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Cyclopentadienyl–metal chemistry in the Wilkinson Group, Harvard, 1952–1955

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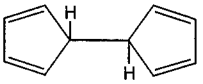
Geoffrey Wilkinson joined the chemistry faculty of Harvard University in September 1951. He had only to make the short trip down Massachusetts Avenue from MIT where he had been a postdoctoral research associate. He had been hired because the Harvard chemistry department had decided to look into the possibility of adding radiochemistry to its academic program, and Wilkinson had made a name for himself by identifying more new radioisotopes than any other person before or since while working in Seaborg's laboratory in Berkeley. A young Seaborg Ph.D., Richard Diamond, was simultaneously hired as an instructor. At the time, Harvard had a small cyclotron which was especially suited to study nuclear excitation energies because of its ability to deliver beams of precise energies. Wilkinson thus began with his first graduate student, Rodman A. Sharp, to carry out such studies. However, as he later told me, he had already decided that he wanted to leave the field of nuclear chemistry and return to inorganic chemistry, and the next graduate students he took, Richard Whipple and myself, and a year later John Birmingham, wanted to do inorganic chemistry. In fact, Geoff never took another student in nuclear chemistry or radiochemistry, which left Rod Sharp as kind of the odd man out in our group.

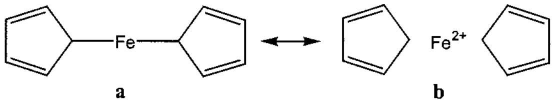
I got a very early start on research, in the fall of 1951, seeking an efficient and convenient way to make anhydrous rare earth chlorides, in finely divided form, which could then be used as starting materials for other syntheses. This project never reached fruition because shortly after I returned from the long Christmas and New Year holiday, Geoff was agog with a completely different idea. A paper which had appeared in the December 15 issue of Nature was entitled 'A New Type of Organo-Iron Compound' by T.J. Kealy and P.L. Pauson [1]. Neither of these names meant anything to him (they were at Duquesne University) but the new compound really got his attention.

We soon learned that P.L. (Peter) Pauson was an organic chemist who had been attempting to use the reaction of $FeCl_3$ with the cyclopentadienyl Grignard reagent to make dihydrofulvalene (**I**) by a reaction well known to proceed, in other cases, according to Eq. (1). Instead, a volatile orange solid, analyzing as $C_{10}H_{10}Fe$, was obtained.



I

$$6RMgBr + 2FeCl_3 \longrightarrow 3R_2 + 2Fe + 3MgCl_2 + 3MgBr_2 \tag{1}$$



II

Kealy and Pauson proposed for this a more or less conventional structure, R–Fe–R, but rationalized its stability as compared to the non-existence of any other R_2Fe compound, by invoking resonance with an ionic structure as shown in II. Geoff's chemical intuition told him this would not do, and set him to thinking and working on the problem.

On the basis of the publication just discussed, which appeared (nominally) on December 15, 1951, Peter Pauson is usually cited as the discoverer of (as it was later christened by R.B. Woodward and M.C. Whiting) ferrocene. This, however, is not in accord with standard practice, for in February of 1952, the preparation of ferrocene by a different method was reported by Miller, Tebboth and Tremaine in the Journal of the Chemical Society [2]. While their paper appeared later than that of Kealy and Pauson, the priority must go to Miller, Tebboth and Tremaine, since their manuscript had a

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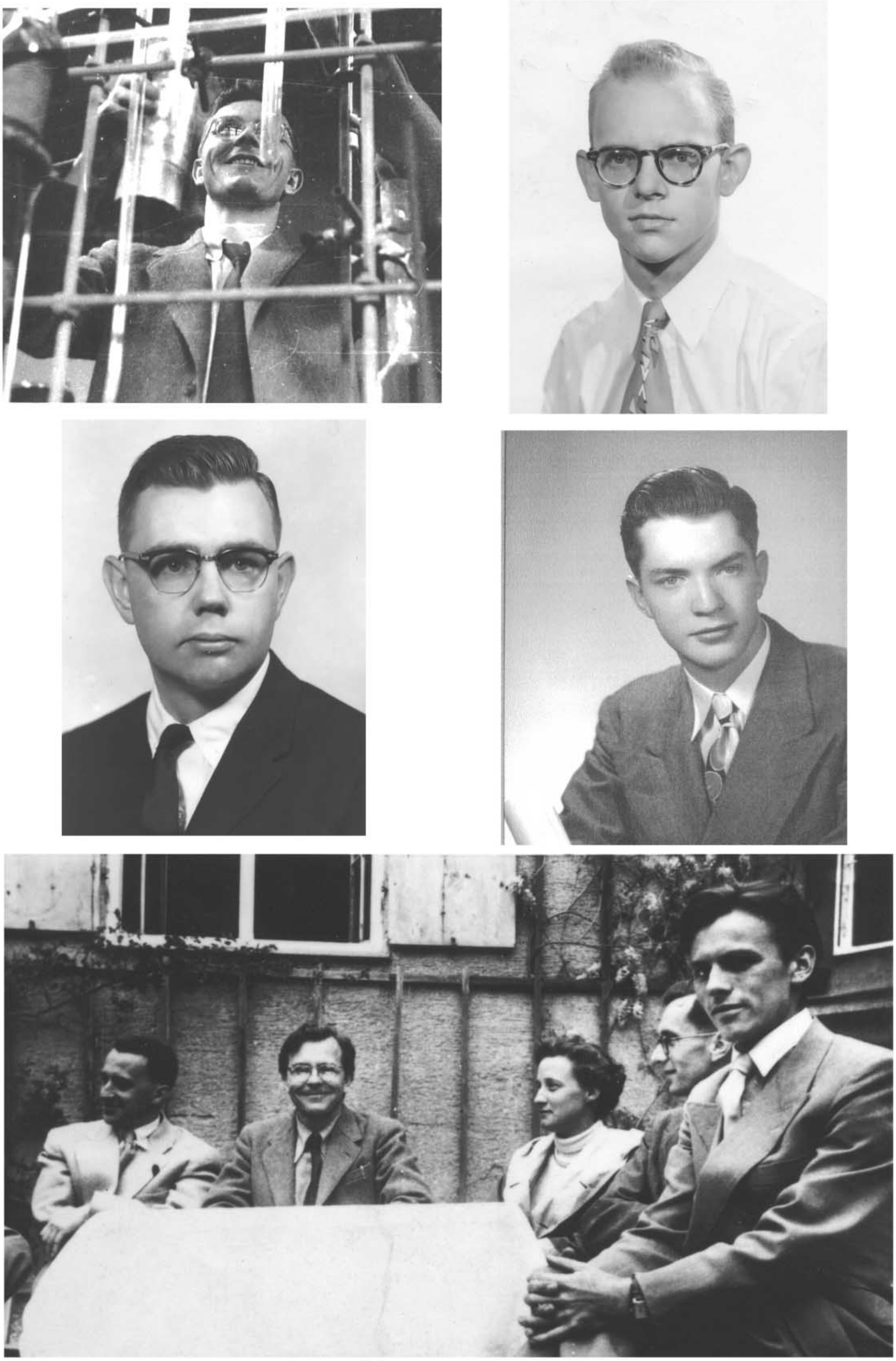


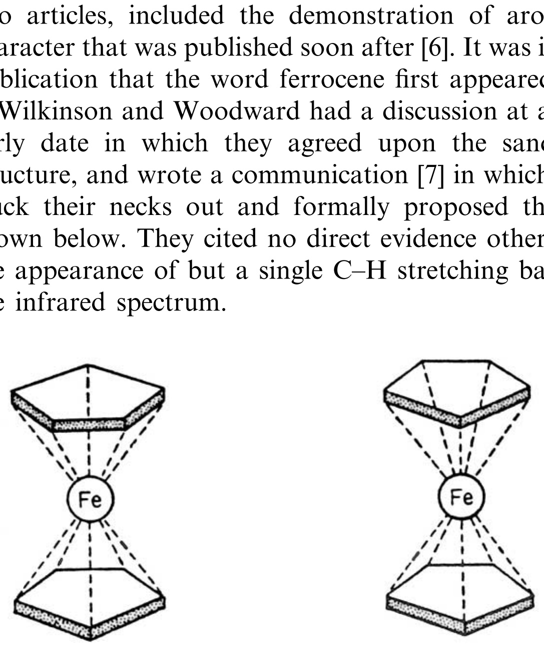
Clockwise from upper left; Geoff Wilkinson in the lab, *ca* 1953; F. A. Cotton, *ca* 1952; J.M. Birmingham, a few years before graduate school; E. O. Fischer, G. Wilkinson, D. Seus, W. Hafner and R. Jira, Munich August, 1954; T. S. Piper, late 1950s.

received date of July 11, 1951, whereas the Kealy and Pauson manuscript was dated August 7, 1951. It may be noted that Miller, Tebboth and Tremaine, who made ferrocene by passing the mixed vapors of cyclopentadiene and its dimer over a Haber catalyst held at 300 °C, characterized it by elemental analysis and a molecular weight measurement. They too pointed out that "Compounds containing only carbon, hydrogen and iron have not hitherto been described," but were content to formulate it as IIa, without expressing any sense of curiosity about its phenomenal (to at least 300 °C) thermal stability. In fact, as later related by Wilkinson [3,4], Miller claimed that he had the compound as early as 1948.

To put all of the above in context, I point out that even to this day no simple dialkyl iron(II) compound has ever been isolated, under any conditions, although a few special diaryls have recently been reported [5].

Geoff immediately set about making a sample of $C_{10}H_{10}Fe$ to see for himself what it was like. He also noted that upon oxidation he got a dark blue cation, which he isolated as the tetrachlorogallate, $C_{10}H_{10}FeGaCl_4$ (why he used this curious anion is explained in Ref. [4]) and as the picrate, $C_{10}H_{10}Fe(C_6H_2N_3O_7)$. It was also shown that the picrate had one unpaired electron. In the meantime, R.B. Woodward, who had also taken a keen interest in Kealy and Pauson's compound, also doubted that it could be what they said it was, and had a couple of people in his group, Mike Rosenblum, a graduate student, who later became a professor at Brandeis University, and Mark Whiting, a postdoctoral fellow from Britain who later became a professor at Bristol University, get to work on it. Exactly what they did first, as related in the following two articles, included the demonstration of aromatic character that was published soon after [6]. It was in this publication that the word ferrocene first appeared.

Wilkinson and Woodward had a discussion at a very early date in which they agreed upon the sandwich structure, and wrote a communication [7] in which they stuck their necks out and formally proposed this, as shown below. They cited no direct evidence other than the appearance of but a single C–H stretching band in the infrared spectrum.



The sandwich structure exactly as depicted by Wilkinson and Woodward [7].

A remarkable feature of this publication is that it has a received date of March 24, 1952 and it appeared in the April 20 edition of the journal. Lest it be thought that this is prima facie evidence of Woodwardian clout, I note that the communications immediately before and after it had received dates of March 22 and March 21. Things have certainly slowed down a lot in this supposedly more efficient electronic age. In this communication the work of Miller, Tebboth and Tremaine was not cited because the journal containing it had not yet arrived in the Harvard chemistry library.

Geoff very soon recognized that molecules similar to ferrocene with other metals might well exist and set about trying to make them. I think that Geoff clearly decided, at a very early date, that his goal would be to make cyclopentadienylmetal compounds of as many transition metals as possible, and he never lost sight of that goal. He also, I believe, clearly focused on measuring physical properties that would be informative as to the electronic structures and bonding in such compounds.

It was in pursuit of the latter objective that I first entered the arena. The phenomenal stability of ferrocene intrigued me and I decided to see if the strength of the ring to metal bonding could be quantitated by determining the heat of formation of ferrocene. By borrowing the necessary apparatus from Professor G.B. Kistiakowsky, and getting a little instruction from him in how to use it, I proceeded to measure the heat of combustion. This done, with some collateral data from the literature and a little bit of arm waving, I arrived at the conclusion that "the combined energies of resonance and carbon to iron bonding… 113 kcal… accords with the unusual stability of ferrocene" [8].

Meanwhile, Geoff, who had no students other than myself (who was otherwise occupied, as I mentioned above) and Whipple to do productive synthetic work, got busy himself and made ruthenocene, $(C_5H_5)_2Ru$ and the ruthenocenium ion [9], as well as the cobalticinium ion [10]. He also 'borrowed' one of Professor James Lingane's graduate students, John Page, and the electrochemistry of the iron, ruthenium and cobalt compounds was elucidated [11].

Some time in early 1953 Geoff got the interesting idea that by passing vapors of cyclopentadiene and a metal carbonyl through a hot tube, carbon monoxide might be displaced by C_5H_5 groups. He tried this himself with the hexacarbonyls of chromium, molybdenum and tungsten, and was rewarded by preparing $(C_5H_5)_2Cr$, a brilliantly red solid that is extremely reactive to oxygen [12]. With $Mo(CO)_6$ and $W(CO)_6$ he got the $C_5H_5M(CO)_6MC_5H_5$ compounds, M = Mo, W. The Mo compound was at first thought to have only five CO groups, but this was later corrected.

Ernst Otto Fischer entered our consciousness late in the spring of 1952 with the appearance of a paper [13] in which he, too, postulated the sandwich (or, as he called it, Doppelkegel) structure. It soon became evident, as a stream of synthetic publications issued from the Munich laboratory, that Wilkinson had a formidable rival for leadership in the field. Since the synthetic skills in the Fischer laboratory were clearly no less than in the Wilkinson laboratory and Fischer appeared to have several good students, to stay abreast would be a challenge. However, in going on with this story, I shall not focus on that aspect of things but simply tell what happened in Wilkinson's laboratory, although parallel work by Fischer will at times be mentioned.

My admiration for the chemistry of E.O. Fischer is on a par with that which I have for the chemistry of Wilkinson. I had the great pleasure of meeting him for the first time in July of 1954 when I was on a tour through Germany, staying mostly in Youth Hostels (Jugendherbergen). On arrival in Munich, in July of 1954, I went to see him and he proved to be a gracious and charming host. He insisted that I stay at his house where his housekeeper washed all of my clothes. More importantly, I spent two marvelous days in the lab with him and his group, and I also met Walter Hieber. As far as I could see, Fischer's competitiveness, while keen, was lacking in any unfriendly edge.

Sometime in the academic year 1951–1952, Richard Whipple joined the Wilkinson group. Whipple was from the University of Michigan and was soon known in the group as Whippledick. However, it took a while for him to get going and I went off to Los Alamos National Laboratory for the summer of 1952, so Wilkinson was essentially on his own in doing preparative chemistry until September of 1952.

In September of 1952, another interesting thing happened: Peter Pauson turned up at Harvard, supported by a grant from the DuPont company. This had, apparently, been planned well before the first Harvard publications on ferrocene. It proved to be a very happy coincidence, however, for Peter participated in the work of the Wilkinson group as well as doing things on his own. Thus, by September of 1953, he had submitted a paper on the synthesis of substituted ferrocenes [14] and also written a paper with Geoff [15] which reported the first bis-indenyl compounds, those of iron(II) and cobalt(III).

During the 1950–1951 year at MIT, Geoff had had an undergraduate, John Birmingham, work with him on some senior research. John had gone off to do a Ph.D. at Iowa State University and spent the year 1951–1952 there. However, he was not satisfied there and when he saw the Wilkinson, Rosenblum, Whiting and Woodward paper [7], he began to think about coming to Harvard to work with Geoff. In the summer of 1952 he wrote to Geoff about this and Geoff immediately persuaded the chemistry department to admit him in September of 1952. So Geoff had three graduate tudents to work on cyclopentadienylmetal chemistry when the fall semester began in 1952.

During a very busy fall of 1952, John Birmingham, Whipple and I began to provide some preparative results aimed at extending the range of cyclopentadienyl chemistry. Thus, in January of 1953 a communication [16] was submitted in which we reported $(C_5H_5)_2Ni$, $(C_5H_5)_2Ni^+$, $(C_5H_5)_2TiBr_2$, $(C_5H_5)_2Ti(picrate)_2$, $(C_5H_5)_2ZrBr_2$, $(C_5H_5)_2VCl_2$ and $(C_5H_5)_2V(picrate)_2$. By February of 1953 we reported [17] the preparation of compounds containing the $(C_5H_5)_2Rh^+$ and $(C_5H_5)_2Ir^+$ ions. Geoff's vision that cyclopentadienyl metal chemistry should encompass just about all of the transition metals was being confirmed. These preparations were not, however, Harvard exclusives. Independently and at about the same time, Fischer's group also reported $(C_5H_5)_2Ni$ and $(C_5H_5)_2Co$.

I continued work on the nickel compounds and by September of 1953 we were able to submit a very detailed report on $(C_5H_5)_2Ni$ and the $(C_5H_5)_2Ni^+$ cation [18]. In this we presented the results of detailed magnetic studies, which I had made at Brookhaven National Laboratory, of $(C_5H_5)_2Ni$ and the picrate of $(C_5H_5)_2Ni^+$ as well as a thermodynamic study of $(C_5H_5)_2Ni$. Also reported here was the preparation of the exceedingly air-sensitive $(C_5H_5)_2Co$ by the reaction of cyclopentadiene vapor with $Co_2(CO)_8$ in a tube furnace. In the meantime, Geoff himself had used a similar method to prepare $(C_5H_5)_2Cr$, as mentioned above.

Somewhere toward the end of 1953 we lost Whipple. He decided, for reasons I can no longer recall, to drop his pursuit of the Ph.D., left with a Master's degree, and took a job with Dow Chemical Company. He later became an educator in Africa, and he died in the early 1990s.

An important event occurred at the end of 1953. Geoff had been married in the summer of 1952 to Lise Skou, a plant physiologist from Denmark. He was entitled to a one-semester sabbatical leave and decided to take it in Copenhagen during the Spring of 1954. Of the three industrial fellowships I had in the years 1952–1955, by extraordinary good luck the one I had in 1953–54 permitted me to work away from Harvard, so I went with him. Of course, we were both determined to get a lot of work done in Copenhagen, and we did. The conditions in Jannik Bjerrum's laboratory where we worked were ill-suited to preparative organometallic chemistry, but we made the best of it. Fortunately, Geoff had money from the Guggenheim Foundation with which we could buy glassware and other apparatus not available in Bjerrum's lab.

In Copenhagen we wrote three papers between early February and mid-June. One of these, based on work we had done before leaving the United States, concerned $C_{10}H_{10}Mg$ and $C_{10}H_{10}Mn$ [19]. Probably the most important thing reported in this note was that there was a better general preparative method for biscyclopentadienylmetal compounds than any of those previously used. This was by reaction of anhydrous metal halides with a solution of NaC_5H_5 in THF. However, we also reported the preparation and properties of $C_{10}H_{10}Mg$ and $C_{10}H_{10}Mn$. The preparation of the latter by a different method had been earlier reported by Fischer, but it was not well characterized. It proved to have very complex magnetic behavior that was only fully unraveled much later.

There is an amusing story concerning the brown, high-spin form of $C_{10}H_{10}Mn$. It had actually been made for the first time in the fall of 1953 and Geoff had taken a sample of it, in a sealed tube, along with samples of other cyclopentadienyl compounds that had been made in his laboratory, to give a lecture. This first specimen had been obtained as an oily liquid, and he believed that $C_{10}H_{10}Mn$ was a liquid at room temperature. An overnight train trip was required to get to his destination (I seem to recall it was Pittsburgh), and when Geoff gave his talk the next day he referred to this curious compound as a highly paramagnetic liquid and invited people to come and see it. However, he had not looked at it himself since his arrival, and it had turned to a crystalline solid, presumably due to having been agitated overnight on the train.

We also reported [20] compounds containing the first bis-cyclopentadienylmolybdenum and bis-cyclopentadienyltungsten species, namely, $(C_5H_5)_2MoCl^+$, $(C_5H_5)_2MoCl^{2+}$ and $(C_5H_5)_2WCl^{2+}$. We submitted this paper to Zeitschrift für Naturforschung in German and it was published that way, but the editor kindly requested us to submit papers in English in the future, because it had taken a great deal of his time to make ‘our German’ into acceptable German. We obliged him by sending another manuscript, in English, discussing and comparing various views of the bonding in bis-cyclopentadienylmetal compounds [21]. Publishing in a German journal was what Geoff called “taking the war to the enemy.”

We also began a lot of new work in Copenhagen, but this did not get written up for publication until we had returned to Harvard in the fall of 1954. In the meantime John Birmingham and Stan Piper had been beavering away, so Geoff had his hands full in the autumn of 1954 getting papers written. From this point on I shall not attempt to give a strictly chronological account but instead outline what was done by the individuals in the group. I base my account on both the publications [22] and the content of the Ph.D. theses of John Birmingham (May 1955) and Stan Piper (December 1955).

John Birmingham’s work lay in three main areas: biscyclopentadienyl compounds of the Group 4 and 5 elements, Ti, Zr, V, Nb, Ta; cyclopentadienyl compounds of Sc, Y and the lanthanides; biscyclopentadienylrhenium hydride.

A preliminary report of the Group 4 and 5 compounds [16] was submitted in January of 1953. Also included in this note were some things that Peter Pauson and I had done. A full report of John’s work [23] was not submitted until April of 1954 (while Geoff and I were in Copenhagen). John prepared the $(C_5H_5)_2TiX_2$ compounds with $X = F$, Cl, Br and I as well as $(C_5H_5)_2Ti(OH)Br$ and $(C_5H_5)_2Ti(OH)$(picrate). He also showed that the green $(C_5H_5)_2Ti^+$ ion could be obtained by reduction with zinc and that it had, as expected, one unpaired electron. He also prepared $(C_5H_5)_2ZrX_2$ ($X = Cl$, Br).

For the Group 5 elements he made $(C_5H_5)_2VX_2$ ($X = Cl$, Br), which he showed could be reduced to give the $(C_5H_5)_2V^+$ ion (with two unpaired electrons), but not oxidized. With niobium and tantalum the $(C_5H_5)_2MBr_3$ compounds were obtained. All of these new compounds were characterized by elemental analyses and infrared spectra, the normal methods of the day, but no crystal structures were obtained, as was also normal at that time.

As all readers of this journal will recognize, the compounds just described were the lineal ancestors of today’s marvelous so-called single-site catalysts for olefin polymerization. They were discovered, I would like to emphasize, not by people who had written a grant proposal to work on olefin polymerization, but by people who were funded to do fundamental research that had no predictable practical use.

John, in 1972, founded Boulder Scientific Company which is now a major commercial producer of cyclopentadienylmetal compounds and metallocene catalysts for the polyolefin industry and industry in general.

John Birmingham also initiated the study of cyclopentadienyl compounds of the lanthanides. In November of 1954, a preliminary note [24] on the $(C_5H_5)_3M$ compounds of Sc, Y, La, Ce, Pr, Nd, Sm and Gd was submitted. Again, it is hard to believe, but this note appeared before the end of the same year. We should have such efficiency today! On the basis of their chemical behavior, “instantaneous and quantitative reaction with ferrous chloride in tetrahydrofuran solution to give ferrocene,” these compounds were described as ionic. However, they were also described as volatile, subliming “above 220° at 10^4 mm.” This apparent inconsistency was not discussed. In August of 1955 a full paper [25] was submitted on the $(C_5H_5)_3M$ compounds, which included those of Dy, Er and Yb as well as all those reported previously. Here the structures were suggested to be “ionically bonded molecules.”

There is one contribution from John Birmingham that stands out in my mind more than the others. As already described, early in the summer of 1954 I visited E.O. Fischer in Munich. Later that summer, just before he came home, Geoff also paid him a visit (see photograph). During their exchange of information, Fischer told Geoff about a curious compound which he had prepared with the idea of getting $(C_5H_5)_2Re$. The problem he encountered was that his product was diamagnetic, whereas $(C_5H_5)_2Re$ could not possibly be so. Geoff sent an air letter to John instructing him to make some so they could have a look at it. In the fall of 1954 John worked on this substance and we all discussed the mystery of why it was diamagnetic. I did not remember any mention of its having already been made by Fischer, until John recently reminded me of this. I had thought it was first made at Harvard.

I do remember very well a discussion that Geoff, John and I had with Bill Moffitt, a theoretician who was then an Assistant Professor at Harvard, to see if he could think of any way out of the magnetism dilemma. We asked Bill if it was possible that due to strong spin-orbit coupling the magnetism could be quenched and he said “not as I understand quantum mechanics.” The possibility that the compound could be a dimer, $C_{10}H_{10}Re–ReC_{10}H_{10}$,was, of course, checked, but isopiestic molecular weight measurements by John ruled this out.

The break came because in the fall of 1954 John was taking a course taught by Eugene Rochow, who was excited about the then very new field of NMR spectroscopy. This gave John the idea that a hydrogen atom might be bonded to the rhenium atom and that NMR could provide proof of this. At the time, Harvard did not yet have an NMR spectrometer, but Geoff found out that there was a brand new Varian 30 MHz spectrometer at the DuPont Experimental Station in Wilmington, and arranged for them to look at a sample of ‘$C_{10}H_{10}Re$.’ It was soon found that there was a sharp resonance in the region expected for the ten cyclopentadienyl hydrogen atoms, but a careful search revealed another signal, of about one-tenth the intensity, far upfield. Accordingly, Wilkinson and Birmingham [26] concluded that “the most reasonable structure… would seem to be one similar to that of ferrocene…” with an additional “hydrogen atom (which) is presumably buried in the electron density surrounding the metal atom in the exposed region between the cyclopentadienyl rings.” It may be noted that this communication was received May 12 and appeared in the June 20 issue.

In a contemporaneous study of the mass spectra of bis-cyclopentadienyl metal compounds [27], that of the rhenium compound was also run and it showed a parent ion peak one mass unit higher than that of $C_{10}H_{10}Re$.

This discovery was a very fruitful one because $(C_5H_5)_2ReH$ was the first molecular transition metal hydride to be studied by ^{1}H-NMR and led to further work by Geoff and myself [28] on the classical metal carbonyl hydrides, $HCo(CO)_4$ and $H_2Fe(CO)_4$, which we showed also to have extremely high-field chemical shifts, even though they behave as acids (which $C_{10}H_{10}ReH$ did not). Several years later, at Imperial College, Geoff published a more detailed study of $C_{10}H_{10}ReH$, taking advantage of the NMR expertise of his colleague, Leslie Pratt [29].

John Birmingham made a few other contributions to the work of the Wilkinson group. While I did some more work on the magnetic properties of $(C_5H_5)_2Mn$, John studied the behavior of $(C_5H_5)_2Mg$ and its use as a preparative reagent for other $(C_5H_5)_2M$ compounds, and both of these studies were published in one paper [30] in 1956. With the participation of a new graduate student, Albert K. Fischer, John studied non-aqueous reductions of some cyclopentadienylmetal compounds which showed, inter alia, that $(C_5H_5)_2TiCl$ and $(C_5H_5)_2V$ could be prepared [31]. Finally, John and Dietmar Seyferth showed that direct reaction of metal halides and cyclopentadiene in the presence of a base such as triethylamine could give cyclopentadienylmetal compounds (i.e. ferrocene and $(C_5H_5)_2TiCl_2$), albeit in very poor yields [32].

In September of 1954, however, there was another addition to the group, Stan Piper. T. (for Theron). Standish Piper (always called Stan) was not a lucky man. He and I both entered upon graduate study in September of 1951, but Stan was 2 years older than I. At an earlier age he had faced the same problem that I and every other young man had faced in the late 1940s and early 1950s: the military draft. My own response was: if they can succeed, without the least cooperation from me, in getting me into the Army, so be it, but let’s just wait and see. Stan, on graduating from high school, had decided to get the threat behind him and had enlisted for 2 years. The wisdom of this was doubtful, since neither I nor anyone else in my cohort was ever drafted.

At Harvard, Stan chose Eugene G. Rochow for his Ph.D. research mentor, but he regretted his choice and in his second year took the awkward step of switching to Wilkinson. He soon made it clear, at least to me, that he was not satisfied with Wilkinson either. He would have preferred to do research that was much more physical in nature, and when he began his independent career at the University of Illinois, he did just that, taking up polarized single-crystal spectroscopy.

At one point, in keeping with his physical inclination, Stan decided that it would be interesting to look at the EPR spectrum of cobaltocene by doping it into a single crystal of ferrocene. He spent a great deal of time and effort preparing a suitable crystal and orienting it on the probe to go into the cryostat of an EPR spectrometer in the applied physics laboratory directly across Oxford Street from the Mallinckrodt chemistry laboratory. As I said, Stan was not a lucky man. Instead of measuring the EPR spectrum, he discovered that ferrocene undergoes a major first-order phase transition somewhere between room temperature and the temperature to which he was trying to cool his painstakingly prepared crystal. It simply blew up. However, in spite of his physical inclinations, Stan proved to be a perfectly competent preparative chemist and made several important contributions to the work of the Wilkinson group, all in the area of monocyclopentadienylmetal compounds. I shall discuss these presently.

Stan's bad luck, sadly, continued after he went to Illinois. He undertook, for what purpose I never learned, nor could I imagine, preparation of a very large quantity of $[(C_5H_5)(C_6H_6)Fe]ClO_4$. This was an extremely dangerous thing to do, especially as he was aware that during his period at Harvard, a postdoc of Woodward, Ernest Csendes, had made a substantial quantity of ferrocinium perchlorate and it had exploded, causing him serious injury. As I heard the story, Stan made about 100 g of his perchlorate, which he separated into two 50 g lots. Well, 50 g of Stan's material detonated and Stan was taken to the hospital with severe though not life-threatening injuries. In the course of treatment, he contracted a virulent hepatitis and died.

Stan Piper's work was almost entirely concerned with compounds of the $(C_5H_5)MXYZ$ type, in which there is only one η^5-C_5H_5 ring (to use current notation) attached to a metal atom, together with a collection of other ligands, such as CO, NO, halogen atoms, or alkyl groups. As readers will recognize, over the years compounds of this type have become as important as, or more important than, the bis-cyclopentadienylmetal compounds. Table I of Piper's Ph.D. thesis gives a list of the 36 compounds that he made and characterized. However, to a very significant extent Piper was in heavy competition with Fischer's group, who published, during this same period, a number of similar compounds. Often, Fisher's synthetic approach began with dicyclopentadienyl metal compounds, which were caused to react with carbon monoxide. A partial list of compounds made by Fischer and coworkers is: $C_5H_5V(CO)_4$ [33], $(C_5H_5)_2Cr_2(CO)_6$ [34], $C_5H_5Mn(CO)_3$ [35], $C_5H_5Co(CO)_2$ [36], C_5H_5NiNO [37], and $C_5H_5Mo(CO)_3H$ [34].

The first publication of Piper's work [38] was submitted in December of 1954, to the newborn journal, Journal of Inorganic and Nuclear Chemistry. Prior to Stan's work, $C_5H_5Mo(CO)_6MoC_5H_5$ and $C_5H_5W(CO)_6WC_5H_5$ were the only monocyclopentadienylmetal carbonyl compounds reported [12], although, as noted above, Fischer et al. independently made others while Piper was doing his work. The preparative methods used by Piper were generally different from those used by Fischer et al., even for compounds common to both programs. In this first paper the compounds $[C_5H_5Fe(CO)_2]_2$ and $C_5H_5Co(CO)_2$ were prepared by direct reaction of $Fe(CO)_5$ and $Co_2(CO)_8$ with a mixture of C_5H_6 and its dimer. Some other compounds reported were prepared as follows:

$$[C_5H_5Fe(CO)_2]_2 + HCl + O_2 \rightarrow C_5H_5Fe(CO)_2Cl$$

$$C_5H_5Fe(CO)_2Cl + NaCN \rightarrow C_5H_5Fe(CO)_2CN$$

$$MnCl_2 + C_5H_5MgBr + CO \rightarrow C_5H_5Mn(CO)_3$$

$$C_5H_5Mn(CO)_3 + NaNO_2 + HCl + PtCl_4 \rightarrow [C_5H_5Mn(CO)_2NO]_2PtCl_6$$

$$(C_5H_5)Ni + NO \rightarrow C_5H_5NiNO$$

I did very little, if any, of the preparative work reported in this paper [38], but I did do some of the magnetic and spectroscopic measurements. However, my major (?) contribution was to provide assurance that the number and positions of the CO and NO stretching bands observed in the infrared spectra were in accord with the structures proposed for these compounds. A further study of infrared spectra of mixed cyclopentadienyl/carbonyl compounds, in which Andrew D. Liehr (a student of Moffitt's) participated was also published about this time [39]. Stan then went on to make $C_5H_5Cr(NO)_2X$ (X = Cl, SCN), $C_5H_5Fe(CO)_2I$ and $(C_5H_5)_3Mn_2(NO)_3$ [40].

The most important work done by Piper was the preparation of compounds having alkyl groups attached to C_5H_5M moieties [41–44]. At the time this work was done, it was still uncertain whether transition metal to carbon sigma bonds could be stable. Therefore, the reports of very stable compounds containing such bonds were very novel and exciting. The first paper [41] (submitted in August 1955) reported the reaction:

$$C_5H_5Cr(NO)_2Cl + CH_3MgI \rightarrow C_5H_5Cr(NO)_2CH_3$$

as well as reactions producing $C_5H_5Cr(NO)_2CH_2Cl$, $C_5H_5Cr(NO)_2C_5H_5$ and $C_5H_5Fe(CO)_2C_5H_5$. The latter had just previously been reported also by Pauson [45], who was now back in England. This same compound, later studied in more detail, provided one of the prototypical examples of fluxional organometallic molecules [46].

A few months later, Piper and Wilkinson showed [42] that $C_5H_5Mo(CO)_3R$ compounds ($R = CH_3$, C_2H_5) could be conveniently made by reaction of $C_5H_5Mo(CO)_3Na$ with RI, and also reported $C_5H_5Mo(CO)_3Cl$ and $C_5H_5Mo(CO)_2NO$; they also showed that by using $C_5H_5Fe(CO)_2Na$, prepared from $[C_5H_5Fe(CO)_2]_2$, $C_5H_5Fe(CO)_2R$ compounds were easily accessible. They noted that "There would now seem to be no reason, in principle, why alkyl and aryl derivatives of other transition metals such as V, Cr and Ni cannot be made" and pointed also to "the possibility of forming compounds with bonds from the metal atom to elements such as P, Si, O etc..." They soon confirmed their own prediction by reporting $C_5H_5Fe(CO)_2Si(CH_3)_3$ [47].

In a large (20 page) paper [44] giving fuller details of their earlier work, the ^{1}H-NMR spectrum, at room temperature, of what was believed to be (η^5-

C_5H_5)Fe(CO)$_2$(η^1-C_5H_5) was reported. It showed a single line for the η^5-C_5H_5 ring (as expected), but also a single line (slightly broader) for the five hydrogen atoms of the other C_5H_5 ring, instead of the expected A_2B_2X pattern anticipated. In order to account for this without abandoning the idea that the initially proposed formula is correct, they proposed that the η^1-C_5H_5 ring in (η^5-C_5H_5)Fe(CO)$_2$(η^1-C_5H_5) "may be regarded as rotating… at a rate greater than the expected chemical shift (difference)," but it was not until a decade later that this was shown to be correct [48]. Stan Piper also did work leading to two other publications [49,50].

Before finishing this brief history I must also mention one more graduate student, L. Todd Reynolds, who started work only in the fall of 1954, and who did not, I believe, ever finish a Ph.D. thesis. Reynolds prepared the first cyclopentadienylactinide compounds [51], $(C_5H_5)_3MCl$ (M = Th, U), and a few compounds containing methylcyclopentadienyl groups [52].

Dibenzene chromium is a compound that was not made in the Wilkinson group, but I mention it here because it was not something Geoff had not thought about. The crude analogy between having a chromium atom sandwiched between two benzene molecules (which gives an 18-electron molecule) and having an iron atom sandwiched between two C_5H_5 radicals occurred to him in the fall of 1952, and he asked the newly-arrived Bill Moffitt what he thought. Bill said he did not see any chance that such an arrangement could be stable when it could easily revert to solid chromium and stable benzene molecules. So Geoff was convinced that it was not worth further effort and went on with cyclopentadienyl metal chemistry. It was, therefore, quite an unwelcome surprise to him when, in 1955, Fischer and Hafner [53] reported a successful designed synthesis of $(C_6H_6)_2Cr$.

Actually, some time before Fischer's work appeared, we learned that Harold Zeiss (an Assistant Professor at Yale) and his student, Minoru Tsutsui (who later became my colleague at Texas A&M), had reexamined the 'polyphenylchromium' compounds of Franz Hein and concluded, with some input from Lars Onsager, that they were sandwich compounds. I have described this situation in some detail in the review I published in June of 1955 [54]. Thus, the first syntheses of metal arene compounds actually date to at least as early as 1919, when Hein published his first paper on 'polyphenylchromium' compounds [55].

The final topic on which I would like to comment concerns the Nobel Prize that was awarded jointly to Wilkinson and Fischer in 1973. The subject matter was one of the best choices the Nobel committee ever made: the opening up of cyclopentadienylmetal chemistry is one of the most profoundly original and important developments in the history of chemistry, and Wilkinson and Fischer were the ones responsible for it. It is now known [56] that R.B. Woodward expressed extreme disappointment that he was not included. I think he was wrong to feel that way. After publishing two preliminary communications dealing exclusively with ferrocene, Woodward left the area, although M. Rosenblum did continue to explore ferrocene chemistry and eventually another paper [57] appeared. The citation by the Nobel Prize committee reads: "for their pioneering work, performed independently, on the chemistry of the organometallic so-called *sandwich compounds*" (emphasis added; note the plural). In short, I think the 1973 Nobel Prize in Chemistry went to the right people for the right reasons.

What went on in Wilkinson's lab (and also in Fischer's) was science at its best and most exciting. Two young but mature chemists first recognized, with the announcement of the existence of $C_{10}H_{10}Fe$, that something remarkable had been observed and, second, they had the imagination as well as the experimental skill to go off in hot but rational pursuit of the consequences of the originally serendipitous discovery. There are, of course, other ways in which important and exciting research gets done, but this particular paradigm, perceptive pursuit of the implications of an accidental discovery, is hard to beat for excitement. It was a great privilege to have started my own career in this way.

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