Ferrocene: Ironclad History or Rashomon Tale?**

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A critical stance is essential to science. Proving other people wrong is a favorite private and public satisfaction—there is nothing some scientists like better. But, excess zeal discounted, doubt serves as a powerful impulse to the advancement of knowledge. We document it here with the discovery of the structure of ferrocene, a story which also plays up the virtue of the spoken word.[1] We base it on various published (and most fragmentary, if not mutually inconsistent!) accounts, supplemented with some very helpful correspondence from colleagues.

Two groups independently reported at the very end of 1951 preparation of a compound $C_{10}H_{10}Fe$ from cyclopentadiene. Kealy and Pauson published their contribution in the December 15, 1951 edition of *Nature*, while Miller, Tebboth, and Tremaine's account of their independent (and apparently earlier) preparation of the identical compound, with the same "traditional" formulation (what would today be called a di-σ-complex), appeared a little later in the *Journal of the Chemical Society*.[2]

Let's turn to the reception of those two papers in the Chemistry Department at Harvard University. As soon as it arrived in the library, during the first couple of weeks in January 1952, R. B. Woodward apparently saw the Kealy and Pauson piece. And he had a hunch that the structure was wrong. He set a graduate student, Myron Rosenblum, preparing not only ferrocene, but also analogues from other transition metals and cyclopentadiene. For this Rosenblum needed ruthenium trichloride. He went to Geoffrey Wilkinson, who had recently taken up an Assistant professorship at Harvard, to ask for a sample of ruthenium. Wilkinson "*rather brusquely wanted to know*" what Rosenblum needed it for.[3] Wilkinson writes:[4]

> *"…Mike Rosenblum came into my laboratory asking if I had got any ruthenium. I can't remember what I said, except that I think it was along the lines of 'let me tell you what you want it for.' "*

Clearly, Wilkinson had already also seen the Kealy and Pauson paper and had decided to study this problematic structure of ferrocene.[4]

Wilkinson continues:

> *"However, the upshot was that Woodward and I had lunch at the Harvard Faculty Club on Monday[5] and sorted things out. The possibility that the C_5H_5 ring in the iron compound could possibly undergo Friedel–Crafts or other aromatic reactions simply had not dawned on me, but other than the structure, this seemed to be Bob's main interest, whereas mine was to go on to other transition metals."*

One can only bemoan the fact that Woodward left no account of the discovery, and apply all the reservations the science historian has painfully had to learn of the construction of history (yes, even by the very participants) after the fact. Myron Rosenblum offers a some what different perspective on the directions taken by the protagonists:[3]

> *"Woodward certainly had an interest in extending the metallocene series vertically along the periodic table and possibly horizontally as well, since I set up four reactions simultaneously on January 31st. These involved the reactions of $NiCl_2$, $CoCl_2$, $CrCl_3$, and $RuCl_3$ with cyclopentadienylmagnesium bromide. From my research notebook I see that I had actually made two attempts to prepare anhydrous $RuCl_3$ on January 16th, five days prior to my first preparation of ferrocene itself. But in any event, Woodward and Wilkinson had apparently reached a private agreement which apparently left this initiative (extending the ferrocene family) to Geoff."*

Woodward's contribution to the ferrocene story (and dare one identify this as the main contribution, too?) was the divination of the sandwich structure, and a beautiful piece of insight about its aromaticity. Of the latter Rosenblum writes: [3]

> *"On a Thursday evening, March 13th (1952), as we were taking our seats before that evening's seminar, we were chatting about some of the chemistry of this new substance, when [RBW] suggested simply, almost matter-of-factly, that I might want to try a Friedel–Crafts reaction on this new substance.…I put off doing the reaction until Monday, March 17th…the product was a beautiful red crystalline material with an enormous carbonyl stretching absorption in the infrared. "*

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[**] Akira Kurosawa's classic film "Rashomon" depicts a violent event (a rape and murder in a forest) as seen by four participants. In his autobiography (A. Kurosawa, *Something Like an Autobiography*, Vintage Books –Random House, New York, **1983**, p. 183). Kurosawa writes of the difficulty his co-workers had understanding the complex plot. He told them: "This film is like a strange picture scroll that is unrolled and displayed by the ego…you can't understand the script at all, but that is because the human heart itself is impossible to understand."

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The correct ferrocene structure and its aromaticity were most rapidly published in the form of a communication in *Journal of the American Chemical Society*;[6] the coauthors were aside from Wilkinson and Woodward, Rosenblum and Mark C. Whiting (a postdoctoral associate in the Woodward group, who joined the research effort).

Meanwhile, during the spring of 1952, E. O. Fischer was independently studying the structure of ferrocene in his laboratory at the Technische Hochschule in Munich (with W. Pfab). Basing his conclusions on evidence from X-ray crystallography, and on very reasonable bonding notions, he also concluded that the molecule was best formulated as an iron(II) atom in-between two cyclopentadienide rings as ligands. Fischer and his co-workers immediately synthesized the ferrocenium cation, and started exploring cognate molecules such as the corresponding cobaltocene.[7]

The structures proposed by Wilkinson, Woodward, Rosenblum, Whiting, Fischer, and Pfab were truly revolutionary. Contemporary chemists were shocked; here is a recent account by one of the greatest of structural chemists, J. D. Dunitz: [8]

> *"One afternoon, I opened the Library copy of JACS [in Cambridge, England] and came across R. B. Woodward's proposal that the molecule consists of two parallel cyclopentadienyl rings with the iron atom sandwiched between them. I was skeptical. Nothing like this had ever been seen before. On my way out of the Library I met Leslie [Orgel] and asked if he had seen this astonishing proposal. He was as skeptical as I was. When we found that the compound was relatively easy to prepare in crystalline form, I decided to determine its crystal structure and so demonstrate the incorrectness [our emphasis] of the proposed molecular-structure. Within a few weeks, it became clear to us that Woodward's proposal was correct after all. There was no doubt about it."*

Leslie Orgel went on to devise a MO description of this novel structure, which he published together with Dunitz's structure determination. The title of their paper contained the "sandwich" descriptor.[9–11] Which stuck.[12]

Thus the ferrocene story unfolded: a conjectured structure was intuitively doubted, refuted, and replaced with what we now know as the true structure. But the true structure was deemed so unusual that it itself led to an attempt at refutation. Which failed, and thereby became an outstanding piece of corroborative evidence.

Our story is hardly complete! There is something to be learned (will it be done before the traces vanish?) of the complicated interactions that the experimentalists whose names we have mentioned above had with the theoreticians around them.[13] And the sandwich structure was apparently suggested by William von E. Doering to Peter Pauson in September 1951, before the synthesis was published![14]

Also from the outset it was clear that this incredible breakthrough, opening up a whole new field within organometallic chemistry, was worthy of recognition. It led to the award of the Nobel Prize to both Wilkinson and Fischer. Woodward was inexplicably left out; he complained, of course to no avail. Access to the deliberations of the Nobel Committee still decades in the future, Thomas Zydowsky has nevertheless uncovered the fascinating correspondence that ensued, one that will also reveal Woodward's perspective on the initial discovery. But for that story you will have to wait.[15]

We are grateful to many who have shared their memories and writings with us, most importantly Myron Rosenblum, Peter Pauson, Tom Zydowsky, Mark Whiting, Jack Dunitz, and F. Albert Cotton.

[1] We expand here upon a segment from a recent paper aimed at sociologists, "The Say of Things": R. Hoffmann, P. Laszlo, *Soc. Res.* **1998**, *65*, 653–693.

[2] T. J. Kealy, P. L. Pauson, *Nature* **1951**, *168*, 1039–1040; S. A. Miller, J. A. Tebboth, J. F. Tremaine, *J. Chem. Soc.* **1952**, 632–635. For a description of the chemistry and chronology of these two papers, see G. B. Kauffman, *J. Chem. Educ.* **1983**, *60*, 185–186.

[3] Letters from Professor Myron Rosenblum, Brandeis University, to Roald Hoffmann of September 9, 1998, and March 29, 1999.

[4] G. Wilkinson, *J. Organomet. Chem.* **1975**, *100*, 273–278; Wilkinson dates the visit by Rosenblum to Saturday, January 31st. However, from the evidence in Rosenblum's notebook, the visit predates January 16, 1952. January 30th, 1952 was a Wednesday.

[5] The evidence of the Rosenblum notebooks would seem to indicate January 19 and 21 for those dates.

[6] G. Wilkinson, M. Rosenblum, M. C. Whiting, R. B. Woodward, *J. Am. Chem Soc.* **1952**, *74*, 2125–2126.

[7] E. O. Fischer, W. Pfab, *Z. Naturforsch. B* **1952**, *7*, 377–379.

[8] J. D. Dunitz, *Origins Life and Evolution of the Biosphere* **1997**, *27*, 421–427. See also "Forty Years of Ferrocene": J. D. Dunitz in *Organic Chemistry*: *Its Language and Its State of the Art* (Ed.: M. V. Kisakurek), Verlag Helvetica Chimica Acta, Basel, **1993**, pp. 9–23.

[9] L. E. Orgel, J. D. Dunitz, *Nature* **1953**, *171*, 121–122.

[10] A third group independently determined the structure of ferrocene: P. F. Eiland, R. Pepinsky, *J. Am. Chem. Soc.* **1952**, *74*, 4971.

[11] Peter Pauson, private communication, recalls that he had crystals of ferrocene in the fall of 1951. He was trying to decide whether to ask Jack Dunitz, or the senior organic crystallographer of the time, J. Monteath Robertson (real or adopted Scotsmen all). Pauson decided on Robertson. Who, according to Pauson, took the crystals to…Cornell, where he asked Lynn Hoard if someone could look at them. The crystals were assigned to a beginning graduate student, who failed to solve the structure.

[12] The felicitous coining of the name "ferrocene" is due to Mark Whiting and occurs in the second Harvard paper, R. B. Woodward, M. Rosenblum, M. C. Whiting, *J. Am. Chem. Soc.* **1952**, *74*, 3458. Apparently "ferrozene" was an early favorite (e-mail from M. C. Whiting to Roald Hoffmann, May 4, 1999).

[13] Wilkinson, for instance recounts that William Moffitt, a great young theoretician of the time, told him that the binding of benzene to a transition metal was "not on" (ref. [4], footnote on p. 278).

[14] See footnote 41 of P. L. Pauson, *Q. Rev.* **1955**, 391–414.

[15] T. M. Zydowsky [tmzinc@aol.com], *Chemical Intelligencer*, in press.

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