Journal of Organometallic Chemistry, 100 (1975) 273—278

THE IRON SANDWICH. A RECOLLECTION OF THE FIRST FOUR MONTHS

GEOFFREY WILKINSON

Chemistry Department, Imperial College of Science & Technology, London, SW7 2AY (Great Britain)

In early September of 1951, I arrived at 12 Oxford Street, Cambridge, Mass., as a new Assistant Professor in the Harvard Chemistry Department. I owed my appointment largely to my nuclear background. Harvard had originally intended to appoint a tenure member in nuclear chemistry, a plan which did not materialize, and had settled for myself and an Instructor, Dick Diamond, a newly graduated Ph.D. from Seaborg's laboratory in Berkeley. I was given a laboratory in the Mallinckrodt Laboratory, and I went to work collecting chemicals and apparatus and built myself a small vacuum line.

I had the job of teaching courses on inorganic chemistry and nuclear chemistry and the former started at once. I had never previously given more than a couple of seminars, and although I had begun to do inorganic work the previous year at M.I.T. on PCl_3 and PF_3 complexes, I had never given a lecture on inorganic chemistry. So, gathering what was then the inorganic bible, Sidgwick's, *The Chemical Elements and their Compounds*, as well as Pauling's, *Nature of the Chemical Bond*, the book I had been brought up on at Imperial College, Emeléus and Anderson's, *Modern Aspects of Inorganic Chemistry*, and whatever else was available, such as, Yost, Russell and Garner's books on rare earths and the Groups V and VI elements, I set to work to be at least one lecture ahead of the students. I wrote my notes at an old roll-top desk that Ron Vanelli, the Departmental executive officer, had found for me in the sub-basement of the Mallinckrodt Laboratory. That it belonged originally to Theodore W. Richards* probably had little to do with subsequent events; however,it had character, and I was reminded of a lecture on atomic weights given by my predecessor H.V.A. Briscoe at Imperial College in 1939, in which he remarked that he always considered himself a disciple of Richards with regard to his own studies on determination of atomic weights. Subsequently, I spent much time with my feet up on that desk and well remember in 1955 working out in this condition the significance of

---

* Nobel Prize in Chemistry, 1914, "for his accurate determining of the atomic weight of a large number of elements".

Stan Piper's observations that $C_5H_5Fe(CO)_2C_5H_5$ had only two proton resonances, one sharp, one a bit broad, instead of the one for the π-C_5H_5 ring and a more complex set of lines for the σ-C_5H_5 ring, whereas the infrared spectrum showed not only the aromatic C—H stretch of π-C_5H_5 but also other C—H stretches*.

There was also a practical laboratory connected with the inorganic course, Chem. 150, and fortunately Bob West, a Ph.D. student of Gene Rochow's, had been the teaching assistant the previous year. Consequently he was able to relieve me of some of the pain and get the course moving. The lectures I gave that fall may not have been the most polished but at least one student was enticed out of what he had come to Harvard to do, physical chemistry with George Kistiakowsky, and after he had done this course requirements, Al Cotton started research with me the following spring.

In, and among, the writing chores I managed to get some experimental work done. I acquired some nickel and iron carbonyls, the only ones then commercially available, and began to continue my M.I.T. work on PR_3 substitution. However, I also began to look at reactions of the carbonyls with unsaturated compounds. This was largely because of my reading about Zeise's salt, Reihlen's butadieneiron carbonyl, and silver olefin complexes in Emeléus and Anderson and in Sidgwick. I was quite convinced that the ethylene must be bound sideways to platinum and butadiene must be a *cis* chelate, as is now well established. I began to repeat the Reihlen work, collected other unsaturated compounds and made the red bis(acrylonitrile)nickel (it was described several years later by Schrauzer). My main recollection of that fall term however, was Chairman Kistiakowsky's Departmental party, as classical a booze-up as I have ever been to, and later on, nearer Christmas, going skiing to Stowe in Vermont with Vanelli and Kistiakowsky, both of whose expertise terrified me; I recollected the story that Linstead (later Rector of Imperial College) when at Harvard, had also once gone skiing with Kistiakowsky and came back on crutches, so I stuck to the easy slopes.

One other recollection of the fall remains, the reading of page 84 in Sidgwick (I began at the beginning with my lectures and of course the alkali metals came early on) where he describes the cyclopentadienide ion and writes, "we have a structure not unlike the neutral benzene molecule; a perfectly symmetrical molecule with five similarly placed CH groups and at the same time six more valency electrons than are required to maintain single links in the molecule ....". I knew from the good books that metal phenyls and alkyls were unstable and the thought crossed my mind if it would be different using C_5H_5; one of those experiments put aside for the future that one should have done when first thought of. Later on, Woodward told me he had seen, which I didn't, in the titles of papers to be published in the *Journal of the Chemical Society* (they did that in those days) a paper on "Dicyclopentadienyliron" (this was the

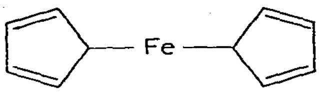
---

* I had been an enthusiastic photographer when about fifteen, and knew that if one took a photograph of a spinning wheel at say, 1/1000th sec exposure it would be sharp, whereas at 1 sec, it would be blurred. It was this analogy with the observation of a molecule on the very short time scale of infrared measurements and on the time scale of nuclear magnetic resonance, orders of magnitude longer, that led me to the idea of the σ-ring moving around by a 1,2 shift, or, in the later term, "ring whizzing".

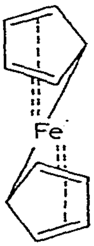
celebrated Miller*, Tebboth and Tremaine paper) and he wondered what the hell that could be. If we had only got together we could have made the compound ourselves weeks before the Kealy and Paulson note in *Nature* arrived at Harvard.

So the story for me actually began on a Friday, I think 30th January, 1952. I normally went into the Departmental Library lateish on Friday afternoons, and as usual I picked up *Nature*, in which I found the celebrated note by Kealy and Pauson (T.J. Kealy and P.L. Pauson, *Nature*, 168 (1951) 1039, December 15th issue, received 7th August, 1951).

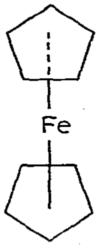
On seeing the structure I, which was also the one Miller, Tebboth and Tremaine had drawn in their paper which appeared later, I can remember immediately saying to myself "Jesus Christ it can't be that!". Now I don't know why it was not the Sidgwick view quoted above that first occurred to me but the chelate diene type structure, but I remember scribbling out on a piece of paper the structure II in which both double bonds were coordinated, and almost immediately afterwards III, as the significance of the resonance structures (I had been much impressed by Pauling) dawned and the equivalence of the carbons became obvious, "It's a sandwich". The thing that really excited me was the thought that if iron did this, the other transition metals must also form sandwich compounds.



(I)



(II)



(III)

---

* In about January of 1958 I went to the Technical College at Slough, Buckinghamshire, to give a lecture to the local section of the Royal Institute of Chemistry. The chairman turned out to be Sam Miller. After the lecture, he offered to drive me back to London, but on reaching Heathrow airport the fog was so dense it took us another three hours to reach Notting Hill. I had walked the last mile in front of the car shouting instructions to Sam who had his head out of the window. He finally abandoned his car and we both walked home, myself only a half a mile, but he had to go to Golders Green. I never saw him again. During this nightmare drive, he recounted their attempts to react olefins and nitrogen over iron catalysts to give amines, during which they happened to use dicyclopentadiene and obtained $C_{10}H_{10}Fe$. This was in 1948 at the laboratories of the British Oxygen Company at Morden in south west London. Miller was an organic chemist (he died in 1970, see *Chemistry in Britain*, (1971) 252) mainly interested in acetylenes, and admitted they did not recognise what an unusual compound they had. It was only after another couple of years that they decided to do a little more work and write the paper that eventually appeared (S.A. Miller, J.A. Tebboth and J.F. Tremaine, *J. Chem. Soc.*, (1952) 632, received 11th July, 1951). Miller also sent me his only remaining copy of the original British Oxygen Company report but unfortunately this vanished in the chaos following Eddie Abel's attempt to oxidise a silanol with chromic oxide which led to an explosion and fire that wrecked the laboratories and my office. Eddie was more concerned to save the actinide chapter of the first edition of the textbook that I had given to him to read that morning, most of which went out through the windows.

Of course I had no idea what the properties of cyclopentadiene were or whether you could buy it in bottles, and I decided I had better see an organic chemist fast. Unfortunately I was going somewhere for dinner so didn't have much of a chance. As I found out the following day, sometime the same Friday evening, before his usual weekly seminar, Bob Woodward had also seen the *Nature* note. Having actually seen the name dicyclopentadienyliron before, as I note above, it didn't take him long to come to the same conclusion about the structure, but I think essentially from the point of view of the equivalence of the carbons in the anion (cf. Sidgwick). He discussed this at his seminar and set one of his Ph.D. students on the problem. The first I knew of this was on Saturday when Mike Rosenblum came into my laboratory asking if I had got any ruthenium. I can't remember what I said, though I can remember being more than considerably annoyed, except that I think it was along the lines of "let me tell you what you want that for". However, the upshot was that Woodward and I had lunch at the Harvard Faculty Club on Monday 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 after the structure, this seemed to be Bob's main interest, whereas mine was to go to other transition metals. We discussed how to prove the structure and agreed that if the infrared spectrum showed only one C—H stretch and if the compound was diamagnetic that would be enough. Since Woodward had done a lot of work with dicyclopentadiene, there was plenty on hand and so Mike Rosenblum was able to get going quickly. Within a day or so we had our first batch of $(C_5H_5)_2Fe$, and he measured the infrared spectrum on the department's sole Perkin—Elmer 21 while I measured the magnetic susceptibility on a Gouy balance that Paul Bartlett had built for work on the triphenylmethyl radical.

Recognising that $(C_5H_5)_2Fe$ had divalent iron I thought it should be possible to oxidise it. Kealy and Pauson had reported that "It dissolves in dilute nitric acid or concentrated sulphuric acid forming a deep red solution with strong blue fluorescence". When the Miller, Tebboth and Tremaine paper arrived they had shown that CCl_4 solutions react with bromine to a "dark green precipitate which dissolved in water to give a blue aqueous solution containing "ferrous (sic!) and bromide ions". I was able to oxidise $(C_5H_5)_2Fe$ in several ways and it was easy to show that a blue +1 cation $(C_5H_5)_2Fe^+$ was obtained that gave precipitates with large uninegative ions like silicotungstate. I went on to look at reactions with halogens, $FeCl_3$ etc., most of which never were written up. The beautiful blue crystals cf $(C_5H_5)_2Fe^+GaCl_4^-$ that were mentioned in our first note arose because of reaction of $(C_5H_5)_2Fe$ with $FeCl_3$ as an oxidising agent. I then tried $AlCl_3$ and $GaCl_3$, which clearly didn't react, so I stuck some cotton wool in the top of the test tubes. When I looked at them a week or so later, there were the crystals, evidently formed slowly by hydrolysis of $GaCl_3$ and air oxidation.

I was now anxious to get on to the other metals. Since we were making cyclopentadienylmagnesium bomide from ethereal ethylmagnesium bromide and cyclopentadiene, it seemed that a metal compound soluble in organic solvents might be better than the halide in cases other than iron, titanium, and I thought the acetylacetonates were a good prospect. So the second sandwich compound, the first I made myself, was $(C_5H_5)_2Ru$ made from $Ru(acac)_3$. I only had about

300 mg of the compound but it was enough for analysis, infrared spectrum and so on.

About this time Al Cotton had decided to work with me and had started off trying to make a lower halide of scandium. Being somewhat physically orientated and, I think, trying to avoid synthesis as much as possible, he suggested measuring the heat of combustion of $(C_5H_5)_2Fe$. This seemed worthwhile so we borrowed a bomb calorimeter from the Physical Chemistry teaching laboratory and a calibrated platinum resistance thermometer from Kistiakowsky and bought some NBS standard benzoic acid. Al spent the rest of the term, till he went off in June to a summer job at Los Alamos, measuring the heat combustion.

About the beginning of March I had to go back to M.I.T. to give a brief talk on their lecture program for industrial sponsors and in addition to the work I had done at M.I.T. I mentioned some of the work I was now doing. There was a certain amount of scepticism but I remember George Scatchard saying that we could well be right, which cheered me up. One of the visitors was Gene Brimm and from what he said it was clear that Union Carbide were very interested, and we began a tentative sort of exchange of information. I only found out about the efforts in other industrial companies much later.

At M.I.T. I also tried to interest the X-ray crystallographers, none of whom at that time were in Chemistry, but in Geology, in doing the structure of $(C_5H_5)_2Fe$. They showed no interest at all so I then tried Harvard Medical School and again drew a blank. I also had drawn a blank in another direction as shortly after we recognised the sandwich structure I talked to a visiting theoretician who was spending a sabbatical year at Harvard and whom I had got to know quite well. I said surely there must be some fancy way of describing the bonding, *d* orbitals and all that, but I guess he must have known too much quantum mechanics because the only sort of reply I got was to the effect that "God does work some wonders these days doesn't he". The first of more than one interesting experience with theoretical chemists*.

I had by this time, now gone on to cobalt, and well remember the delight when I ran $Co(acac)_3$ into the Grignard solution and it went bright yellow. It didn't take long to get the yellow aqueous solution of $(C_5H_5)_2Co^+$ and some salts to show that they had the now characteristic infrared spectrum, as well as very high stability.

Since Lingane in Analytical Chemistry was well equipped for electrochemical studies, it struck me that the $(C_5H_5)_2Fe \rightleftharpoons (C_5H_5)_2Fe^+$ system was worth comparing with other Fe^{II}—Fe^{III} compounds, as were the Ru and Co species, so I got one of Lingane's students, a Canadian, John Page, to help with the polarography and this seemed to come out reasonably well.

During all this spring I was, of course, giving not only inorganic lectures but nuclear chemistry lectures and was still having to try to keep one lecture

---

* A few months after Bill Moffit came to Harvard in the fall of 1952 I asked him what was the chance of benzene binding to a transition metal, as I thought that since it had six π-electrons like $C_5H_5^-$ there was a possibility. He went away and came back some time later saying he didn't think it was on. So having implicit faith in theoretical chemists at that time, I forgot all about it. Some time later Lars Onsager came up from Yale to give a physical chemistry seminar and came in to see me to ask the very same question because Harold Zeiss, then at Yale, had had the idea that Hein's polyphenylchromium compounds were benzene sandwiches, as turned out to be the case. This taught me the lesson that one should not be deterred from doing an experiment because somebody says it won't work.

ahead. I was working at least twelve hours a day and seldom got back to my lodgings before two in the morning. I had hoped to press on to other metals more quickly, but I had to round off what I had on hand since I was leaving on about the 7th or 8th June, going first to England and then to Denmark to get married.

Woodward and I had written up the first note on the structure within a few weeks of starting work (G. Wilkinson, M. Rosenblum, M.C. Whiting and R.B. Woodward, *J. Amer. Chem. Soc.*, 74 (1952) 2125, received 24th March, 1952) and in May I got the rest ready for sending off to the Journal.
F.A. Cotton and G. Wilkinson, *J. Amer. Chem. Soc.*, 74 (1952) 5764, received 6th June, 1952. The heat of combustion of ferrocene.
G. Wilkinson, *J. Amer. Chem. Soc.*, 74 (1952) 6146, received 12th June, 1952. The preparation and some properties of ruthenocene and ruthenicinium salts.
G. Wilkinson, *J. Amer. Chem. Soc.*, 74 (1952) 6148, received 12th June, 1952. The preparation and some properties of the cobalticinium salts.
J.A. Page and G. Wilkinson, *J. Amer. Chem. Soc.*, 74 (1952) 7149, received 12th June, 1952. Polarographic studies.
Although these papers went by referees without trouble, I had a little bother over nomenclature with one of them. I had, perhaps unwisely, adapted for the other metals, the name ferrocene, invented for $(C_5H_5)_2Fe$, by Mark Whiting, then a postdoctoral fellow working with Woodward on the organic reactions. Their note (R.B. Woodward, M. Rosenblum and M.C. Whiting, *J. Amer. Chem. Soc.*, 74 (1952) 3458, received 2nd June, 1952) in which the name ferrocene was proposed clearly hadn't gone to my referee and he could not have seen their note as it had not appeared.

This was the end of the first really exciting four months, I now had a hiatus of three months at a critical time and when I returned to Harvard in September I not only found Peter Pauson newly arrived from Kharasch's laboratory in Chicago as a postdoctoral fellow with Woodward, but there was also a report from the European section of the Office of Naval Research with the ominous news that someone else I had never heard of, was in the game. On 20th June, 1952, E.O. Fischer and W. Pfab had submitted their note to the *Zeitschrift für Naturforschung*, B, 7 (1952) 377.