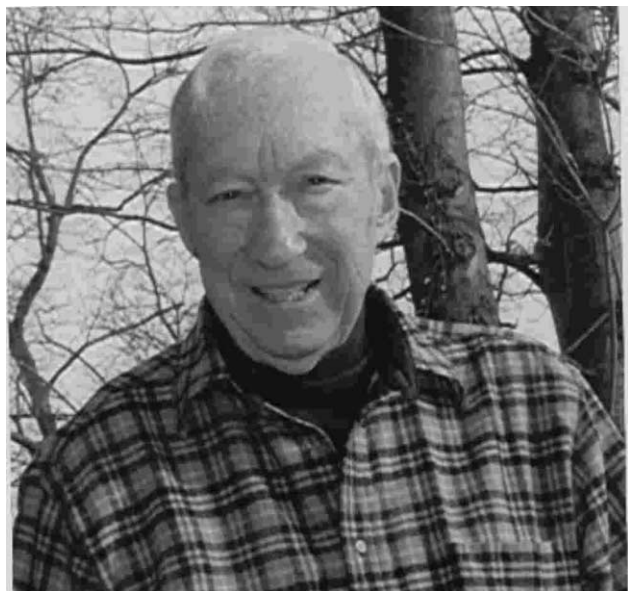


The early ferrocene days—a personal recollection

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(Myron Rosenblum, 2000)

I came to Harvard as a graduate student in September 1949 and by the summer of 1950 had joined Bob Woodward's group to work on the synthesis of fulvalene. Aromaticity was a subject which continued to occupy Woodward's interest throughout his career, and fulvalene, a highly unsaturated C_{10} hydrocarbon at the time unknown, was of some general theoretical interest. As fortunate fate would have it, I was not destined to prepare fulvalene, which turned out to be a substance of exquisite reactivity and doubtful aromaticity [1].¹ The synthesis of fulvalene was first achieved in 1959 by

¹Theoretical chemistry was yet in its early predictive state, as can be seen in the following statement taken from this paper. "From Table III we notice that the resonance energy of fulvalene, although considerably less than that of its very stable isomers naphthalene and azulene, is almost twice that of fulvene (22 kcal), and it seems likely that fulvalene is reasonably stable and not too reactive chemically. Indeed the fact that it is so far unknown may be connected with the fact that no direct attempt to prepare it can be found in the literature".

Doering and Matzner [2], and subsequently by DeMore, Pritchard and Davison [3]. This elusive substance appears to be detectable spectroscopically only at high dilution in solution or at very low temperatures. Instead, a truly aromatic compound of an entirely different sort awaited.

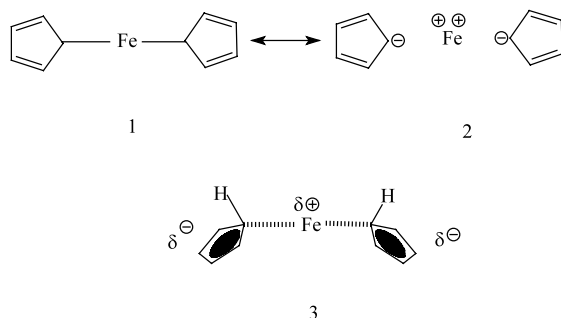
My lab space was in Converse 108, a large room at the end of the building, with five lab bays. The room is now much diminished from its former state through serving in part as a corridor to the Conant building. I occupied a lab bay at the end of the room. Jerry Meinwald, then a graduate student, worked in the next bay. Franz Sondheimer and Mike Cava, both postdocs, in turn occupied the next two bays, and finally Irving Osvar, who was a special assistant assigned to prepare synthetic intermediates for Woodward's strychnine synthesis, worked in the bay at the other end of the lab.

Woodward frequently made the rounds of his labs, and it was therefore not surprising when he appeared in the lab one morning in January 1952. This must have been toward the middle of the month, since the first entry in my research notebook related to the ferrocene work is dated January 16, 1952.² Our approach to the synthesis of fulvalene involved the use of dicyclopentadiene and cyclopentadiene intermediates, and I recall that he asked me whether I had seen a paper, which appeared in *Nature* on a new cyclopentadiene-iron compound. I had not. He then proceeded to outline the results of Kealy and Pauson's [4] experiments and finally drew out on the 2 × 4 ft. blackboard, which was mounted on the wall at the end of my lab bay, in architecturally exact Woodwardian form, the now accepted structure of ferrocene. This structure showed the iron atom nested neatly between two cyclopentadienyl rings, with each of the carbon atoms being bonded by dashed lines to the central metal. He then said something like "This, I believe is the correct structure. Why don't you take off a few days, make this stuff, and let's have a look at it".

²I am indebted to one of my former graduate students, Don Ciappenelli who, at the time of Woodward's death, was the department administrator at the Harvard chemistry department. He very kindly arranged to return my research notebooks to me.

Curiously, the first entry in my lab book pertaining to the ferrocene work is marked as ‘ruthenium–dicyclopentadienyl’, so it seems likely that we had also discussed the possibility of preparing congeners of the iron compound. In any event, I first attempted unsuccessfully to prepare anhydrous RuCl_3 by evaporating an aqueous solution of the salt and then heating the residue at higher temperatures. It must have been during this time, and possibly before January 21, when I set up the reaction to prepare Kealy and Pauson’s iron compound, that I went to see Geof Wilkinson [5].³ He had recently come from MIT, and seemed like a reasonably good bet to know where I could obtain a sample of an anhydrous ruthenium salt. Wilkinson’s office was in a small room in Mallinkrodt, and after introducing myself and posing the request, I remember that he shot back sharply, and in a somewhat annoyed voice “what do you want that for”?

As for iron dicyclopentadienyl, this was prepared in an experiment begun on Monday, January 21, following the procedure reported by Kealy and Pauson, using cyclopentadienylmagnesium bromide and ferric chloride. By the next day some 8 g of purified product had been obtained, and its reversible oxidation had been marked. During the course of the next several weeks the UV and IR spectra of the new compound were taken, and its resistance to hydrogenation and to reaction with maleic anhydride was established. The new compound also proved to be remarkably stable to heat. Attempted destruction by passing its vapors through a tube heated at 470° left it unscathed. In their paper, Kealy and Pauson [4] had proposed that the remarkable stability of the new iron compound might be attributed to “the tendency of the cyclopentadienyl group to become ‘aromatic’ by acquisition of a negative charge, resulting in important contributions from the resonance form 2 and intermediate forms”.



It therefore was of interest to determine its dipole moment, since contributions from such dipolar forms would be expected to confer an appreciable dipole moment on the substance even for a formally linear

C–Fe–C system (3). Such measurements were well out of the realm of my experience. However, with the help A. Weissberger’s compendium of physical methods, and the good fortune of finding a heterodyne beat apparatus in Eugene Rochow’s laboratory, I spent the week of February 25th carrying out the precise measurements needed in these calculations, and had the result: $0.05 \pm 0.1\text{D}$, in time for the annual party at Woodward’s home. Chemistry was an excluded topic of conversation at these festivities, but I felt that it would not be entirely out of place to quietly transmit what I believed was an important piece of information. When I arrived at the house, I was greeted by Woodward himself, and in as calm and matter-of-fact a voice as I could muster, I said: “the dipole moment is effectively zero”. He smiled slightly, nodded his head, and I passed by and into the party.

By the middle of March the first of two communications had been sent off to JACS, proposing the sandwich structure for the new iron compound. Confirmation of its essential correctness was not long in coming. Before the year was out, Fischer and Pfab [6] in Germany, and Eiland and Pepinsky [7] in this country had independently confirmed Woodward’s structural proposal through x-ray diffraction studies. A third paper by Dunitz and Orgel [8], also showing the sandwich structure, appeared shortly thereafter.

I recall an amusing incident that occurred during the period when we were still deeply involved in an exploration of the redox properties of the new substance. One day, Woodward came into the lab, neatly dressed as he typically was, in a powder blue jacket and darker matching blue tie. He was clearly eager to do some quick bench work and poured an acidic aqueous solution of ferrocenium salt, which I had at hand, into a small separatory funnel. I gave him the requested bottle of ferrous salt and, not waiting to dissolve the salt in water in a separate operation, he removed a small sample of this salt and popped it deftly into the separatory funnel. A brief and vigorous shake of the separatory funnel brought about a surprising result. Instead of dissolving, the small chunk of salt neatly punched its way through the glass wall carrying some of the solution with it onto his suit. Fortunately, I had a clean lab towel at hand. He quickly dampened this under the tap and, after vigorously wiping the front of his jacket, flung the towel down on the bench and without another word hurried from the lab.

The suggestion that the new iron compound might possess aromatic character came about in the course of a casual and brief conversation I had with Woodward just before one of his Thursday evening seminars near the Ides of March. As we were taking our seats for the evening’s chemical adventures, he mentioned in an offhand manner that I might want to attempt a Friedel–Crafts reaction on the compound. The entry

³ This was probably on Saturday, January 19th, since Wilkinson, in his recollections, notes that I came to see him on a Saturday.

into my research notebook shows that I put off doing that acetylation experiment until the following Monday, March 17. By the next day, I had a new bright red crystalline substance, with an infrared spectrum in which the largest single feature was an intense carbonyl peak at 6 μm . I recall hurrying into his office and triumphantly spreading the spectrum out on his desk—to his evident pleasure. The felicitous name ‘ferrocene’, for the new aromatic substance, was suggested by Mark Whiting.

As for the congeners of ferrocene, I went back and on January 16, 1952, made a satisfactory sample of anhydrous RuCl_3 by passing a mixture of CO and Cl_2 over Ru metal at 360° [9]. Unfortunately, this material was highly insoluble in organic solvents and an attempt, made on January 31, to convert this to ruthenocene in the presence of cyclopentadienylmagnesium bromide came to naught. Ruthenocene was later prepared by Wilkinson using the more soluble complex $\text{Ru}(\text{acac})_3$ [10]. However, the idea of extending the synthesis of congeners of ferrocene across the periodic table was clearly very much in the air at the time. On the same day that I set up the ruthenium experiment, I also set up three other, very colorful experiments on my bench, involving reactions of cyclopentadienyl Grignard with NiCl_2 , CoCl_2 and CrCl_3 . These too came to naught since, in retrospect, the standard organic aqueous workup procedure used was inadequate to the task of isolating these chemically very reactive metallocenes. I wonder at times whether Woodward might not have taken a greater interest in pursuing this line of research had these experiments been more successful. In any event, these synthetic sorties were never repeated. Woodward had apparently reached a private agreement with Wilkinson, leaving the extension of the metallocene series to him, and I turned my attention to the study of the organic chemistry of ferrocene.

By the spring of the following year, when I concluded my lab work, the preparation of a large number of

acylated ferrocenes and their transformation products had been carried out. This was accomplished working jointly with Mark Whiting and Ernest Csendes, a newly arrived Woodward postdoc. Peter Pauson, who had recently come to Harvard as an independent research fellow and had experienced a renewed interest in his offspring, prepared a number of otherwise inaccessible arylferrocenes directly from arylcyclopentadienes. The aromatic chemistry of the ferrocene was by now firmly established and a good beginning toward understanding its basic chemistry had been made. During this period too, early evidence for the low rotational barrier in ferrocene was adduced through a careful study of the number of $\text{C}_{10}\text{H}_8\text{AB}$, $\text{C}_{10}\text{H}_7\text{A}_2\text{B}$ isomers. Woodward never wrote these results up for publication, since his principal interest lay elsewhere, in the intellectual drama and art of complex organic synthesis. It was not until almost 5 years had gone by, and after I had presented him with the completed manuscript, which he accepted without change, that the evidence pertaining to the rotational barrier in ferrocene was finally published. I believe this was in fact his last publication on the subject of metallocene chemistry.

References

- [1] R.D. Brown, *Trans Faraday Soc.* 46 (1950) 151.
- [2] (a) W. Doering, E. Matzner, *Theoretical Organic Chemistry*, Kekule Symposium, Butterworths, London, 1959, p. 35;
(b) W.E. Doering, *Abstracts of 16th National Organic Chemistry Symposium*, Seattle, 15–17 June, 1959, p. 22.
- [3] W.B. DeMore, H.O. Pritchard, N. Davidson, *J. Am. Chem. Soc.* 81 (1959) 5874.
- [4] T.J. Kealy, P.L. Pauson, *Nature* 168 (1951) 1040.
- [5] G. Wilkinson, *J. Organometal. Chem.* 100 (1975) 273.
- [6] E.O. Fischer, W. Pfab, *Z. Naturforsch. Teil b* 7 (1952) 377.
- [7] P.F. Eiland, R. Pepinsky, *J. Am. Chem. Soc.* 74 (1952) 4971.
- [8] J.D. Dunitz, L.E. Orgel, *Nature* 171 (1953) 121.
- [9] Jolly, *Comptes Rendu* 114 (1892) 291.
- [10] G. Wilkinson, *J. Am. Chem. Soc.* 74 (1952) 6146.