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Recollections of the arrival of ferrocene

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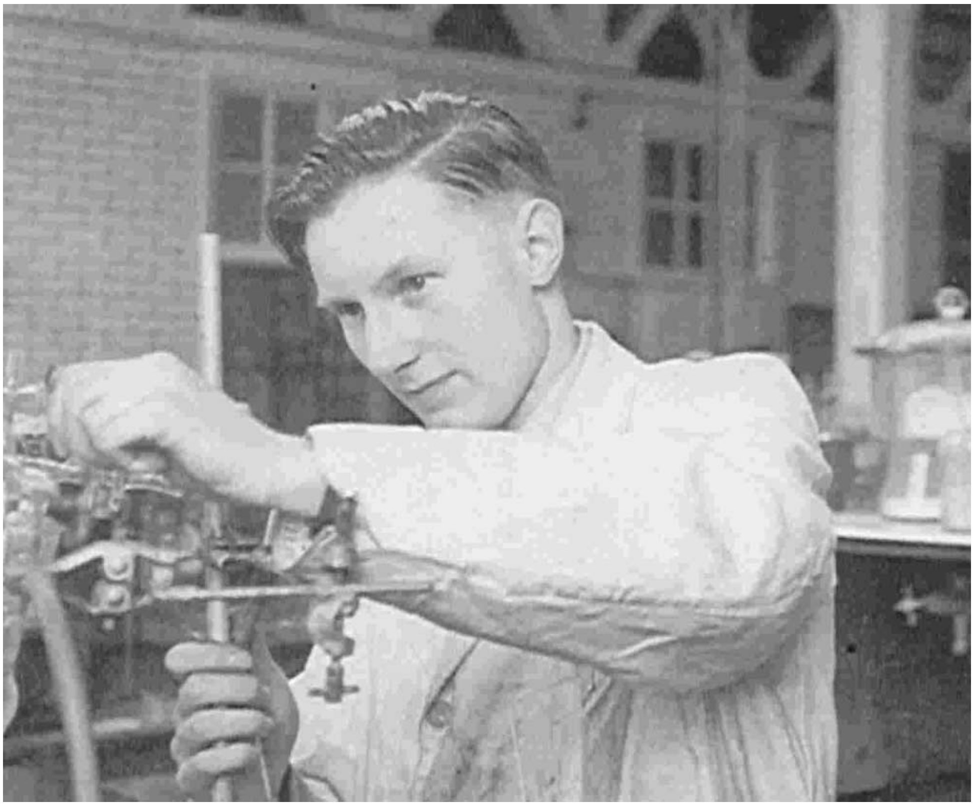

(Mark Whiting ca. 1952)

My interest in transition-metal organometallic chemistry began at Imperial College London in 1946 when I was asked by my supervisor, E.R.H. Jones, to work on the Reppe carboxylation of acetylenes with nickel carbonyl [1]. Some experiments were also carried out with iron pentacarbonyl. By the summer of 1951, I had obtained a lectureship, a tenured post, at the University of Manchester, but was preparing for a transatlantic voyage in order to work as a postdoctoral fellow with R.B. Woodward—already a name to conjure with.

In July or August 1951 I received, as a Fellow of the Chemical Society, my monthly copy of *J. Chem. Soc.* with an enclosure entitled 'Papers Received'; at that time JCS sent out each month a list of the titles and authors of papers sent in. One of these was 'Di*cyclo*pentadieneiron,' by S.A. Miller, J.A. Tebboth, and J.F. Tremaine [2]. Evidently a compound $Fe(C_5H_5)_2$ existed, surely analogous in a sense to $Fe(CO)_5$.

I arrived at Harvard in September 1951 and worked at first on a variant of the Woodward steroid synthesis. After returning from a snowy Christmas with friends of my sister in Grand Rapids, Michigan, I found an air letter from my Manchester colleague Kathleen Farrer containing an accurate précis of Peter Pauson's description of di*cyclo*pentadienyliron, made from ferric chloride and *cyclo*pentadienyl magnesium bromide, and

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evidently the compound I already knew of. When *Nature* reached Harvard later in the month, after the usual sea crossing, Bob Woodward at once appreciated the importance of this substance (as I had not), and it became a major topic of conversation within the group. We soon predicted dibenzenechromium, di*cyclo*butadienylnickel, mixed cycloarenecarbonyls, etc., and first Mike Rosenblum and then I (to my delight) were allowed to switch work to this area. Meanwhile, we learned that, along the corridor, Geoffrey Wilkinson had also become interested in it.

When I made my first batch of the new compound, I ran its infrared spectrum in carbon tetrachloride solution and saw that (at Baird prism-monochromator resolution) the C–H stretching band was a sharp singlet, actually sharper than benzene, which indicates that all the C–H bonds were identical, as we had expected. Mike had run the spectrum in chloroform, as was normal practice in the Woodward group, and the C–H absorption of the solvent had obscured the region. I also satisfied myself that the conversion of the orange petrol-soluble compound to a blue water-soluble material was an oxidation—the view originally held by the other three workers but which had fallen into disfavour. This led to the 'three yellow solutions' experiment, a neat trick: solutions were prepared of the new compound and *p*-benzoquinone in ether and of picric acid in methanol. Mixing any two had little effect, but mixing all three produced a beautiful dark green precipitate of what we called ferricinium picrate. It was this that led me to suggest amending the name 'ferrozene', which we had begun to use, to 'ferrocene'.

By this time, Mike Rosenblum had effected the first aromatic substitution; using carbon disulphide as solvent, acetyl chloride and aluminium chloride (a heterogeneous system) converted ferrocene into diacetylferrocene. I repeated the experiment with methylene chloride as solvent, giving a homogeneous system, and easily separated the product into mono-acetylferrocene and a diketone fraction which itself was separated with great difficulty into Mike's compound, the main component, and another isomer. By now we had recognised an infrared band at about 10 μm as characteristic of unsubstituted *cyclo*pentadienyl rings (C–H out of plane bending). It was present in the mono-acetyl compound and the new diacetyl compound, but it was absent from the main isomer. Obviously, the first acetyl group deactivates the ring in which it is present, which confirms the analogy with benzenoid aromatic substitution.

A good deal of time was spent exploring the chemistry of ferrocene. Geoffrey Wilkinson, in particular, worked on the generalisation of this chemistry to other metals, especially making cobalticinium salts. But when I returned to Manchester in October 1952, there were many other things I wanted to do and I was happy to leave the field in the hands of the Woodward–Wilkinson–Rosenblum and Pauson groups. However, I did re-enter it briefly at Oxford, where Barry Nichols and I observed the formation of the arenechromium tricarbonyls—a potentially enormous group of compounds. Meanwhile, developments have fully vindicated Bob Woodward's belief that ferrocene was a most important milestone.

References

[1] E.R.H. Jones, T.Y. Shen, M.C. Whiting, J. Chem. Soc. 48 (1951) 763, 766.
[2] S.A. Miller, J.A. Tebboth, J.F. Tremaine, J. Chem. Soc. (1952) 623.