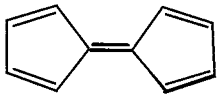

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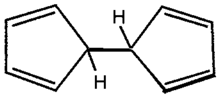

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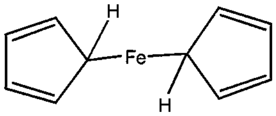

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On completion of my degree, I had moved to Duquesne University[3] in 1949. There, I read with interest, but also scepticism, R.D. Brown's paper (*Nature*, 1950), which suggested that fulvalene (**3**) might show aromatic properties. The challenge to either prove or

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[1] Discoverer of the Stevens Rearrangement, the McFadyen–Stevens aldehyde synthesis, and the Bamford–Stevens reaction.

[2] Best remembered for the Haworth phenanthrene synthesis.

[3] This Catholic university in Pittsburgh was better known for its basketball team than for its academic achievements. Its chemistry students were mostly pre-meds, but it offered BS and MS degrees in chemistry although not yet PhD. I had applied in response to an advertisement in *Chemical and Engineering News* and, after their first selected candidate withdrew at short notice, I was offered the post of Assistant Professor without interview.

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disprove his suggestion was heightened by my belief that the compound might be accessible in just two steps: the coupling of two molecules of cyclopentadienylmagnesium bromide to give the dihydro compound **4**, followed by dehydrogenation. This, therefore, was the project I offered to Tom Kealy when he expressed an interest, in 1951, in working with me for his MS degree.

The reductive coupling of Grignard reagents RMgX by transition metal halides to give hydrocarbons R–R is a general reaction that is known to be particularly easy when R is an allylic group. Although other halides, e.g. $CoCl_2$, were regarded as better, we chose $FeCl_3$ for two reasons: (i) It is a common and ether-soluble reagent in its anhydrous form, whereas all the other candidates would have had to be made from hydrates; and (ii) if fulvalene were truly aromatic, the oxidising power of Fe(III) might suffice to effect the dehydrogenation step and thus give us fulvalene in a one-pot process.

(T.J. Kealy)

Tom and I did the crucial experiment together one day in July 1951: making EtMgBr in ether, at the same time cracking the dimer of and redistilling cyclopentadiene, which was then added to the Grignard solution to displace ethane and generate cyclopentadienylmagnesium bromide, finally adding the $FeCl_3$. Standard workup of this mixture by pouring onto ice and ammonium chloride produced a yellow ether layer—not the yellow aqueous layer expected if the iron(III) had remained unreduced. Moreover, a few drops of the yellow solution that had escaped onto the outside of the separating funnel evaporated, leaving yellow crystals. Could we have made a yellow hydrocarbon, perhaps even the desired fulvalene? It seemed too good to be true.

We soon had a batch of purified crystals and, not wishing to imply that the results should add up to 100%, these were sent for C,H microanalysis as containing C, H, and O. When the results came back a few days later, the large deficit from 100% clearly required an element heavier than oxygen and it needed little arithmetic to find that these results accurately fitted $C_{10}H_{10}Fe$. We now had to analyse for iron, both qualitatively and quantitatively. The compound dissolved in strong sulphuric acid but was largely recovered unchanged on dilution. We had to boil with strong nitric acid before we could get the standard qualitative tests for iron to work, and even this was insufficient to give accurate quantitative results. These were only obtained after fuming to dryness with $HClO_4$.

What was this remarkable substance we had made? We were well aware of the common belief that bonds between transition metals and hydrocarbon groups would always be unstable—based on the failure of all recorded attempts to form such links. Yet, here we had a compound, formed from two C_5H_5 units and an iron atom, which was not only isolable but also stable to high temperatures and unaffected by water and by both strong acids and alkalis. True, we knew of the exceptions to the alleged non-existence of organo-transition metal compounds: Zeise (1827) had made $K[PtCl_3(C_2H_4)]$ and some methylplatinum compounds had been described—but platinum was seen as 'atypical'; Hein (1919) had described 'polyphenylchromium salts' and Reihlen (1930) had reacted iron pentacarbonyl with butadiene to give $C_4H_6Fe(CO)_3$. These substances tended to be ignored simply because their structures were unknown.

Whatever our product might be, it was clearly something very novel and unexpected, and we therefore reported our findings in a note to *Nature*—despatched within a week of getting that C,H analysis. We wrote the structure as **5**.

I attended the large IUPAC Congress in New York a couple of months later and there handed a sample of our crystals to J.M. Robertson, the distinguished X-ray crystallographer who was Professor of Physical Chemistry at Glasgow University.

Soon several people independently guessed the correct structure. The first of these was W. von E. Doering, whom I visited at Columbia University immediately after the IUPAC Congress and told about our finding. Unfortunately, I failed to understand his suggestion, which included the possibility that magnetic susceptibility might provide evidence; I was too reluctant to expose my ignorance and my lack of understanding and was content to await the definitive answer expected from X-ray work. In the meantime, through circumstances beyond his control,[4] no results were forthcoming from Robertson before several others undertook X-ray structural work after our note appeared in *Nature*. Ironically, one of these was Jack Dunitz, next to whom I was sitting at the IUPAC meeting while listening to Robertson's talk and waiting to give him the sample.

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[4] Robertson was on his way to Cornell University as that year's 'Baker Lecturer' and preoccupied with writing the book which was expected of holders of this visiting appointment.

In those days, the Chemical Society published lists of papers accepted for publication in its journal. About a month before our *Nature* note was due, I read of a paper on 'Dicyclopentadienyliron' by Miller, Tebboth and Tremaine of the British Oxygen Co. I wrote to Dr. Miller and told him that we appeared to have the same compound, and so it proved when he sent me a proof copy of the *J. Chem. Soc.* paper. It also showed that they had used a radically different route and that their paper had been submitted before we ever tried the reaction, but it was to appear in the February 1952 issue of *J. Chem. Soc.*, whereas *Nature's* faster method of publication gave us the apparent precedence with a 1951 publication date. In an accompanying note Miller mentioned that they had had the compound for about 3 years. Even this, however, was quite possibly not the first preparation. The following tale was told about a year later by E.O. Brimm of Linde Air Products. Brimm, who had done some work on metal carbonyls and other organometallics, was one of several industrial chemists who, on reading our report, wanted to make some of the compound. Therefore he enquired of a colleague at Union Carbide (Linde's parent company) whether they had any cyclopentadiene. The reply that they no longer did so was accompanied by the statement that, some years previously, they had terminated work on the cracking of cyclopentadiene because a yellow sludge clogged the iron pipes they used. They had not attempted to isolate or analyse this but had kept a bottle of it; it was ferrocene. The British Oxygen group's synthesis was, in fact, not dissimilar as it involved passing cyclopentadiene over a heated, iron-containing ammonia synthesis catalyst.

As is well-known, the correct structure of dicyclopentadienyliron was put forward in two independent publications: one by E.O. Fischer and W. Pfab, the other by G. Wilkinson, M. Rosenblum, M.C. Whiting, and R.B. Woodward. Both groups had repeated our preparation and made physical measurements that strongly supported the 'Doppelkegel' or 'sandwich' structure but fell short of full proof. Fischer relied chiefly on preliminary X-ray data indicating that the molecules are centrosymmetric, while the Harvard group cited the single C–H frequency in the IR and the diamagnetism. Only weeks went by before two independent complete X-ray structure determinations were published.[5]

At Woodward's suggestion that the compound might be aromatic, Whiting and Rosenblum went on to show that it readily undergoes Friedel–Crafts acylation and, on this basis, suggested the name 'ferrocene'—with the 'ene' ending implying aromaticity. We had indeed prepared a novel, non-benzenoid aromatic, but a very unexpected addition to that class!

Both Fischer and Wilkinson very soon started adding bis-cyclopentadienyls of other transition metals; Tom Kealy had tried nickel and cobalt but was thwarted by the insolubility of their anhydrous halides, which prevented their reaction with the ethereal solution of cyclopentadienylmagnesium bromide. Fischer overcame this problem by turning to the hexammine complexes of these metals and Wilkinson by using the acetylacetonates.

In the meantime I was spending the academic year 1951–1952 at the University of Chicago as a postdoctoral fellow working on peroxide chemistry with M.S. Kharasch. My next move was to Harvard where I was appointed to a 'Du Pont Fellowship' to work independently. Although my application for this had been based on a scheme to synthesise the alkaloid colchicine (a tropolone), Professor Bartlett, as Chairman of the department, made clear that I was free to do whatever I liked. It cannot have been unexpected that by then I was anxious to play a part in the work on metallocenes which was in full swing in both Woodward's and Wilkinson's laboratories.

En route to Harvard, I visited the Du Pont laboratories at Wilmington. There, Dr Victor Weinmayr was doing work on the organic chemistry of ferrocene. On talking about other metals, he told me that nickel worked and that I should feel free to use this information provided that I did not disclose its source. Combining this hint with what I knew already, I therefore employed nickel acetyl acetonate in my first experiments at Harvard and, by the time Wilkinson and Cotton both returned from their summer vacations, I was able to show them a sample of the beautiful emerald-green crystals of nickelocene. They showed that it is paramagnetic and we extended our joint studies to the benzo derivatives of ferrocene and of the cobaltocenium cation, which I prepared from indene by similar techniques, leaving them to do all the physical measurements.

During this and the following 2 years, Fischer and Wilkinson made bis-cyclopentadienyl–metal and cyclopentadienylmetalcarbonyl compounds of most of the transition metals. It seemed almost inevitable that they were in constant competition as to who would be first with the next, fairly obvious target.[6]

At the end of my year at Harvard, I returned to the UK to take up a lectureship in organic chemistry at Sheffield University. There, I soon had the benefit of PhD students to do all the hard work for me. We concentrated on the organic aspects. The first student (G.D. Broadhead), after showing that ferrocene undergoes acetylation very much faster than anisole, found that it would undergo formylation under Vilsmeyer

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[5] By Dunitz and Orgel and by Eiland and Pepinsky.

[6] This competition effectively ceased in 1955, when Fischer's success (with W. Hafner) in making bis-benzenechromium led him to concentrate heavily on arene complexes.

conditions (as also shown independently by Rosenblum) and then tried azo-coupling, thereby finding the unexpected arylation. The second student (B.F. Hallam), after some work on cyclopentadiene–iron carbonyl complexes, took on the task of verifying my belief that Reihlen's above-mentioned butadienetricarbonyliron is also a π-complex. By repeating its preparation and also making the cyclohexadiene complex, he opened up the whole field of olefin, diene, and triene complexes—but that is the beginning of a larger story beyond the scope of the present topic.

It was undoubtedly the availability of good methods of structure determination coupled with the greater theoretical understanding which made possible the explosive growth of interest in organo-transition metal chemistry following directly from the discovery of ferrocene, whereas the earlier findings had led nowhere. Personally, I feel extremely lucky to have been involved from the start and I owe a huge debt of gratitude to a succession of co-workers who made it possible for me to participate with great enjoyment in these developments throughout these 50 years.