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Cover Essay

Bis(benzene)chromium. 1. Franz Hein at the University of Leipzig and Harold Zeiss and Minoru Tsutsui at Yale

I. Introduction

When, in 1918, Franz Hein in his laboratory at the University of Leipzig carried out a reaction of 3 molar equiv of phenylmagnesium bromide in diethyl ether at −10 °C with 1 equiv of anhydrous chromium trichloride, he started a research project that was to consume him for the rest of his life. It had been his intention to prepare triphenylchromium, but the chemistry went awry, led to much confusion, and did not get sorted out until the mid-1950s, as we shall see. Inextricably related to this work was the synthesis of our cover molecule, bis(benzene)chromium, by Ernst Otto Fischer and Walter Hafner in 1955. This essay brings the story of the bis(arene) complexes of Cr(0) and Cr(I), starting with the early work of Hein and continuing on to the present day.

Chromium is a transition metal in group 6 of the periodic table, with a ground-state electron configuration of $[Ar]3d^5 4s^1$. At the time that Hein started his research, it was not at all certain that an organic chemistry of the transition metals (involving M−C covalent bonds) could be developed. However, even much earlier, as soon as main-group organometallic reagents that were sources of nucleophilic organic groups had been prepared by Frankland and, later, Grignard, attempts to do so were carried out. As was noted in the recent $C_2H_5ZnI/(C_2H_5)_2Zn$ cover molecule essay,[1] diethylzinc and dimethylzinc were recognized very early on to be generally useful reagents for the alkylation of the main-group-element halides such as those of tin, lead, mercury, boron, aluminum, arsenic, and antimony. Extension of this new synthetic methodology to the preparation of alkyl derivatives of other metals and metalloids (e.g., silicon[2]) followed, but in these early days of organometallic chemistry, alkyl compounds of only main-group elements could be prepared. Of course, there was interest in using the dialkylzincs in the synthesis of alkyl derivatives of what later became called the transition metals. (Mendeleev's periodic table did not come until 1869.) In fact, in 1859 Hallwachs and Schafarik[3] speculated about the possible existence of the ethyl derivatives of chromyl chloride and uranyl chloride, which they wrote as CrO_2Aet and U_2O_2Aet, respectively.[4] Some isolated, unsuccessful attempts to prepare transition-metal alkyls also were reported at that time, but most negative results probably did not show up in the literature. In 1861, Wanklyn and Carius described reactions of diethylzinc in diethyl ether solution with cuprous iodide (written as Cu_2I), silver chloride, and ferrous iodide (written as Fe_2I_2).[5] In none of these reactions was there any evidence for the formation of stable ethyl derivatives; in all cases, gases (ethane, ethylene, butane) were evolved. The solid product of the $(C_2H_5)_2Zn/FeI_2$ reaction, a black, metallic-appearing powder, gave off dihydrogen when it was heated or treated with water. The authors, on the basis of H_2-evolution studies, suggested that it was a mixture of metallic iron and an iron hydride (written as Fe_2H_2). The latter, they suggested, might react with chlorides and oxides of other elements to replace Cl and O by H. The attempted alkylation of platinum halides with diethylzinc by Frankland also was unsuccessful.[6] A very vigorous reaction took place with formation of metallic platinum, but no stable ethylplatinum compounds were isolated. Such investigations became more numerous with the advent of the Grignard reagent in 1900. Only a few years later, Pope and Peachey[7] reported the preparation of the first stable transition-metal alkyl derivative, trimethylplatinum iodide, by addition of a solution of $PtCl_4$ in diethyl ether, with cooling, to a diethyl ether/benzene solution containing a 2-fold excess of CH_3MgI, followed by hydrolytic workup. Crystallization from benzene gave $(CH_3)_3PtI$ as a bright yellow, crystalline powder.

These and the other early attempts, mostly unsuccessful, to prepare alkyl and aryl derivatives of transition metals have been summarized by Krause and von Grosse[8] and by Cotton.[9]

However, in this essay, we are concerned specifically with the organic compounds of chromium. Sand and Singer[10] in 1903 reported unsuccessful attempts to prepare the methyl analogues of the two compounds mentioned by Hallwachs and Schafarik in 1859. In both cases, the reaction of CH_3MgI with the respective chlorides, UO_2Cl_2 and CrO_2Cl_2, was followed by hydrolytic workup. The results were inconclusive: any uranium−methyl and chromium−methyl compounds that might have formed could well have been readily hydrolyzed. Equally unsuccessful were the experiments of Bennett and Turner,[11] who studied the reaction of $CrCl_3$ with 3 molar equiv of C_6H_5MgBr with the goal of preparing triphenylchromium. The $CrCl_3$ was added to

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[1] Seyferth, D. *Organometallics* **2001**, *20*, 2940.
[2] Seyferth, D. *Organometallics* **2001**, *20*, 4978.
[3] Hallwachs, H.; Schafarik, A. *Ann.* **1859**, *33*, 206.
[4] Partington mistakenly reported the latter as a compound that actually had been isolated: Partington, J. R. *A History of Chemistry*; Macmillan: London, 1964; Vol. 4, p 511.
[5] Wanklyn, J. A.; Carius, L. *Ann.* **1861**, *120*, 69.
[6] Frankland, E. *J. Chem. Soc.* **1861**, *13*, 188.
[7] Pope, W. J.; Peachey, S. J. *J. Chem. Soc.* **1909**, *95*, 571.
[8] Krause, E.; von Grosse, A. *Die Chemie der metall-organischen Verbindungen*; Gebrüder Bornträger: Berlin, 1937; Chapter X, pp 766−788.
[9] Cotton, F. A. *Chem. Rev.* **1955**, *55*, 551.
[10] Sand, J.; Singer, F. *Justus Liebigs Ann. Chem.* **1903**, *329*, 190.
[11] Bennett, G. M.; Turner, E. E. *J. Chem. Soc.* **1914**, *105*, 1057.

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the solution of C_6H_5MgBr in diethyl ether "with continual shaking and cooling". The reaction mixture then was heated on a water bath for 1.5 h and later hydrolyzed ("with ice-cold water and dilute acid"). Ether extraction gave biphenyl as the only reported product. The authors rationalized the formation of this product in terms of a reduction of Cr(III) to Cr(II) (eq 1) and

$$2CrCl_3 + 2C_6H_5MgBr \rightarrow C_6H_5\text{-}C_6H_5 + 2CrCl_2 + MgCl_2 + MgBr_2 \quad (1)$$

used this reaction synthetically with benzylmagnesium bromide, α-naphthylmagnesium bromide, and *p*-tolylmagnesium iodide to prepare the respective coupled products. In the case of isoamylmagnesium iodide, the yield of diisoamyl was "unsatisfactory". An attempted cross-coupling reaction ($ArMgBr + Ar'MgBr \rightarrow Ar{-}Ar'$) gave only the symmetrical coupling products. These experiments were doomed to failure: the organochromium products that might have been formed would not have survived the reflux step.

II. The Phenylchromium Compounds of Franz Hein, Leipzig, 1918−1936

Despite the rather unpromising results of Sand and Singer and of Bennett and Turner on the methylation of CrO_2Cl_2 and the arylation of $CrCl_3$, respectively, with the appropriate Grignard reagent, Franz Hein, who had just obtained his Ph.D. at the University of Leipzig in 1917 and who was staying there to carry out the research for his *Habilitation* (which would allow his entrance into an academic career), chose to reexamine the action of phenylmagnesium bromide on $CrCl_3$. His initial results were submitted for publication as a preliminary communication on November 15, 1918, 4 days after the end of World War I and 5 days after the birth of Ernst Otto Fischer, the codiscoverer of our cover molecule. Hein's communication reported (without giving any preparative details) that the action of C_6H_5MgBr on anhydrous $CrCl_3$ gave a mixture of products, the major one of which was an orange, amorphous solid which could not be crystallized but which formed a 1:1 adduct with $HgCl_2$.[12] This organochromium product, Hein said, could "with reasonable certainty" be of the formula $(C_6H_5)_5CrBr$ on the basis of its elemental analysis (C, H, Br, Cr) (which was not so good) and that of its $HgCl_2$ adduct (only Cr and Hg, which were fine). An ebullioscopic molecular weight determination showed $(C_6H_5)_5CrBr$ to be monomeric in chloroform. It was found to be stable toward water but not toward acids. To Hein, the presence of six substituents on the Cr atom of his product and its orange color suggested that a Cr(VI) compound had been formed. It seemed to him that a valence disproportionation must have occurred, and he wrote eq 2 to represent the reaction. This was

$$5C_6H_5MgBr + 4CrCl_3 \rightarrow (C_6H_5)_5CrBr + 2MgBr_2 + 3MgCl_2 + 3CrCl_2 \quad (2)$$

strange and unexpected, but, as he said, it was known that the action of RMgBr on $PbCl_2$ resulted in the formation of R_4Pb and metallic lead, which also was a valence disproportionation. In apparent confirmation of $(C_6H_5)_5CrBr$ as a Cr(VI) derivative was Hein's finding that a Cr(VI) starting material, CrO_2Cl_2, also reacted with PhMgBr to give $(C_6H_5)_5CrBr$. Therefore, in its early days, this novel organochromium chemistry, while surprising, seemed to make sense.

Hein's communication ended with a promise to provide full details at a later date and a sentence that sounds rather quaint today: "I therefore direct to all my esteemed colleagues in this area the request to leave to me the organochromium compounds for my further study."[13] It would seem that chemists worldwide respected this request (if they did not, it did not do them any good), for Hein had the organochromium area all to himself—until the early 1950s.

The first full paper, entitled "Pentaphenylchromhydroxyd", appeared in 1921.[14] Full details of the preparation of Ph_5CrBr now were provided. The reaction itself sounds fairly easy to carry out: the workup, however, is something else. Hein's procedure was as follows: To a fairly dilute solution of C_6H_5MgBr in diethyl ether, cooled with an ice−salt mixture (−10 °C), must be added a suspension of sublimed, anhydrous $CrCl_3$ in diethyl ether with vigorous shaking. The reaction mixture, which becomes intensely brown-black, then is stirred, with continued cooling, for 2.5−3 h. When the reaction is complete, the reaction mixture, consisting of a brown-black sticky mass and a supernatant solution which has become lighter in color, is treated immediately with a 95% H_2SO_4/ice mixture. The red-brown phenylchromium products in the main appear as an emulsion in the ether layer. The multistep workup is time-consuming and complicated, but finally the product, which Hein calls the "crude bromide", is obtained as an orange-brown, amorphous powder. A major byproduct, separated by ether extraction, was biphenyl. It is noteworthy that no mention is made that air must be excluded during the reaction or workup procedures. The crude bromide yields were not high, not more than 20% based on $CrCl_3$ charged. Insufficient cooling gave lower yields, and adequate mixing of the reactants and the already formed product during the first $^1/_2$ h also is important. Otherwise, even with strong cooling, an explosively rapid exotherm can boil away all the ether within a few minutes. Then, commented Hein, of course the yield is zero.

The crude bromide was rather nasty stuff—it obviously was a mixture of phenylchromium compounds, Hein said, whose composition was variable and depended on the reaction and workup conditions. It always was amorphous; the many different attempts to crystallize it invariably failed. It was thermally unstable, being decomposed by only mild heating. It was oxidized by air over time in solution and in the solid state but was stable under an atmosphere of carbon dioxide. It was decomposed by acids, and it was light-sensitive. These properties, especially its amorphous nature, made the crude bromide very difficult to work with. One must admire Hein's tenacity and patience.

Examination of the ethanol-soluble portion of the crude bromide showed that it was impure and that it

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[12] Hein, F. *Ber. Dtsch. Chem. Ges.* **1919**, *52*, 195.

[13] "... ich richte daher an die verehrten Fachgenossen die Bitte, die Chromorganoverbindungen mir zur weiteren Bearbeitung überlassen zu wollen."

[14] Hein, F. *Ber. Dtsch. Chem. Ges.* **1921**, *54*, 1905.

contained organic impurities. An apparently pure derivative in the form of a marginally stable, also amorphous, 1:1 adduct with $HgCl_2$ could, however, be obtained, and this appeared to confirm Hein's assumption that the major component of the crude bromide was $(C_6H_5)_5CrBr$. (I reproduce Hein's formulas in this part as he wrote them. When they had been shown to be the incorrect formulations (Section III), I will write them in quotation marks.) Removal of the $HgCl_2$ as HgS by treatment of the adduct solution in pyridine with H_2S gave, after a difficult purification procedure, ostensibly "pure" $(C_6H_5)_5CrBr$ as the hemietherate. This material also could not be crystallized.

Further investigation of the chemical properties of $(C_6H_5)_5CrBr$ showed it to have saltlike properties. The action of silver nitrate in aqueous−alcoholic solution precipitated AgBr, while treatment with Reinecke's salt, $(NH_4)_2[(H_3N)_2Cr(SCN)_4]$, resulted in precipitation of a pentaphenylchromium Reineckate. Shaking of a solution of $(C_6H_5)_5CrBr$ in ethanol with moist silver oxide resulted in precipitation of AgBr and formation of pentaphenylchromium hydroxide. After several unsuccessful approaches, it was found that the reaction of KOH with the crude bromide in absolute ethanol, followed by addition of an equal volume of diethyl ether, resulted in complete precipitation of KBr, leaving a solution of $(C_6H_5)_5CrOH$. Further multistep procedures finally gave an aqueous solution of the pure hydroxide, from which it crystallized in the form of gold-orange flakes in low yield (1−2 g from 80 g of starting $CrCl_3$). These crystals contained 4 mol equiv of water which could be removed in two stages, by storage over $CaCl_2$ and then over P_2O_5 in vacuo. The completely anhydrous hydroxide was deep olive green and rather unstable. This color change was found to be reversible on rehydration. Hein's suggested formula was $[(C_6H_5)_5Cr(H_2O)_2]OH{\cdot}2H_2O$. The hydroxide was found to be as strongly basic as an alkali metal hydroxide, on the basis of its chemistry and electrical conductivity in anhydrous methanol.

Up to this point, Hein's results, while surprising and unexpected, are internally consistent. Noteworthy are the great experimental difficulties that Hein experienced and the great sensitivity to experimental conditions in obtaining these results that Hein noted. After having read this paper, none of Hein's "esteemed colleagues" would have felt any desire to intrude in this area of organometallic chemistry!

The second full paper[15] brought new results that were even more surprising and unexpected. To prepare other salts of the $(C_6H_5)_5Cr^+$ species, the purified hydroxide was treated with salts or with acids. The expectation was the reaction shown in eq 3. The products, however,

$$Ph_5CrOH + MX \rightarrow Ph_5CrX + MOH \qquad (3)$$

surprisingly, were *tetraphenyl*chromium salts. Thus, treatment of a chloroform solution of the hydroxide with an excess of HI or aqueous KI gave the red-brown, crystalline $(C_6H_5)_4CrI$. Prepared in a similar manner was the orange tetraphenylchromium bromide. The orange-red perchlorate, $(C_6H_5)_4CrClO_4$, was rather unstable in the solid state. On a warm day it tended to explode spontaneously after a few hours. Gentle heating and mild shock also caused it to explode. It also was light-sensitive, the decomposition causing a color change to gray-green and the formation of biphenyl. Treatment of $(C_6H_5)_5CrOH$ with aqueous $(NH_4)_2Cr_2O_7$ yielded the gold-orange $[(C_6H_5)_4Cr]_2Cr_2O_7$, which also was explosive. A tetraphenylchromium Reineckate also was prepared. Electrolysis of an aqueous alcoholic solution of $(C_6H_5)_4CrI$ resulted in deposition of orange crystals on the cathode (to which Hein ascribed the formula $[(C_6H_5)_4Cr]_x$), which dissolved to give a strongly basic solution. The tetraphenylchromium hydroxide, however, could not be isolated. The big question associated with this chemistry was: what happened to the fifth phenyl group? In a search for organic products in the aqueous phases and the residues from the chloroform extractions of the $(C_6H_5)_4Cr$ salt preparations, a substantial amount of phenol was found. Hein speaks of the possibility of adventitious oxidation of an intermediate "free" phenyl group (a phenyl group *in statu nascendi*, he called it). However, in a footnote, the reader is informed of recent (i.e., 1921) experiments using completely anhydrous pentaphenylchromium hydroxide to prepare such salts with strict exclusion of oxygen and moisture during all operations in which phenol was not formed. Instead, other (unspecified) aromatic products were formed in goodly quantity. One was left none the wiser concerning the fate of the lost phenyl group.

Hein considered the chromium in the $(C_6H_5)_4CrX$ salts to be pentavalent, although Cr(V) compounds were virtually unknown. Because the X substituents were only loosely bonded to Cr, he ascribed to Cr coordination number 4 in the tetraphenylchromium salts.

During the course of his studies with the pentaphenylchromium compounds, Hein came to suspect that other phenylchromium compounds were lurking in the solutions that he was studying. In particular, in the reaction of the crude bromide with Ag_2O, other products were formed, in addition to the $(C_6H_5)_5CrOH$ noted earlier. Evaporation in vacuo of the intensely orange aqueous mother liquors from the pentaphenylchromium hydroxide preparation left a dark red, viscous concentrate, which on cooling gave orange crystals of what proved to be pentaphenylchromium carbonate hexahydrate—the only pentaphenylchromium-derived product that apparently had not lost a phenyl group. An even more water-soluble product also was present.[16] Evidence for this was provided by the intense color of the aqueous syrup that remained after the $(C_6H_5)_5Cr$ carbonate had been removed. Attempts to isolate this soluble product were not successful. In this concentrated form, the products were not stable. On the other hand, on dilution with water, stable but light-sensitive solutions were obtained. These were strongly basic, absorbed CO_2, and reacted with aqueous silver nitrate to precipitate Ag_2O. On reaction with many acids and alkali-metal salts, orange, amorphous, oily precipitates were formed, among them the chloride, bromide, iodide, cyanide, nitrate, perchlorate, picrate, and Reineckate. All were soluble in organic solvents such as chloroform and ethyl acetate, in contrast to the base from which they were derived. The base solutions were oxidized slowly by air and rapidly by hydrogen peroxide. With great difficulty, an

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[15] Hein, F. *Ber. Dtsch. Chem. Ges.* **1921**, *54*, 2708.

[16] Hein, F. *Ber. Dtsch. Chem. Ges.* **1921**, *54*, 2727.

orange-red, crystalline, hydrated Reineckate finally could be prepared, $(C_6H_5)_3Cr[Cr(NH_3)_2(SCN)_4]\cdot H_2O$ (analysis for C, H, S, Cr). Under special conditions, the monohydrate could be dehydrated over H_2SO_4 in vacuo. The anhydrous Reineckate, however, decomposed rather quickly on exposure to air to give a black-brown-violet solid that smelled intensely of biphenyl (often noted when the penta- and tetraphenylchromium compounds decomposed) and benzene (which Hein found so noteworthy that he followed it with "(!)"). Also prepared was the air-sensitive $(C_6H_5)_3CrI\cdot(C_2H_5)_2O$ and the crystalline, poorly stable $(C_6H_5)_3CrClO_4$. The latter exploded readily on gentle warming or when lightly tapped. Hein regarded the triphenylchromium compounds as Cr(IV) derivatives, although no other examples of this oxidation state were known at that time. Curiously, under some conditions (overly long reaction times or insufficient cooling), the product of the $3C_6H_5MgBr + CrCl_3$ reaction was triphenylchromium bromide rather than the pentaphenylchromium bromide. Hein concluded that both bromides were formed as primary products in the reaction; therefore, triphenylchromium bromide was not a secondary product.

The results summarized above constitute Hein's *Habilitations* research. He appears to have done it all by himself, starting in 1918 and completing it in 1921. At this point, the results did not seem to make very much sense. Hein had prepared members of three families of polyphenylchromium compounds, $(C_6H_5)_5CrX$, $(C_6H_5)_4CrX$, and $(C_6H_5)_3CrX$, where X was hydroxide or various mononegative anions. Surprisingly, the compounds in all three families were orange-red, reminscent of Cr(VI) as in chromate salts. The most stable of these, in all three families, which could be isolated as at least microcrystalline solids, were those compounds that contained a large anion such as the Reineckate, perchlorate, and iodide. All appeared to be salts and often were soluble in water or aqueous alcohol. The usual product of their decomposition was biphenyl, but benzene also had been found. The remarkable conversion of $(C_6H_5)_5CrOH$ to $(C_6H_5)_4CrX$ compounds gave phenol in substantial quantity, thus apparently accounting for the fifth phenyl group. The low yield of the crude bromide, ~20%, could be explained on the basis of eq 2, which limited the yield to 25%. Apparently, Hein did not use the then already available Schlenk techniques in his phenylchromium chemistry to perform the standard chemical operations under an inert atmosphere but, rather, carried out his experiments without exclusion of air, the available ether vapors at room temperature and below serving as a not very effective inert atmosphere in the reaction flask.

At this point, there was only one thing Hein could do: press on and try to gather more information that might help to solve the mystery of his phenylchromium compounds.

Before we consider his further organochromium research, it is of interest to tell something about Franz Hein (1892−1976) (Figure 1).[17] He was born in Grötzingen (Baden) in Germany. After his high school *Abitur* in Leipzig, he studied chemistry at the University of Leipzig, where he carried out his Ph.D. research with Hantzsch and Schäfer on two topics, triphenylmethane derivatives and optical studies on bismuth compounds, completing it in 1917. He stayed in Leipzig as *Assistent* and, after 1920, as *Oberassistent*, working on his *Habilitation*. He became a professor in 1923. His years at the University of Leipzig were very fruitful. Not only did he work on the phenylchromium compounds but also, after his *Habilitation*, he started work on the electrochemistry of organometallic systems.[18,19] This involved the study of diethylzinc and also of di-*n*-propylzinc and triethylaluminum as solvents for alkali metal alkyls (C_2H_5M with M = Li, Na, K and C_6H_5Li and $C_6H_5CH_2Li$). Such solutions contained Wanklyn-type species which were strong electrolytes in the zinc and aluminum alkyl solutions, e.g., eq 4. Conductivity

Figure 1. Franz Hein, University of Leipzig, 1935 (University of Leipzig Archives, by permission, Dr. G. Wiemers, Director).

$$C_2H_5Na + (C_2H_5)_2Zn\ (\text{excess}) \rightarrow Na^+[(C_2H_5)_3Zn]^- \tag{4}$$

studies showed that Faraday's law was obeyed. Organic free radicals were discharged at the anode on electroly-

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[17] Biographical reports: (a) Wolf, F. *Jahrbuch 1975/76*; Sächsische Akademie der Wissenschaften, **1979**, 229−239. (b) Oesper, R. E. *J. Chem. Educ.* **1953**, *30*, 313. (c) Kurras, E. *Z. Chem.* **1962**, *2*, 161. (d) Hennig, H. In *Wege und Perspektiven der Wissenschaft*; Haase, G., Ed.; Akademie-Verlag: Berlin, 1976; pp 264−267. (e) Beyer, L.; Hoyer, E. *Nachr. Chem.* **2000**, *48*, 1493.

[18] Some of this work of Hein was mentioned in the cover essay on $EtZnI/Et_2Zn$.[1]

[19] (a) Hein, F. *Z. Elektrochem.* **1922**, *28*, 469. (b) Hein, F.; Wagler, K.; Segitz, F. A.; Petzschner, E. *Z. Anorg. Allg. Chem.* **1924**, *141*, 161. (c) Hein, F.; Meininger, H. *Z. Anorg. Allg. Chem.* **1925**, *145*, 95. (d) Hein, F.; Segitz, F. A. *Z. Anorg. Allg. Chem.* **1926**, *158*, 153. (e) Hein, F.; Schramm, H. *Z. Phys. Chem.* **1930**, *149*, 408. (f) Hein, F.; Schramm, H. *Z. Phys. Chem.* **1930**, *151*, 234. (g) Hein, F.; Pauling, H. *Z. Elektrochem.* **1932**, *38*, 25. (h) Hein, F.; Pauling, H. *Z. Phys. Chem.* **1933**, *165*, 338.

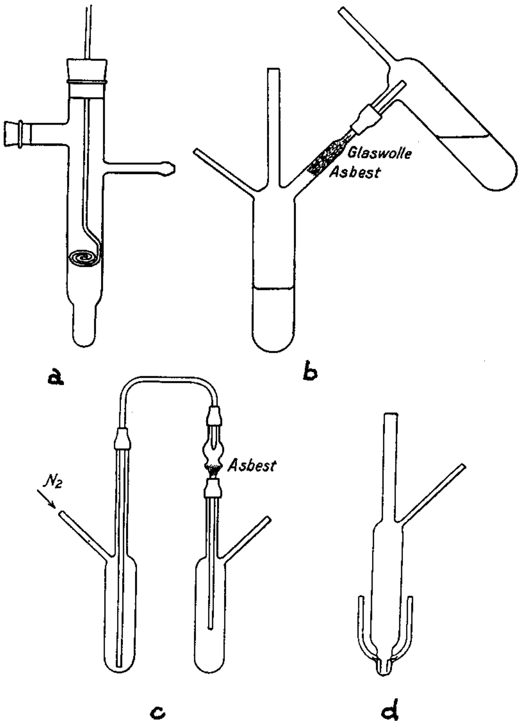

Figure 2. Hein's Schlenkware:[19b] (a) reaction vessel; (b) vessels for filtration; (c) transfer/filtration system; (d) apparatus for conductivity measurements. Reprinted by permission, Wiley-VCH Verlag GmbH.

sis of the $C_2H_5M/(C_2H_5)_2Zn$ solutions, and they were found to dissolve the anodes of metals such as Zn, Al, Pb, and Cd to form the respective metal alkyls: a new metal alkyl synthesis. Such metal alkyl/diethylzinc solutions were highly sensitive toward air and moisture, and Hein had to exclude all traces of air and moisture using Schlenk-type glassware (Figure 2).

In 1941, Hein began a new project in organometallic chemistry that he pursued sporadically until 1965: the preparation and study of main-group-metal derivatives of metal carbonyls, compounds that contained a main-group−transition-metal σ bond.[20] Thus, for example, by reactions of $Fe(CO)_5$ and $H_2Fe(CO)_4$ with organometallic hydroxides were prepared compounds such as $(CH_3Hg)_2Fe(CO)_4$, $[R_2PbFe(CO)_4]_2$ ($R = CH_3, C_2H_5$, n-C_3H_7, n-C_4H_9, C_6H_5), $[(C_2H_5)_3Pb]_2Fe(CO)_4$, $[(C_6H_5)_3Sn]_2Fe(CO)_4$, and $[(C_6H_5)_2SnFe(CO)_4]_2$. Also prepared were $(C_6H_5)_3SnCo(CO)_4$, $(C_6H_5)_2Sn[Co(CO)_4]_2$, and $(OC)_3FeTlFeH(CO)_4$.

Hein's research interests also included aspects of other organometallic, inorganic, coordination, and analytical chemistry. Among these were studies of the Cr(II) halides, the preparation of $[Cr(\alpha,\alpha'\text{-bipyridyl})]ClO_4$, and the preparation of silver permanganate, which was found to be a useful analytical reagent for the determination of H_2 at room temperature.

Hein stayed at the University of Leipzig until 1942, when he moved to the University of Jena to become Director of the Institute for Inorganic Chemistry. In March 1945, the Chemical Institutes in Jena were destroyed in an air raid. Hein returned to Jena after war's end in 1946, and he played an important part in the reconstruction of the Chemical Institutes. He held the chair in inorganic chemistry until his retirement in 1959.

In his further research on organochromium chemistry, after his *Habilitation*, Hein was aided by student co-workers. The goal of this work was to solve the mystery of the three polyphenylchromium families: to understand the reactions that led to their formation and their structure and bonding. By the time the first stage ended, with a paper submitted in April 1939, the mystery had not been solved, but some further interesting results had been obtained.[21]

A noteworthy finding was that tetraphenylchromium iodide could be reduced to tetraphenylchromium, the first neutral organochromium compound with only organic substituents.[21c] Electrolysis of $(C_6H_5)_4CrI$ in oxygen-free liquid ammonia under purified nitrogen at −40 to −50 °C resulted in deposition on the platinum cathode of an orange-red, crystalline solid which was iodine-free and whose Cr analysis agreed with that required for $(C_6H_5)_4Cr$. This product was extremely reactive and was thermally unstable even at room temperature. Its thermal decomposition gave biphenyl as the organic product. It dissolved completely, with reaction, in alcohol, giving a basic solution from which $(C_6H_5)_4CrOH$ could be obtained in quantitative yield. It was air-sensitive, becoming sticky and darker in color. Provided that appropriate precautions were taken to exclude air and moisture, tetraphenylchromium was found to dissolve in dry pyridine without reaction to give stable, red-brown solutions.[21j] Determination of the molecular weight of tetraphenylchromium in pyridine solution showed it to be monomeric. The electrolysis of pentaphenylchromium hydroxide in liquid ammonia also proceeded with loss of a phenyl group (as had its reactions with acids and salts). Tetraphenylchromium, identical with that derived from $(C_6H_5)_4CrI$, was obtained.

The same electrolysis procedure could be applied as well to triphenylchromium iodide. Triphenylchromium, even less thermally stable than the tetraphenyl compound, deposited on the cathode in the form of an amorphous, brown-yellow, air-sensitive solid that contained some ammonia. Solution in alcohol resulted in formation of triphenylchromium hydroxide. Triphenylchromium also was obtained as a yellow-brown precipitate by chemical reduction of $(C_6H_5)_3CrI$ by sodium in liquid ammonia.

Hein's initial interpretation of the $C_6H_5MgBr/CrCl_3$ reaction is shown in eq 2: i.e., the valence dispropor-

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(20) (a) Hein, F.; Pobloth, H. *Z. Anorg. Allg. Chem.* **1941**, *248*, 84. (b) Hein, F.; Heuser, E. *Z. Anorg. Allg. Chem.* **1942**, *249*, 293. (c) Hein, F.; Heuser, E. *Z. Anorg. Allg. Chem.* **1947**, *254*, 138. (d) Hein, F.; Heuser, E. *Z. Anorg. Allg. Chem.* **1947**, *255*, 125. (e) Hein, F.; Scheiter, H. *Z. Anorg. Allg. Chem.* **1949**, *259*, 183. (f) Hein, F.; Kleinert, P.; Jehn, W. *Naturwissenschaften* **1957**, *44*, 34. (g) Hein, F.; Jehn, W. *Liebigs Ann. Chem.* **1965**, *684*, 4.

(21) Publications between 1924 and 1939: (a) Hein, F.; Schwartzkopf, O. *Ber. Dtsch. Chem. Ges.* **1924**, *57*, 8. (b) Hein, F.; Spaete, R. *Ber. Dtsch. Chem. Ges.* **1924**, *57*, 899. (c) Hein, F.; Eissner, W. *Ber. Dtsch. Chem. Ges.* **1926**, *59*, 362. (d) Hein, F.; Späte, R. *Ber. Dtsch. Chem. Ges.* **1926**, *59*, 751. (e) Hein, F.; Reschke, J.; Pintus, F. *Ber. Dtsch. Chem. Ges.* **1927**, *60*, 679. (f) Hein, F.; Reschke, J.; Pintus, F. *Ber. Dtsch. Chem. Ges.* **1927**, *60*, 749. (g) Hein, F.; Pintus, F. *Ber. Dtsch. Chem. Ges.* **1927**, *60*, 2388. (h) Hein, F.; Späte, R. *Kolloid-Z.* **1926**, *39*, 236. (i) Hein, F.; Schwartzkopf, O.; Eissner, W.; Hoyer, K.; Klar, K.; Clauss, W. *Ber. Dtsch. Chem. Ges.* **1928**, *61*, 730. (j) Hein, F.; Markert, E. *Ber. Dtsch. Chem. Ges.* **1928**, *61*, 2255. (k) Hein, F.; Schwartzkopf, O.; Eissner, W.; Hoyer, K.; Klar, K.; Clauss, W.; Just, W. *Ber. Dtsch. Chem. Ges.* **1929**, *62*, 1151. (l) Hein, F.; Retter, W. *Z. Phys. Chem. A* **1931**, *156*, 81. (m) Hein, F. *J. Prakt. Chem.* **1932**, *132*, 59. (n) Hein, F. *J. Prakt. Chem.* **1939**, *153*, 160.

tionation 4Cr(III) → Cr(VI) + 3Cr(II). To see if this was indeed correct, Hein, Reschke, and Pinkus[21f] sought evidence for the formation of a Cr(II) product. Such a product should reduce aqueous acid to give H_2 but not water. Experimentally it was found that addition of neutral water under a CO_2 atmosphere to a $C_6H_5MgBr/CrCl_3$ reaction mixture released substantial amounts of H_2 very vigorously, while subsequent addition of aqueous HCl released even more. As a result, it was suggested that C_6H_5MgBr also reacts with $CrCl_2$ (eq 5),

$$4C_6H_5MgBr + 4CrCl_2 \rightarrow (C_6H_5)_4CrCl + 3CrCl + 2MgCl_2 + 2MgBr_2 \quad (5)$$

which was confirmed by experiment. In an experimental footnote in this paper,[21f] the reaction and subsequent workup are described as having been carried out with rigorous exclusion of air under carefully deoxygenated nitrogen. However, phenylchromium compounds were produced. Details about yield were not reported, since these were not preparative experiments.

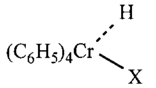
Some efforts also were expended in order to obtain an understanding of the $(C_6H_5)_5CrOH \rightarrow (C_6H_5)_4CrX$ conversion by the action of acids and salts.[21k] The initial experiments suggested that the hydroxide actually might be the phenoxide $(C_6H_5)_4CrOC_6H_5$, although Hein had other thoughts about that. The reaction of a very carefully prepared and purified $(C_6H_5)_5CrOH$ hydrate with KBr in a water−chloroform mixture gave phenol in an amount equivalent to the organochromium starting material used, as well as traces of biphenyl. A similar result was obtained in a reaction carried out under nitrogen of the $(C_6H_5)_5CrOH$ hydrate with KI in anhydrous ethanol. Hein wrote eq 6 to describe the

$$(C_6H_5)_5CrOH + KX + H_2O \rightarrow (C_6H_5)_4CrX + C_6H_5OH + KOH + (H) \quad (6)$$

former reaction. Hein's conclusions were as follows. The quantitative yield of phenol indicates that it is not produced by an oxidation process (as he had thought initially) but, rather, by a reaction of the eliminated phenyl group with water. That phenol was produced in 100% yield in the second experiment shows that it is the neighboring water of hydration that reacts with the leaving phenyl group. An experiment was carried out to test this idea. The reaction of pure, water-free, olive brown $(C_6H_5)_5CrOH$ in chloroform solution with anhydrous KI or ZnI_2 gave a much lower yield of phenol, for which, according to eq 7, a maximum yield of 50% would be expected.

$$2(C_6H_5)_5CrOH + 2KX \rightarrow 2(C_6H_5)_4CrX + K_2O + C_6H_5OH + (H) + (C_6H_5) \quad (7)$$

Equation 6 got Hein and his students into the proverbial can of worms. Among the products was a hydrogen atom, yet no H_2 gas evolution was ever observed. So what happened to $H^{\bullet}$? It was concluded that it was somehow coordinated to the $(C_6H_5)_4Cr$ salt that had been produced. A series of experiments that Hein characterized as "difficult, troublesome, time-consuming and requiring much preparation" was carried out under a pure nitrogen atmosphere in sealed Schlenk tubes. Hein suggested that if hydrogen (nascent?) was produced and somehow trapped in the reactions of eqs 6 and 7, then such reaction mixtures might have reducing power; for instance, they might reduce methylene blue. Accordingly, $(C_6H_5)_5CrOH$ and NH_4Cl in aqueous solution were allowed to react in the presence of methylene blue. Alternatively, methylene blue was added to a solution of $(C_6H_5)_4CrCl$. In both cases, a part of the methylene blue was reduced. This reduction, it was found, could be catalyzed by $Pd/CaCO_3$ or $Pd/BaSO_4$ or by UV irradiation. These reductions were taken as evidence for the formation of H in the reacting system. The fact that preformed $(C_6H_5)_4CrCl$ reduced methylene blue was strange indeed, and Hein suggested that the hydrogen was bonded to the Cr atom, writing formula **1**, mentioning in support of this idea the chromium hydride reported by Weichselfelder and Thiede 3 years earlier as being formed in a 3 $C_6H_5MgBr/CrCl_3$ reaction carried out in the presence of dihydrogen (eq 8). Hein



1

$$3C_6H_5MgBr + CrCl_3 + 3H_2 \xrightarrow[22\ h]{Et_2O} \text{“}CrH_3\text{”} + 3C_6H_6(?) + 3MgBrCl \quad (8)$$

mentioned also that detectable amounts of H_2 were given off when a $(C_6H_5)_4CrX$ compound was carefully warmed in high vacuum.[21m] A sample of $(C_6H_5)_4CrCl$ that had been "dehydrogenated" by reaction with methylene blue was essentially unchanged: it had the same color, melting point, and other properties. Furthermore, it could be rehydrogenated at room temperature and atmospheric pressure in ethanol solution using a Pd catalyst. Admittedly, these experiments were done on a small scale (0.6 g of $(C_6H_5)_4CrCl$ in one example) and involved uptake of very small quantities of H_2 (7−8 cm^3 at STP), but they were carried out carefully using the apparatus shown in Figure 3 and they were repeatable. A problem in these experiments was that both in the methylene blue reductions and in the hydrogen absorptions, the H_2 released or taken up amounted to no more than 20% of the calculated value; therefore, there is a question about what these experiments really mean. In previous reviews of Hein's work, this puzzling aspect of tetraphenylchromium halide and hydroxide chemistry received more than casual mention only in ref 8.[23,26]

Hein's other research in the 1921−1939 period involved further studies of the $(C_6H_5)_5CrOH \rightarrow (C_6H_5)_4CrX$ conversion (some 50 examples were investigated, 40 of

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(22) Weichselfelder, T.; Thiede, B. *Justus Liebigs Ann. Chem.* **1926**, *447*, 64. The identity of "CrH_3" is based on H_2 absorption measurements during the reaction and on measurements of H_2 evolution on treatment of the reaction mixture with dilute H_2SO_4 and oxidation of any Cr(II) present with 0.1 N $K_2Cr_2O_7$. Organic products were not identified.

(23) Reference 8 (pp 768−783) gives the best, most detailed account of Hein's work up to 1937. Other accounts are found in refs 9, 24, and 25.

(24) Zeiss, H. In *Organometallic Compounds*;ACS Monograph Series 147; Zeiss, H., Ed.; Reinhold: New York, 1960; Chapter 8, pp 380−425.

(25) Uhlig, E. *Organometallics* **1993**, *12*, 4751.

(26) The question remains: is this property of the "$(C_6H_5)_4CrX$" prepared by Hein's Grignard procedure real? It was never mentioned again in Hein's later papers.

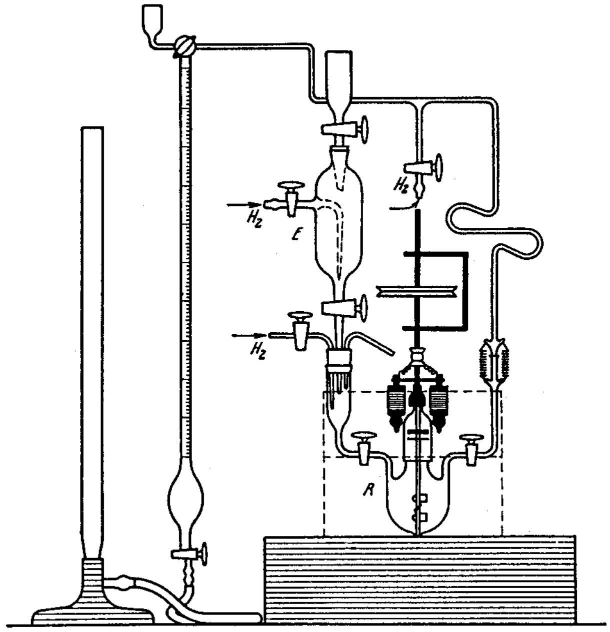


Figure 3. Hein's apparatus for measuring H_2 uptake by $(C_6H_5)_4Cr$ chloride and iodide solutions in diethyl ether.[21k] Reprinted by permission, Wiley-VCH Verlag GmbH.

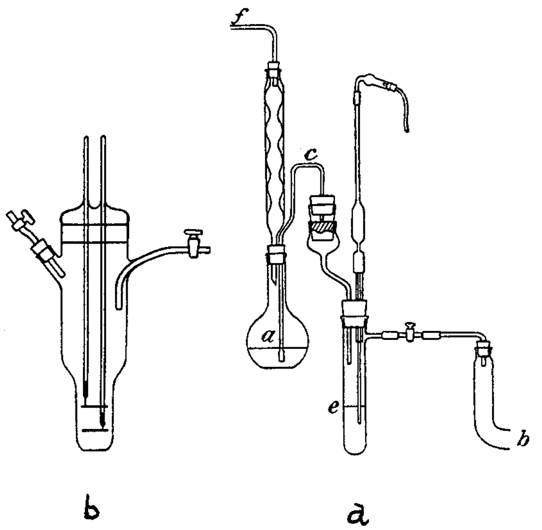


Figure 4. (a) Apparatus for preparing $(C_6H_5)_nCrX$ solutions with exclusion of air and moisture. (b) Conductivity apparatus.[19c] Reprinted by permission, Wiley-VCH Verlag GmbH.

which gave tetraphenylchromium derivatives), the use of inorganic chromium compounds other than $CrCl_3$, $CrCl_2$, and CrO_2Cl_2 as starting materials in the reaction with C_6H_5MgBr, the preparation of other arylchromium compounds (*o*- and *p*-tolyl, *m*-chlorophenyl, *m*-xylyl and α-naphthyl), and studies of the electrical conductivity (Figure 4) of various phenylchromium salts and hydroxides (that the latter are strong electrolytes is shown in Figure 5). Hein gave a summary of his phenylchromium research in 1932,[21m] since this appeared to be the end of the road. Many experiments had been done, a large amount of information had been gathered, but an understanding of the phenylchromium compounds still had not been achieved.

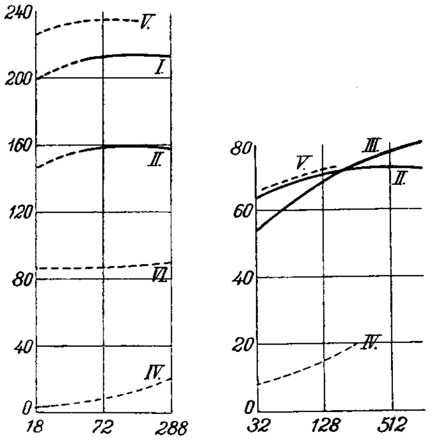
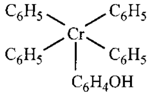
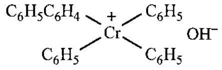
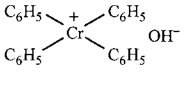
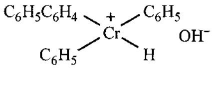
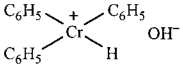
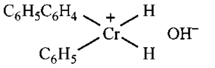


Figure 5. Molar conductivities of $(C_6H_5)_nCrOH$ at 25 °C: (a) in water; (b) in methanol. Legend: (I) $(C_6H_5)_3CrOH$; (II) $(C_6H_5)_4CrOH$; (III) $(C_6H_5)_5CrOH$; (IV) NH_4OH; (V) NaOH.[19c] Reprinted by permission, Wiley-VCH Verlag GmbH.

Table 1

Hein's Formulations	TYPE I	TYPE II
$(C_6H_5)_5Cr^+OH^-$		
$(C_6H_5)_4Cr^+OH^-$		
$(C_6H_5)_3Cr^+OH^-$		

In 1936, the first researchers other than Hein devoted some time to a study of the phenylchromium compounds (at least they were the only ones who published anything). Klemm and Neuber, at the instigation of Hein, undertook an investigation of the magnetic behavior of representatives of the three phenylchromium families,[27] samples of which were provided by Hein. Those chosen were ones that had been isolated in analytically pure form: the pentaphenylchromium hydroxides (hydrates and anhydrous) and anthranilate, the tetraphenylchromium iodide, the triphenylchromium Reineckate, and the diethyl etherate of the iodide. All were used immediately after their preparation to avoid any decomposition. The results were very surprising: all compounds examined were paramagnetic with magnetic moments of around 1.73 μ_B, indicating the presence of one unpaired electron, and obeyed Curie's Law. This was not in agreement with Hein's suggestion of valence states VI, V, and IV, respectively, for the penta-, tetra-, and triphenylchromium families. Klemm and Neuber suggested that all three phenylchromium families contain the rare Cr(V) valence state. Two series of formulations were suggested: type I, in which the organic groups all were phenyl, and type II, in which one of the organic groups was biphenylyl (Table 1). These formulations were in agreement with some experimental facts: the members of all families had essentially the same magnetic moment, the same orangeish color, and approximately the same UV/vis absorption spectra. However, the presence of hydrogen substituents in some formulas and of biphenylyl groups in the type II formulas was a problem. Klemm and

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(27) Klemm, W.; Neuber, A. *Z. Anorg. Allg. Chem.* **1936**, *227*, 261.

Neuber were not especially happy with either of their formulations; neither was Hein, as he said in a note that followed immediately after the Klemm/Neuber paper.[28] Further synthetic chemistry, Hein said, e.g., experiments using mixtures of C_6H_5MgBr and $C_6H_5C_6H_4MgBr$, might shed some light on Klemm and Neuber's suggestions. Unfortunately, these do not appear to have been carried out.

At this point, it is useful to take stock and consider the strange properties of the three families of chromium compounds that Hein called penta-, tetra-, and triphenyl derivatives and that he said contained chromium in the penta-, tetra-, and trivalent states, respectively.

(1) All had much the same color − from yellow-orange to orange-red.

(2) All showed an absorption in the UV spectrum at around 350 nm.

(3) All had essentially the same magnetic properties, a magnetic susceptibility of $1.72 \pm 5\%\ \mu_B$.

(4) The claimed pentaphenylchromium hydroxide on treatment with acid or salts for the most part gave *tetraphenyl*chromium salts and phenol. Reaction of tetraphenylchromium hydroxide with acids and salts, on the other hand, gave tetraphenylchromium salts without loss of a phenyl group.

Given these observations, the ideas of Hein about the constitution of the three phenylchromium families did not make much sense at all. It did not seem possible that three different valence states of chromium characterized the three phenylchromium families. However, the results of Klemm and Neuber did not seem to lead anywhere either. Hein's phenylchromium chemistry was full of vexing anomalies and questions; it was a complete mystery. In his 1955 review,[9] Cotton called it "one of the most fascinating and perplexing phases of organometallic chemistry".

We are still some years away from our first encounter with our cover molecule. I have gone into such detail in describing Hein's research during the 1918−1932 period to show how difficult research in "pre-modern" days could be. The chemical literature of the pre-1950 era is full of triumphs of successful structure proofs by means of well-considered synthetic and degradation experiments combined with elemental analyses and deductions based on physical and chemical properties, but there also are examples, such as that of the phenylchromium compounds, where, after years of work, one ended up at a brick wall, with no apparent possibility of further progress at that time. Hein's problems were unusually difficult ones in that his products were of limited, often of low, thermal stability and also were air-sensitive. The main-group organometallic chemists were guided in their research by analogies to the inorganic compounds of their particular elements. This was not the case with Hein's phenylchromium compounds. They seemed to be uniquely different in concept from inorganic chromium compounds. Hein and his students were unsuccessful in reaching their goal, but not for lack of trying. Their synthetic work and studies of reactivity certainly were well done, and they applied all of the limited number of physical techniques that were available at the time: molecular weight measurements, conductivity studies, UV/vis absorption spectroscopy, and magnetic measurements. Unfortunately, structure determination by X-ray crystallography was not available to them. Had it been, their problems might have been solved at an early date. Then there was the fact that no sandwich compounds involving carbocyclic rings and a metal were known when Hein and his students were investigating the phenylchromium compounds. The sandwich structure of ferrocene was not determined until 1952. As Hein said in a paper published in 1956,[29] had he considered in the 1920s and 1930s a sandwich structure for his chromium compounds, he would not have been taken seriously. Grignard reagents in all known cases at that time reacted with metal halides in the sense of a substitution reaction, with transfer of the organic group in RMgX to the metal with no change in the nature and structure of the organic group.

So in 1936, Hein stood in front of his brick wall. He carried out research in other areas of chemistry. He moved to Jena and was bombed out, and his major efforts after the war were devoted to the rebuilding of the Chemical Institute in Jena. However, he did not forget his phenylchromium compounds. He published two papers in 1953 on the thermal decomposition of tetraarylchromium halides[30a] and of $(C_6H_5)_4CrI$ under high vacuum.[30b] The products were biphenyl, a Cr(I) halide, and chromium carbide.

The preparation of ferrocene by Kealy and Pauson by reaction of cyclopentadienylmagnesium bromide with $FeCl_3$ in 1951 and the rapid early development in the 1952−1954 period of cyclopentadienyl−metal chemistry by Ernst Otto Fischer and Geoffrey Wilkinson and their respective students did not lead Hein to consider the possibility of a sandwich-type structure for his phenylchromium compounds. Hein's brick wall remained standing.

Finally, some other, most certainly related, chemistry should be mentioned. In 1926, the same year that Weichselfelder and Thiede reported the reaction of phenylmagnesium bromide with $CrCl_3$ in the presence of H_2,[22] Job and Cassal in France published the results of a $C_6H_5MgBr/CrCl_3$ reaction carried out while bubbling carbon monoxide through the solution.[31] After hydrolytic workup, $Cr(CO)_6$ was found in ∼14% yield among the many products, which included benzaldehyde, benzophenone, benzil, benzoin, diphenylacetophenone, and phenol, as well as others. An organochromium residue similar to that of Hein's also was obtained. However, as further studies of Job and Cassal showed, Hein's initial phenylchromium product, preformed in the $3C_6H_5MgBr + CrCl_3$ reaction, did not react with carbon monoxide. The CO had to be added to the system while the phenylmagnesium bromide and $CrCl_3$ were reacting. Therefore, some other intermediate must be involved. Job and Cassal suggested that complexes of phenylchromium intermediates and CO might be involved, writing no-bond "formulas" such as **2** and **3**. The intermediacy of such complexes, they said, would explain the formation of benzophenone, biphenyl, and some of the other organic products. Hieber and Rom-

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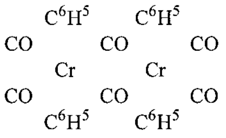
(28) Hein, F. *Z. Anorg. Allg. Chem.* **1936**, *227*, 272.

(29) Hein, F. *Chem. Ber.* **1956**, *89*, 1816.

(30) (a) Hein, F.; Pauling, H. *Z. Anorg. Allg. Chem.* **1953**, *273*, 207. (b) Hein, F.; Bähr, G. *Chem. Ber.* **1953**, *86*, 1171.

(31) Job, A.; Cassal, A. (a) *C.R. Hebd. Seances Acad. Sci.* **1926**, *183*, 58, 392. (b) *Bull. Soc. Chim. Fr.* **1927**, *41*, 814, 1041.



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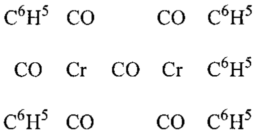

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berg[32] studied this novel $Cr(CO)_6$ synthesis in some detail and also suggested intermediates in which Cr was bonded to phenyl and CO ligands. The Job–Cassal synthesis of $Cr(CO)_6$ was optimized in a study carried out at Yale University during World War II with support from the National Defense Research Committee.[33] Reactions carried out in a glass bomb liner in an autoclave with CO pressures of ~50 atm gave the hexacarbonyl in yields of up to 67%. It was found essential to use an excess of C_6H_5MgBr (5–7.5 mol to 1 mol of $CrCl_3$), to add the C_6H_5MgBr solution to the suspension of $CrCl_3$ in diethyl ether at -70 °C, and to pressurize with CO immediately after the addition had been completed. The only comment of the authors concerning the mechanism of the reaction was "we venture the opinion that none of the mechanisms proposed in the literature for the formation of chromium carbonyl is correct". Harold Zeiss, whom we shall meet in the next section, suggested a possible mechanism for the Job–Cassal reaction in which $(C_6H_5)_3Cr(CO)_3$ is a key intermediate[24]—not too different in concept from the proposed intermediates of Job and Cassal,[31b] **2** and **3**.

III. The Brick Wall Toppled: Zeiss and Tsutsui at Yale, 1951–1954

In 1953, Minoru Tsutsui began his Ph.D. research at Yale University, under the guidance of Professor Harold H. Zeiss, on Hein's phenylchromium compounds. As stated in Tsutsui's dissertation,[34,35] "In the absence of any definitive study of polyphenylchromium compounds, this investigation was undertaken in order to elucidate their constitution and structure." Chromium was not an unfamiliar element to these chemists. The first part of Tstutsui's research at Yale had dealt with the chromic acid oxidation of methyl 8-nitrodehydroabietate.

As might be expected, considering Hein's three 1921 papers, this turned out to be a very difficult project for Tsutsui. As he mentioned some years later,[36] he repeated Hein's procedure for the preparation of the "crude bromide" 52 times. In only three of these was he able to obtain the "crude bromide"; the other 49 were unsuccessful. The procedure that Tsutsui used, however, was different from that of Hein in one important respect: Tsutsui carried out his $C_6H_5MgBr + CrCl_3$ reactions under a *nitrogen* atmosphere—since, in 1953, that was the prescribed procedure for working with air-sensitive organometallic compounds. This change, as we shall see later, in Part 2, was an important one which was responsible for Tsutsui's long run of failed experiments. In fact, the few experiments that did give the "crude bromide" probably were ones in which some air leaked into the apparatus. In any case, Tsutsui was able to collect small amounts of the "crude bromide". From the bromide, he prepared Hein's "pentaphenylchromium hydroxide" and from this the "tetraphenylchromium iodide". From the aqueous phase, a small quantity of "triphenylchromium iodide" was isolated. Thus, now small samples of the key members of Hein's three phenylchromium families were in hand. What was done next is described in Tsutsui's dissertation[31] and in Zeiss' review on "Arene Complexes of the Transition Metals".[24] Their options were limited by the small amount of each compound that was available. In 1953, NMR spectrometers were in the hands of physicists and physical chemists and not generally available to synthetic organic chemists, nor were mass spectroscopy or single-crystal X-ray crystallography routinely available in chemistry laboratories. Therefore, Zeiss and Tsutsui decided to use degradation methods. It was found that reductive cleavage of the Cr–aryl bonds by $LiAlH_4$ (a reagent unknown in Hein's time) occurred readily. It had been found that diphenylmercury reacted with $LiAlH_4$ to give benzene; thus, it was reasoned that the $LiAlH_4$–"phenylchromium" reaction should reductively cleave whatever aromatic substituents were attached to chromium. The reaction of the "crude bromide" with $LiAlH_4$ gave benzene, biphenyl, terphenyl, and higher boiling polyphenyls; as Hein had thought, it was a mixture of various compounds. Similar reduction of "tetraphenylchromium hydroxide" gave 2 molar equiv of only biphenyl; with "triphenylchromium iodide", a 1:1 molar ratio of benzene and biphenyl resulted. The amount of benzene was determined spectrophotometrically: GLC was a technique that became available a few years in the future. "Pentaphenylchromium hydroxide" was cleaved by $LiAlH_4$ to give a 2:1 mixture of biphenyl and phenol. These results essentially demolished Hein's view of the phenylchromium compounds. Assuming that the chromium compounds reacted with $LiAlH_4$ in the same way as did diphenylmercury, then Hein's "tetraphenyl-" and "pentaphenylchromium" compounds could not contain C_6H_5–Cr bonds. Furthermore, "pentaphenylchromium hydroxide" in reality must be a member of the "tetraphenylchromium" series, a phenoxide, which reacted normally with other anion sources. These results also made the Klemm–Neuber type II structures (Table 1) seem more reasonable except for their hydride substituents, which were not expected to be stable to acid and base. The formation of biphenylyl anion in the $LiAlH_4$/"$(C_6H_5)_4CrI$" reaction was eliminated by solvolysis of the reaction mixture with D_2O: no deuterium incorporation into the biphenyl that was formed was observed. However, reduction of "$(C_6H_5)_4CrI$" with $LiAlD_4$ did result in deuterium incorporation in the biphenyl produced: 5.0 D% or one atom of D per molecule of the chromium compound, i.e., per two molecules of biphenyl. The Klemm–Neuber structure for "$(C_6H_5)_4CrI$", by comparison, would result in incorporation of 10 D%, one D per molecule of biphenyl. While these experiments made the Klemm–Neuber structures seem unlikely, they did not lead directly to the correct structure. It was Professor Lars Onsager of

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[32] Hieber, W.; Romberg, E. *Z. Anorg. Allg. Chem.* **1935**, *221*, 321.

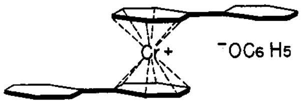
[33] Owen, B. B.; English, J., Jr.; Cassidy, H. G.; Dundon, C. V. *J. Am. Chem. Soc.* **1947**, *69*, 1723.

[34] Tsutsui, M. Ph.D. Dissertation, Yale University, 1954.

[35] Did Zeiss, who joined the Yale chemistry faculty in 1949, know about the research on the Job–Cassal reaction carried out at Yale during World War II,[33] in which Hein's $(C_6H_5)_5CrBr$ was prepared and tested in a reaction with CO? Is this what sparked his interest in Hein's phenylchromium compounds? Intriguing questions to which, I guess, we shall never know the answer.

[36] Tsutsui, M. *Z. Chem.* **1963**, *3*, 215.

Yale University (who was to be awarded the Nobel Prize in chemistry in 1968 for his work on irreversible thermodynamic processes) who made the connection to ferrocene during discussions with Zeiss and Tsutsui. Why not consider a sandwich structure, similar to that of ferrocene? If 12 π electrons could be donated to a zerovalent chromium atom from two neutral aromatic molecules (biphenyl or benzene), then the chromium atom would reach the stable 18-electron krypton configuration. A neutral, diamagnetic bis(arene)chromium compound would result. However, Hein's compounds were paramagnetic and contained +1 cations; therefore, one Cr valence electron had been lost. Zeiss and Tsutsui, in their paper in the *Journal of the American Chemical Society*,[37] drew the structures **4** for Hein's "pentaphenylchromium hydroxide", **5** for "tetraphenylchromium iodide" and **6** for "triphenylchromium iodide". These structures were consistent with all the anomalous observations concerning Hein's phenylchromium compounds noted at the end of the last section, including the electrochemical reduction of **4** and **5** to give what must be the neutral bis(biphenyl)chromium. The results of the experiments with $LiAlD_4$ could be rationalized in terms of D^- attack at one of the biphenyl rings of **4** and **5** to cause decomposition of the respective complex, thus giving one deuterated and one deuterium-free biphenyl molecule.



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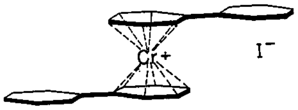

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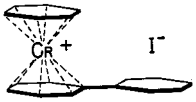

6

This, in 1953, was a rather revolutionary proposal. Of course, ferrocene was known to have a sandwich structure, but it involved two cyclic six-π-electron anions bonded to a divalent cation (in one view of the bonding). Bis(biphenyl)chromium, on the other hand, would have two *neutral* six-π-electron donor molecules bonded to a *zerovalent* chromium atom. As Zeiss and Tsutsui said,[37] "At the outset we were reluctant to believe that aromatic π-electrons could be donated in this manner and that the loss of resonance energy accompanying this process would be offset by the stability associated with the inert gas configuration achieved." Zeiss and Tsutsui had considerable trouble in publishing these results and the conclusions concerning structure and bonding. A footnote in their 1957 *J. Am. Chem. Soc.* paper tells about these difficulties: "The subject matter of this paper was presented in 1954, Abstr., 126th Meeting, Amer. Chem. Soc., p 29–0, Sept. 1954, and also submitted to This Journal as a preliminary Communication. The paper, however, was rejected by the referees chiefly on the grounds of insufficient evidence for our (with Prof. L. Onsager) proposal of the π-complexed biconoidal structure. In 1955, a portion of our results was published in abbreviated form, *Yale Sci Mag.*, *20*, 14 (1955); *Angew. Chem.*, *67*, 282 (1955)." It was only after Fischer and Hafner's paper on the synthesis and isolation of bis(benzene)chromium appeared in Dec 1955 and a paper by Fischer and Seus in Aug 1956 on bis(biphenyl)chromium and the derived cation that the *J. Am. Chem. Soc.* reviewers felt that they could recommend acceptance of the full paper by Zeiss and Tsutsui, which finally appeared in June 1957. It was unfortunate that their Communication was not accepted in 1954, but the peer review system, as we all know, is not perfect.

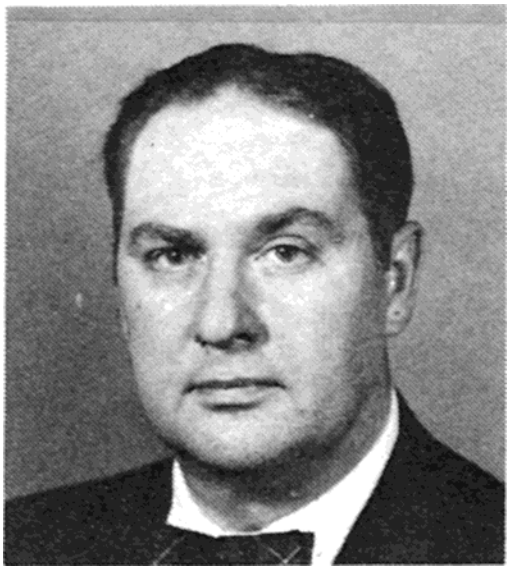

Figure 6. Harold H. Zeiss (from a Monsanto Chemical Co. publication, by permission).

Zeiss and Tsutsui speculated that Hein had missed a fourth family, the "diphenylchromium salts": i.e., salts of the bis(benzene)chromium cation, because these should be even more water-soluble than those of the (benzene)(biphenyl)chromium cation. However, no experiments were done during the course of Tsutsui's dissertation research to explore this possibility.

Therefore, in November 1954, Zeiss and Tsutsui had assembled evidence that invalidated Hein's penta-, tetra-, and triphenylchromium formulations. The alternative that they suggested was in agreement with the experimental facts, and while we have no problems with it today, in 1954 it was not universally accepted. What was needed to convince the doubters was an indisputable structure determination.

We shall encounter Zeiss and Tsutsui again in Part 2, since Zeiss in particular initiated a major research effort in organochromium chemistry and made important contributions to the understanding of the Hein chemistry after he left Yale. At this point, however, the reader may wish to know some details of their careers.

Harold H. Zeiss (1917–1995) (Figure 6) was born in Evansville, IN. He studied chemistry at the University of Indiana (B.S., 1938). After a year of study in Germany (Technische Hochschule München with Hans Fischer, University of Heidelberg with Karl Freundenberg), he

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[37] Zeiss, H. H.; Tsutsui, M. *J. Am. Chem. Soc.* **1957**, *79*, 3062.

Figure 7. Minoru Tsutsui (from a Texas A&M University Chemistry Department brochure, by permission, Professor E. A. Schweikert, Head).

spent 6 years in industry in the United States. He obtained his Ph.D. at Columbia University in 1949, working on the resolution of methylethylisobutylcarbinol and the methanolysis of its optically active hydrogen phthalate under the supervision of Professor W. von Eggers Doering. Academic appointments at Yale University followed (instructor, 1949; assistant professor, 1951). In 1955, he joined the Monsanto Chemical Co., first as a research associate with an independent research group in the Central Research Laboratory in Dayton, OH, and then in 1961 as President and Director of Monsanto Research S.A. in Zürich. This laboratory, with an outstanding international staff, during its existence, made many significant contributions in basic research in organometallic, organophosphorus, and organosilicon chemistry. Monsanto Research S.A. was closed in 1975, and Zeiss spent two more years in the Monsanto Laboratories in St. Louis, MO, before he retired in 1978.

Minoru Tsutsui (1918−1981)[38] (Figure 7) was born in Japan. He obtained a B.A. at the Gifu Agricultural College in 1938 and an M.S. at the Tokyo University of Literature and Science in 1941. During World War II he served in the Japanese Navy. He came to the United States in 1951 as participant in a 3 month summer research program at MIT with J. D. Roberts and subsequently entered graduate school at Yale University. Upon completion of his Ph.D. work in 1954, Tsutsui spent 2 years at the Sloan Kettering Institute and several years (1957−1960) with Zeiss in the Monsanto Laboratories in Dayton. Then followed his academic career, first for 8 years at New York University, where he rose to the rank of full professor. He joined the chemistry faculty of Texas A&M University in 1968. His research focused on organometallic and coordination chemistry and he also participated in the “politics” of chemistry, being active in American Chemical Society and New York Academy of Sciences programs as well as in international cooperative programs with Japan, the USSR, and the People’s Republic of China.

The bis(benzene)chromium story is a long one; therefore, we shall publish it in two parts. At this point, bis(benzene)chromium has not yet been discovered, although the $(C_6H_6)_2Cr^+$ ion has, without doubt, been swimming around in Hein’s aqueous mother liquors since 1918. However, it is already a subject of the thoughts and musings of E. O. Fischer. The next part will bring an account of its discovery and of the further efforts of Fischer, Hein, Zeiss, and Elschenbroich and their respective co-workers to develop the field of bis(arene)metal chemistry.

Acknowledgment. My thanks and appreciation are given to Professor Dr. Lothar Beyer (University of Leipzig), Professor John P. Fackler (Texas A&M), Dr. Ludwig Maier, Dr. William J. Considine, and Ms. Elizabeth Greene (Indiana University) for their help in obtaining information about the protagonists of our story, to Dr. Gerald Wiemers, Director of the University of Leipzig Archives, for the photograph of Franz Hein, to Professor Arnold L. Rheingold for the cover molecule picture, and to Ms. Rhonda Saunders for the cover design.

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[38] Martell, A. E. *J. Coord. Chem.* **1981**, *11*, 133.