

 MILESTONE 10

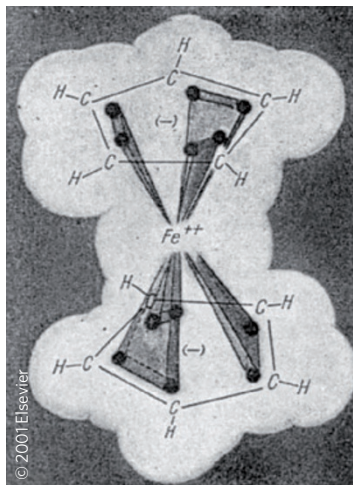
# An iron-clad structure

In 1951, Peter Pauson and his student Tom Kealy set out to make an unusual hydrocarbon called pentafulvalene, in which two cyclopentadiene rings are joined together through a carbon-carbon double bond. Although this particular target eluded them, their experiments resulted in the formation of a remarkably stable compound made of carbon, hydrogen and iron — a compound that arguably started a revolution in organometallic chemistry.

Analytical data revealed that the elemental composition of this unexpected product was consistent with the formula  $C_{10}H_{10}Fe$ , but what was the structure? Because the reaction used a starting material with a five-membered ring, it was reasonable to conclude that the final product simply contained two of these rings — the harder part was figuring out how they were bonded to the iron atom.

Pauson and Kealy suggested a linear structure in which the two rings were bonded to opposite sides of the metal, each through a single carbon atom. The same structure was proposed by Miller, Tebboth and Tremaine in a paper published just a couple of months later (although it had been submitted for publication almost a month earlier) describing a different synthesis of the same compound.

It wasn't long before other chemists started to question the linear structure suggested in these first two reports, most notably Robert Woodward and Geoffrey Wilkinson at Harvard University and Ernst Fischer at the Technische Hochschule in Munich. Woodward and Wilkinson were the first to suggest a sandwich-like



An early drawing of the chemical structure of ferrocene. Figure reprinted with permission from E. O. Fischer and R. Jira *J. Organomet. Chem.* **637-639**, 7-12 (2001)

structure (although they did not use that term), whereby the iron atom sits nestled between the faces of two five-membered rings stacked on top of one another. The supporting experimental evidence was, however, still indirect, with the strongest hint being that the infrared absorption spectrum revealed that all of the C-H bonds were equivalent — which would not be the case in the linear structure.

The first use of X-ray crystallography to help decipher the structure of what had now been

christened 'ferrocene' by Woodward and co-workers was described by Fischer and Wolfgang Pfab later in 1952. Preliminary data about the symmetry of the molecule and the size of the unit cell were much more consistent with the sandwich structure than the linear one. Two further X-ray crystallographic studies finally confirmed the sandwich structure of ferrocene, with the iron atom, indeed providing the metallic filling in a pentagonal antiprism defined by two parallel cyclopentadienyl rings.

These studies finally laid to rest any scepticism surrounding the true three-dimensional arrangement of the 21 atoms in ferrocene, and three years later more precise structural details — including more accurate C-C and C-Fe bond distances — were reported.

It soon became apparent that ferrocene was just the tip of the iceberg and many other metals were found to be suitable fillings for molecular sandwiches. And that wasn't the only part of the sandwich that could be varied — other aromatic systems could be used in the place of the five-membered cyclopentadienyl rings. The importance of the discovery of ferrocene and other sandwich compounds for the field of organometallic chemistry was underlined by the award of the Nobel Prize in Chemistry in 1973 to Fischer and Wilkinson.

Stuart Cantrill, Chief Editor,  
Nature Chemistry

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