Articles

Seventy-Five Years of π-Complexes of Chromium(I)

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Seventy-five years ago, by the reaction of chromium trichloride with phenylmagnesium bromide, Franz Hein first prepared π-arene complexes of chromium(I). Taking into account the analytical data and mindful of the theoretical ideas of the chemistry of his day, he regarded these compounds as polyphenylchromium salts: $(C_6H_5)_5CrX$ (1), $(C_6H_5)_4CrX$ (2), and $(C_6H_5)_3CrX$ (3). Independent of the assumed oxidation states, these salts had the same orange-red color and the same magnetic moment (1.73 μ_B). Cathodic reduction yielded the species $(C_6H_5)_4Cr$ and $(C_6H_5)_3Cr$. In later parallel studies Zeiss and Tsutsui and Fischer (1954–1956) succeeded in determining the correct structure of these polyphenylchromium compounds. Zeiss and Tsutsui reproduced Hein's procedure, and by reducing the products with $LiAlH_4$, they isolated biphenyl, presumably a ligand in the case of 1 and 2, and biphenyl and benzene in the case of 3. On the basis of these results and on the knowledge of the structure of ferrocene, it was Onsager who expressed the idea of the π-sandwich structure of Hein's salts: $1 \equiv [Cr(\pi\text{-}C_6H_5C_6H_5)_2](OC_6H_5)$, $2 \equiv [Cr(\pi\text{-}C_6H_5C_6H_5)_2]X$, and $3 \equiv [Cr(\pi\text{-}C_6H_5C_6H_5)(\pi\text{-}C_6H_6)]X$. Fischer prepared 2 by an independent route, using his reductive Friedel–Crafts method. In 1956, the π-arene structure of 1–3 was proved, but at about the same time $(THF)_3Cr(C_6H_5)_3$, the first (σ-phenyl)chromium complex, was synthesized. Thermolysis of $(THF)_3Cr(C_6H_5)_3$ and subsequent methanolysis yielded 2, 3, $[Cr(C_6H_6)_2]X$, biphenyl, and benzene as the main products. Considering these experimental results, Hähle and Stolze discussed the possible mechanism of this process, which is closely related to Hein's procedure, to prepare the complexes 1–3. Three interdependent reactions were proposed: disproportionation of $Cr(C_6H_5)_3$, reductive elimination of biphenyl, and reductive elimination of benzene. The role of THF as a hydrogen donor in the last process is discussed.

Introduction

Seventy-five years ago, in 1918, the first π-arene complexes of chromium(I),[1] the first π-arene complexes of any transition metal, were synthesized by Franz Hein. Certainly, Hein did not establish the correct structure, but when one considers the then-prevailing theoretical ideas concerning the properties of aromatic compounds, this is quite understandable. The problem of the structure was solved only 48 years later, by H. Zeiss and M. Tsutsui and by E. O. Fischer, W. Hafner, and D. Seus in parallel and complementary studies. Until then, the opinion of coordination chemists concerning Hein's "polyphenyl-chromium salts" was best summarized by Cotton[2] in a review in 1955: "The chemistry of the polyphenylchromium compounds of Hein has long constituted one of the most fascinating but perplexing phases of the organometallic chemistry. The reactions and properties of these substances seem, at face value, so completely unorthodox, and the isolation of the compounds so tedious that there has been scepticism, covert and overt, as to the validity of Hein's claims. Until quite recently, no preparation of any of these compounds had been reported except by Hein himself."

What was the background of these words, and what was the experimental know-how in 1918, when Hein started his work?

First, some biographical data. Franz Hein (1892–1976) studied from 1912 to 1917 at the University of Leipzig, and he had the same supervisor as Alfred Werner (1866–1919), Artur Hantzsch (1857–1935). His thesis dealt with optical studies of bismuth compounds and triphenyl-methane derivatives. Hein was a versatile chemist,[3] with interests both in coordination and in organometallic chemistry. Doubtless, the π-arene complexes of chromium(I) were his most important field of research. He used them as the basis for his habilitation in 1921, and they were his lifelong companions. However, in the 1920s and 1930s he was also active in electrochemistry. He studied the properties of solutions of alkali-metal alkyls in other metal alkyls (zinc diethyl) and described a new (electrochemical) method for the preparation of alkyls of zinc, lead, aluminum, etc.[4] He synthesized the first compounds with a covalent bond between a transition and a main-group metal,[5] such as $(Et_3Sn)_2Fe(CO)_4$, $(Ph_3$-

(3) Oesper, R. E. *J. Chem. Educ.* **1953**, *30*, 313.
(4) (a) Hein, F.; Petzschner, E.; Wagler, K.; Segnitz, F. *Z. Anorg. Allg. Chem.* **1924**, *141*, 161. (b) Hein, F.; Pauling, H. *Z. Phys. Chem. A* **1933**, *165*, 338.
(5) (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.

[⊕] Abstract published in *Advance ACS Abstracts*, October 1, 1993.
(1) Hein, F. *Ber. Dtsch. Chem. Ges.* **1919**, *52*, 192.
(2) Cotton, F. A. *Chem. Rev.* **1955**, *65*, 551.

Pb)$_2$Fe(CO)$_4$, and [(Et$_2$Pb)Fe(CO)$_4$]$_2$, and he discovered the complexes Cu(R$_2$N(CH$_2$)$_2$O)X with a spin-paired binuclear or with a spin-free tetranuclear structure.[6]

In 1923 Hein was appointed assistant professor in inorganic chemistry at Leipzig. In 1940 he received a call to the University of Jena, and in 1946 he was appointed head of the Institute of Inorganic Chemistry at Jena. He retired in 1958.

Historical Facts and Discussion

Synthesis and Studies of the Reactivity of Polyphenylchromium Salts before 1950.
The synthesis of organic compounds of the main-group elements by the reaction of Grignard reagents with binary element halides was well known (for instance, eq 1).[7] Hein attempted the

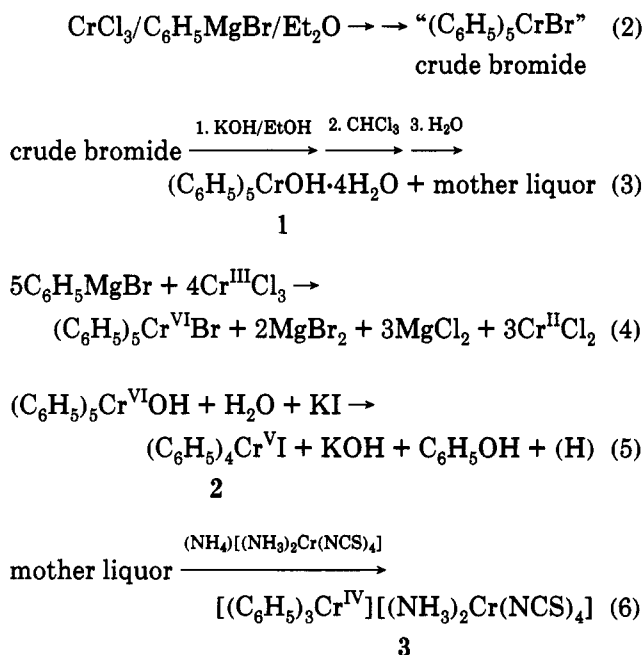$$SnCl_4 + 4RMgBr \rightarrow SnR_4 + 4MgClBr \quad (1)$$

preparation of an organic derivative of chromium by the Grignard procedure[8] (eq 2). He started with 500 mL of a 2 M solution of phenylmagnesium bromide in diethyl ether and, with stirring and cooling with an ice–salt mixture, he added 0.25 mol of chromium trichloride. Stirring and cooling was continued for other 3 h, and then the reaction mixture was stored for 1 day. An oily product separated. The whole mixture was treated with sulfuric acid and ice. In the ether layer a red-brown emulsion formed which in the course of a lengthy procedure yielded an amorphous orange-red powder, "pentaphenylchromium bromide",[9] an unexpected compound indeed. During all steps of the preparation there was admission of air, although it was restricted by the ether vapors over the reaction mixture.

Two amusing details of Hein's first paper[8] are worth mentioning. He writes "The yield is not excellent, scarcely 20% of the chromium trichloride used. It becomes easily lower, whenever care is not taken to insure good cooling and mixing. Otherwise the reaction may proceed explosively with volatilization of all the ether within a few minutes. Then of course, the yield is zero."

"In vacuum over calcium chloride and protected against light, the orange red powder is stable for months. But there is one condition: the outside temperature must not be, as for instance in the summer months, relatively high."

Pentaphenylchromium bromide should be a compound of chromium(VI). Hein knew that his product was impure; he spoke of a "crude" bromide, and therefore he attempted to prepare a pure compound. Finally, he succeeded in the preparation of the "hydroxide" 1 (eq 3), and he regarded pentaphenylchromium bromide as a product of the disproportionation of a chromium(III) compound, with a chromium(II) compound as the other product (eq 4). This would explain why a yield of only 20% was obtained. In 1921, with the hydroxide 1 or with the mother liquor remaining after crystallization of 1 as starting material, the tetraphenyl- and triphenylchromium compounds 2[10] and 3[11] with the supposed oxidation states V and IV were isolated. 2 was believed to be the product of an abnormal

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(6) (a) Hein, F.; Beerstecher, W. *Z. Anorg. Allg. Chem.* **1955**, *282*, 93.
(b) Uhlig, E.; Staiger, K. *Z. Anorg. Allg. Chem.* **1968**, *360*, 39. (c) Hodgson, D. J. *Prog. Inorg. Chem.* **1975**, *19*, 143.
(7) Pfeiffer, P.; Schnurmann, K. *Ber. Dtsch. Chem. Ges.* **1904**, *37*, 319.
(8) Hein, F. *Ber. Dtsch. Chem. Ges.* **1921**, *54*, 1905.
(9) In the following, Hein's nomenclature is used at first. Remember that formulas such as 1–3 etc. are in accordance with elementary analysis.
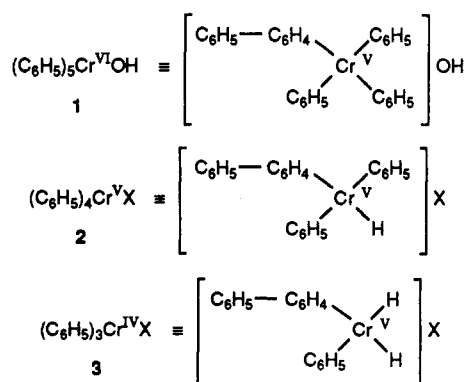(10) Hein, F. *Ber. Dtsch. Chem. Ges.* **1921**, *54*, 2708.
(11) Hein, F. *Ber. Dtsch. Chem. Ges.* **1921**, *54*, 2727.

Scheme I

$$CrCl_3/C_6H_5MgBr/Et_2O \rightarrow \rightarrow \text{``}(C_6H_5)_5CrBr\text{''} \quad (2)$$
$$\text{crude bromide}$$

$$\text{crude bromide} \xrightarrow[]{\text{1. KOH/EtOH} \quad \text{2. CHCl}_3 \quad \text{3. H}_2\text{O}}$$
$$(C_6H_5)_5CrOH\cdot4H_2O + \text{mother liquor} \quad (3)$$
$$1$$

$$5C_6H_5MgBr + 4Cr^{III}Cl_3 \rightarrow$$
$$(C_6H_5)_5Cr^{VI}Br + 2MgBr_2 + 3MgCl_2 + 3Cr^{II}Cl_2 \quad (4)$$

$$(C_6H_5)_5Cr^{VI}OH + H_2O + KI \rightarrow$$
$$(C_6H_5)_4Cr^{V}I + KOH + C_6H_5OH + (H) \quad (5)$$
$$2$$

$$\text{mother liquor} \xrightarrow[]{(NH_4)[(NH_3)_2Cr(NCS)_4]}$$
$$[(C_6H_5)_3Cr^{IV}][(NH_3)_2Cr(NCS)_4] \quad (6)$$
$$3$$

salt formation (eq 5). 3 was precipitated from the mother liquor by addition of Reinecke's salt (eq 6). Phenol was identified as further product of reaction 5. Considerable effort aimed at an exact proof of product (H)[12] (eq 5) met with no success. There were only some indications of a loose bond to a chromium complex, as was expressed by the formulation "(C$_6$H$_5$)$_4$Cr(···H)X.

As already mentioned, in the 1920s and early 1930s Hein was active in a second field of research, the electrochemistry of organometallic compounds in nonaqueous solvents. Consequently, he studied the cathodic reduction of his polyphenylchromium salts, and in liquid ammonia as solvent he prepared by this means tetraphenylchromium and triphenylchromium.[13] He described these compounds as highly unstable, dark brown compounds with a variable content of ammonia:

$$(C_6H_5)_4Cr^+ + e^- \rightarrow (C_6H_5)_4Cr \quad (7)$$

$$(C_6H_5)_3Cr^+ + e^- \rightarrow (C_6H_5)_3Cr \quad (8)$$
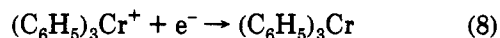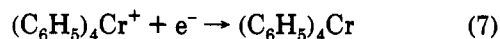
Considering the then-current knowledge of inorganic chemistry in general and what was known about polyphenylchromium salts at the beginning of the 1930s in particular, there was one surprising finding: independent of the different oxidation states which had been claimed by Hein, compounds 1–3 had very similar properties.

(1) All of the compounds (hydroxides or salts) had the same orange-red color. This was unusual in view of the dependence of the color of inorganic chromium compounds on the oxidation state.

(2) All compounds were moderately stable in water.

(3) The cathodic reduction of cations gave the corresponding neutral species.

A fourth finding by Klemm and Neuber was that 1–3 all had magnetic moments of about 1.73 μ_B.[14] According

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(12) Hein, F.; Schwartzkopff, O.; Hoyer, K.; Eissner, W.; Clauss, W.; Just., W. *Ber. Dtsch. Chem. Ges.* **1929**, *62*, 1151.
(13) Hein, F.; Markert, E. *Ber. Dtsch. Chem. Ges.* **1928**, *61*, 2255.
(14) Klemm, W.; Neuber, A. *Z. Anorg. Allg. Chem.* **1936**, *227*, 261.

Chart I

$$(C_6H_5)_5Cr^{VI}OH \equiv \begin{bmatrix} C_6H_5{-}C_6H_4 & & C_6H_5 \\ & Cr^V & \\ C_6H_5 & & C_6H_5 \end{bmatrix} OH$$

1

$$(C_6H_5)_4Cr^VX \equiv \begin{bmatrix} C_6H_5{-}C_6H_4 & & C_6H_5 \\ & Cr^V & \\ C_6H_5 & & H \end{bmatrix} X$$

2

$$(C_6H_5)_3Cr^{IV}X \equiv \begin{bmatrix} C_6H_5{-}C_6H_4 & & H \\ & Cr^V & \\ C_6H_5 & & H \end{bmatrix} X$$

3

to the knowledge of that time, this was an indication of the presence of chromium(V) in all three compounds, as manifested by the formulas in Chart I. Worth mentioning are the formulation of biphenyl as well as phenyl as a ligand and the suggestion of hydride ligands in 2 and 3. Biphenyl, at least, was always a side product of the synthesis of polychromium salts. However, as mentioned above, the hydride ligands were mere guesswork. It is noteworthy that Klemm used valence bond formulation, suggesting, according to our present understanding, σ chromium–carbon bonds.

Structure Determination of the (π-Arene)chromium Complexes (1950–1956). Beginning in 1950, a new era of organometallic chemistry commenced. A milestone was the discovery of ferrocene, obeying the 18-electron rule, by Kealy and Pauson and independently by Miller et al.[15] and the determination of its sandwich structure shortly thereafter by Fischer and Pfab[16] and by Wilkinson, Rosenblum, Whiting, and Woodward.[17] The resulting boom of organometallic chemistry provided a stimulus for renewed studies of the polyphenylchromium compounds, not only in Hein's laboratory at Jena[18] but also in the laboratory of Harold H. Zeiss at Yale University by Minoru Tsutsui. In principle, the latter authors confirmed Hein's results, but the problems they had are expressed in the following remarks:[19] "In only 3 out of over 50 runs did we obtain 'raw bromide' from which 'pentaphenylchromium hydroxide' could be prepared. We attribute these failures to our subsequent care in excluding oxygen from the Grignard flasks (no phenol formed). Many variations of time, temperature, reagent concentrations, added reactants, and chromium trichloride purity were tried without success". However, Zeiss and Tsutsui also performed decisive new experiments which contributed significantly to the elucidation of the structure of polyphenylchromium compounds. They had found that when diphenylmercury is reduced with lithium aluminum hydride, benzene is formed (eq 9) but no C–C coupling to form biphenyl occurred. Therefore, if Hein's chromium salts were bona fide σ-phenyl compounds, benzene should be the only organic product of their reactions with LiAlH₄.

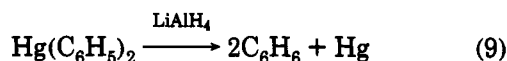$$Hg(C_6H_5)_2 \xrightarrow{\text{LiAlH}_4} 2C_6H_6 + Hg \qquad (9)$$

However, the result of such reactions was quite another one: 1 on reaction with LiAlH₄ gave biphenyl and phenol, 2 only biphenyl, and 3 biphenyl and benzene (Scheme II). By these reactions 1 was shown to be the phenolate 1′ with tetraphenylchromium as the cation. By elemental analysis no decision between 1 and 1′ was possible: 26H in 1 vs 25H in 1′. On the basis of formula 1′, the formation of 2 is understandable (eq 10), and there is no need to find an acceptor of (H) (eq 5). Furthermore, the observed alkaline reaction of 1′ is a result of the hydrolysis of the phenolate.

Scheme II

$$(C_6H_5)_5CrOH \rightarrow$$
$$\mathbf{1}$$
$$C_6H_5C_6H_5 + C_6H_5OH(C_6H_5)_4Cr(OC_6H_5)$$
$$\mathbf{1'}$$

$$(C_6H_5)_4CrI \rightarrow C_6H_5C_6H_5(C_6H_5)_3CrI \rightarrow$$
$$\mathbf{2} \qquad\qquad \mathbf{3}$$
$$C_6H_5C_6H_5 + C_6H_6$$

$$1 + H_2O + KI \rightarrow$$
$$(C_6H_5)_4CrI + KOH + C_6H_5OH + (H) \quad (5)$$
$$\mathbf{2}$$

$$1' + H_2O + KI \rightarrow$$
$$(C_6H_5)_4CrI + KOH + C_6H_5OH \quad (10)$$
$$\mathbf{2}$$

As noted, in the course of his synthesis Hein had not rigorously excluded oxygen. Therefore, the formation of the phenolate during the reaction with phenylmagnesium bromide is not surprising. Of course, in Hein's group the phenolate structure 1′ of pentaphenylchromium hydroxide had been thoroughly discussed.[20] The most important argument against this formulation was the fact that not only "abnormal" but also some "normal" salts of pentaphenylchromium hydroxide had been found.[21] However, looking back, we see that "normal" salts of pentaphenylchromium hydroxide are formed preferably with anions such as anthranilate, which may easily add phenol by hydrogen bonding.

However, the results of the reactions of 1′ or 2 with LiAlH₄ were of even greater importance than the proof of the phenolate structure of 1′. These compounds could not be phenyl compounds but must be biphenylyl compounds.

It is necessary to recall the scientific climate of the mid-1950s. Ferrocene had been discovered in 1951, followed by a stream of metallocenes, synthesized by Fischer and by Wilkinson and their co-workers in a breath-taking competition. Thus, the foundation needed for an explanation of the experimental results of Zeiss and Tsutsui was available, but a special impetus was required to use all of the experiences for a conclusive statement. Zeiss[19] reports that the decisive idea stems from Lars Onsager.

(15) (a) Pauson, P. L.; Kealy, T. J. *Nature* **1951**, *168*, 1039. (b) Miller, S. A.; Tebboth, T. A.; Fremaine, J. F. *J. Chem. Soc.* **1952**, 632.

(16) Fischer, E. O.; Pfab, W. *Z. Naturforsch., B* **1952**, *7*, 378.

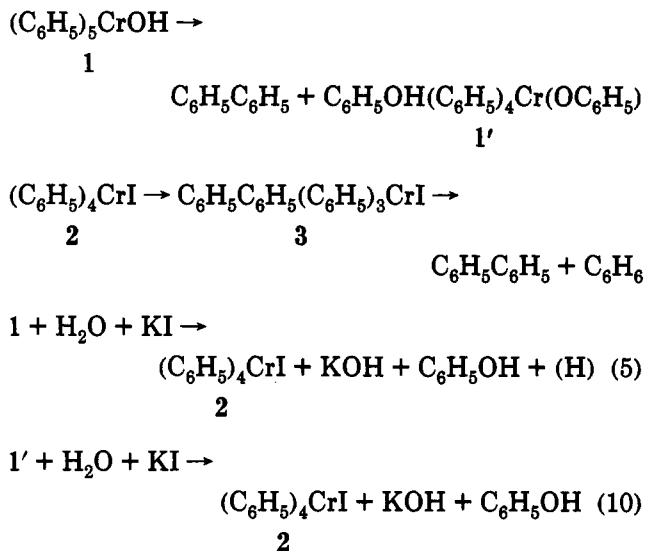(17) Wilkinson, G.; Rosenblum, M.; Whiting, M. E.; Woodward, R. E. *J. Am. Chem. Soc.* **1952**, *74*, 2125.

(18) (a) Hein, F.; Pauling, H. *Z. Anorg. Allg. Chem.* **1953**, *273*, 209. (b) Hein, F.; Bähr, G. *Chem. Ber.* **1953**, *86*, 1171. (c) Hein, F.; Müller, H. *Chem. Ber.* **1956**, *89*, 2722. (d) Hein, F.; Kleinert, P.; Kurras, E. *Z. Anorg. Allg. Chem.* **1957**, *289*, 229. (e) Hein, F.; Fischer, K. W. *Z. Anorg. Allg. Chem.* **1956**, *288*, 279. (f) Hein, F.; Kurras, E. *Z. Anorg. Allg. Chem.* **1957**, *290*, 179.

(19) Zeiss, H. H.; Tsutsui, M. *J. Am. Chem. Soc.* **1957**, *79*, 3062.

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

(21) Hein, F.; Schwartzkopff, O.; Hoyer, K.; Klar, K.; Eissner, W.; Clauss, W. *Ber. Dtsch. Chem. Ges.* **1928**, *61*, 730.

Chart II

$[(C_6H_5)_4Cr]I \equiv$
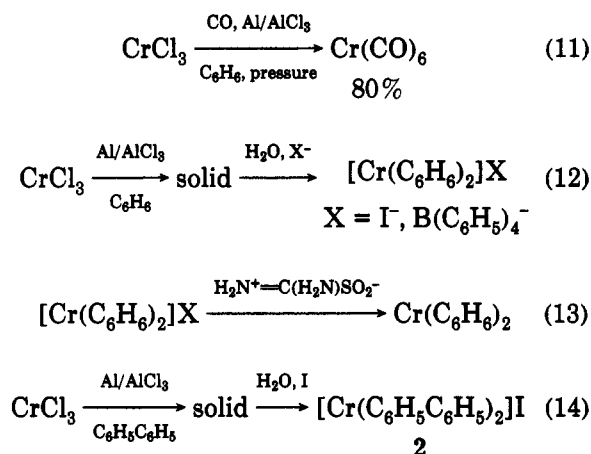**2**

$[(C_6H_5)_3Cr]I \equiv$
3
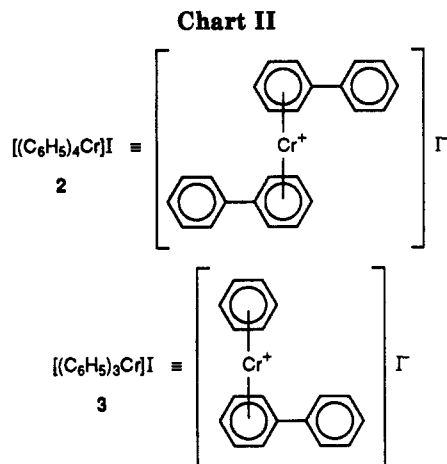
At that time the latter was also a member of the Yale Chemistry Department, and he was very interested in Zeiss's studies. It was he who proposed that Hein's polyphenylchromium complexes are not σ compounds but rather are π complexes (Chart II). To the chemists of that time this was an unconventional proposal. Zeiss first made this proposal in a talk given at the 126th National Meeting of the American Chemical Society in Sept 1954, and in the same year he had submitted a preliminary communication to the *Journal of the American Chemical Society*, which, however, was rejected. Thus, the structure suggestion shown in Chart II was first mentioned in print in Cotton's review, received on Jan 10, 1955.[2]

Of great importance to further development were the seminal studies of E. O. Fischer and W. Hafner on π complexes. They had found that chromium hexacarbonyl could be prepared in high yield by the reaction of carbon monoxide with chromium trichloride in benzene using Al/AlCl$_3$ as a reductant (reductive Friedel–Crafts conditions).[22] When carbon monoxide was omitted, a solid was obtained. Hydrolytic workup gave an amorphous residue and a yellow solution. Precipitation with large anions (eq 12) gave salts of the novel, unprecedented bis(benzene)chromium cation. Reduction of the latter with formamidine sulfinate, one of the strongest reductants in aqueous solution, produced neutral bis(benzene)chromium in the form of deep brown diamagnetic crystals. The analogy with ferrocene in obeying the 18-electron rule was perfect. Evidently Hein had obtained the first neutral π-arene chromium complexes already in 1928 (eqs 7 and 8), but as noted, he did not recognize the real structure at that time.

Doubtless, the synthesis of bis(benzene)chromium was the highlight of Fischer's work at that time. His new method allowed an independent preparation of complex **2** (eq 14),[23] which served to promote the general acceptance of Zeiss' proposal. Finally, on Nov 29, 1956, the *Journal of the American Chemical Society* accepted Zeiss' paper,[19] about 1 year after Oct 11, 1955, the date on which the *Zeitschrift für Naturforschung* received Fischer's paper.[22]
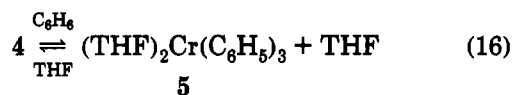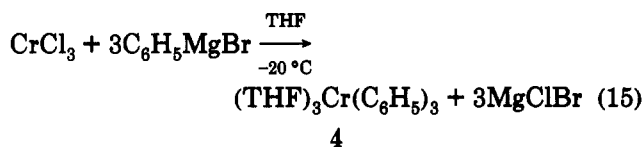
It is noteworthy that the initial structure elucidation of the (π-arene)chromium complexes as key organometallic compounds was achieved only by chemical methods. The X-ray structural analysis of bis(benzene)chromium was made difficult by the high crystallographic space group C_{3i} imposed on the molecule and possibly by orientational

Scheme III

$$CrCl_3 \xrightarrow[C_6H_6, \text{ pressure}]{\text{CO, Al/AlCl}_3} Cr(CO)_6 \quad (11)$$
$$80\%$$

$$CrCl_3 \xrightarrow[C_6H_6]{Al/AlCl_3} \text{solid} \xrightarrow{H_2O, X^-} [Cr(C_6H_6)_2]X \quad (12)$$
$$X = I^-, B(C_6H_5)_4^-$$

$$[Cr(C_6H_6)_2]X \xrightarrow{H_2N^+=C(H_2N)SO_2^-} Cr(C_6H_6)_2 \quad (13)$$

$$CrCl_3 \xrightarrow[C_6H_5C_6H_5]{Al/AlCl_3} \text{solid} \xrightarrow{H_2O, I} [Cr(C_6H_5C_6H_5)_2]I \quad (14)$$
$$\mathbf{2}$$

disorder in the crystal. There was a long controversy about D_{6h}[24] or D_{3d}[25] symmetry. The result of a neutron diffraction study of high-quality crystals (in 1969!) was summarized as follows: "Our results suggest the proposal of D_{3d} molecular symmetry and of elongated C–C distances of about 1.42 Å for di(benzene)chromium".[26]

(σ-Phenyl)chromium Compounds and the Mechanism of Formation of (π-Arene)chromium Complexes in the Course of the Reaction of Chromium Trichloride with Phenylmagnesium Bromide. The assumption of normal σ bonds in compounds **2** and **3** was shown to be incorrect in 1956. However, the renaissance of (σ-organo)chromium compounds followed shortly thereafter. Hein's group prepared ate complexes such as {Li[O(C$_2$H$_5$)$_2$]}$_3$[Cr(C$_6$H$_5$)$_6$],[27] and Zeiss and Herwig[28] obtained the compound which Hein had expected as his product in 1918, triphenylchromium, stabilized by three THF ligands (**4**; eq 15). There is a pathway from **4** as a

$$CrCl_3 + 3C_6H_5MgBr \xrightarrow[-20\ °C]{THF}$$
$$(THF)_3Cr(C_6H_5)_3 + 3MgClBr \quad (15)$$
$$\mathbf{4}$$

$$\mathbf{4} \underset{THF}{\overset{C_6H_6}{\rightleftharpoons}} (THF)_2Cr(C_6H_5)_3 + THF \quad (16)$$
$$\mathbf{5}$$

σ-bonded compound to **2** as a π-complex of chromium(0) which throws some light on the mechanism of formation of **2** and **3** during the course of the reaction of chromium trichloride with phenylmagnesium bromide in ether.[29] However, as the following studies have been done under an argon atmosphere, no direct comparison with Hein's early work is possible. For instance, no formation of the phenolate **1'** is to be expected. Nevertheless, some reaction steps should be the same.

(22) Fischer, E. O.; Hafner, W. *Z. Naturforsch., B* **1955**, *10*, 665.
(23) Fischer, E. O.; Seus, D. *Chem. Ber.* **1956**, *89*, 1809.

(24) (a) Cotton, F. A.; Dollase, W. A.; Wood, J. S. *J. Am. Chem. Soc.* **1963**, *85*, 1543. (b) Ibers, J. A. *J. Chem. Phys.* **1964**, *40*, 3129.
(25) Jellinek, F. *J. Organomet. Chem.* **1963**, *1*, 43.
(26) Förster, E.; Albrecht, G.; Dürselen, W.; Kurras, E. *J. Orgnomet. Chem.* **1969**, *19*, 215.
(27) (a) Hein, F.; Weiss, R. *Z. Anorg. Allg. Chem.* **1958**, *295*, 145. (b) Olmstead, M. M.; Power, P. P.; Shoner, S. U. *Organometallics* **1988**, *7*, 1380.
(28) Zeiss, H. H.; Herwig, W. *J. Am. Chem. Soc.* **1957**, *79*, 6561.
(29) (a) Hähle, H. Thesis, University of Jena, 1965. (b) Stolze, G. Thesis, University of Jena, 1965.

THF, the stabilizing donor of compound 4, is removed in at least two steps. The blue-green, thermolabile compound 5 crystallizes from a concentrated solution of the red complex 4 in benzene (eq 6). When 5 is either heated under vacuum or treated with ether, the residual THF is eliminated. Simultaneously, a "black product" is formed, which is very similar to the product obtained directly when reaction 15 was carried out in diethyl ether instead of THF as solvent.
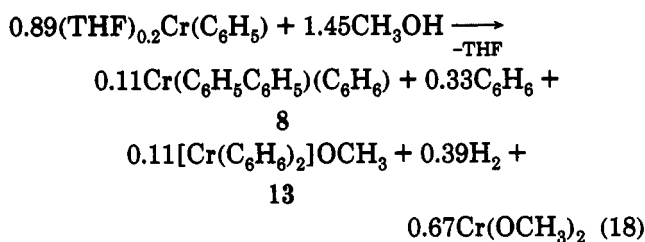
Thermal decomposition of 4 and subsequent methanolysis yield, among others, the π complexes 6 and 8 (Scheme IV). According to the careful and tedious studies of Hähle and Stolze[29] (elementary analysis, determination of solid and volatile products, etc.) the reaction course may be described by eqs 17 and 18 (side reactions are not discussed). Compound 6, biphenyl, and a part of the benzene stem directly from the thermolysis (eq 17) and can be isolated by distillation or by extraction with hexane. There seems to be a causal connection between 6 and 8, as they are formed in equimolar amounts during the thermolysis and the subsequent methanolysis. To explain this fact, a comparison with other (σ-organo)chromium compounds is useful.
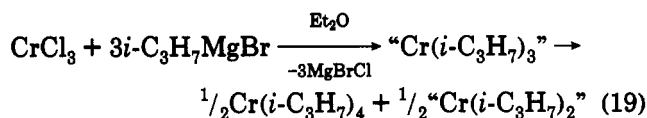
Scheme IV

thermal decomposition

$$(THF)_3Cr(C_6H_5)_3 \xrightarrow[-2.8THF]{} 0.11Cr(C_6H_5C_6H_5)_2 +$$
$$\quad\quad 4 \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad 6$$
$$0.89(THF)_{0.2}Cr(C_6H_5) + 0.67C_6H_5C_6H_5 +$$
$$\quad\quad\quad\quad 7$$
$$0.33C_6H_6 \quad (17)$$

methanolysis

$$0.89(THF)_{0.2}Cr(C_6H_5) + 1.45CH_3OH \xrightarrow[-THF]{}$$
$$0.11Cr(C_6H_5C_6H_5)(C_6H_6) + 0.33C_6H_6 +$$
$$\quad\quad\quad\quad 8$$
$$0.11[Cr(C_6H_6)_2]OCH_3 + 0.39H_2 +$$
$$\quad\quad\quad\quad 13$$
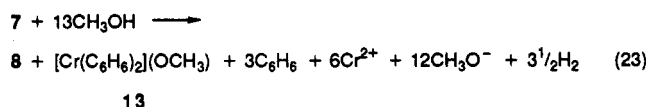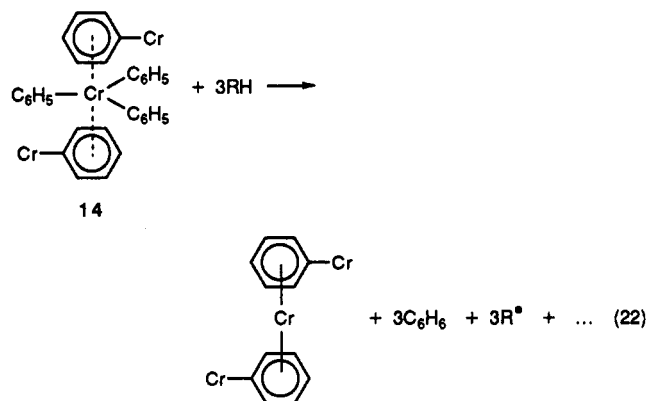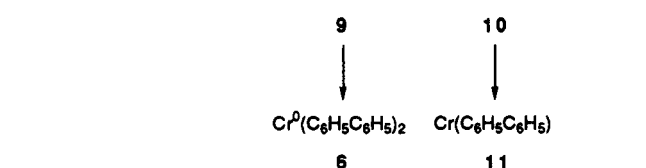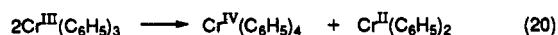$$0.67Cr(OCH_3)_2 \quad (18)$$
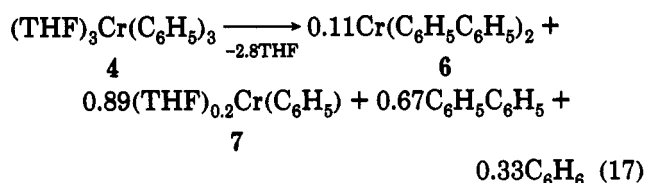
Treatment of chromium trichloride with isopropylmagnesium bromide yields tetraisopropylchromium (eq 19),[30] probably a product of the disproportionation of the intermediate triisopropylchromium. Other tetraorgano-

$$CrCl_3 + 3i\text{-}C_3H_7MgBr \xrightarrow[-3MgBrCl]{Et_2O} \text{"}Cr(i\text{-}C_3H_7)_3\text{"} \rightarrow$$
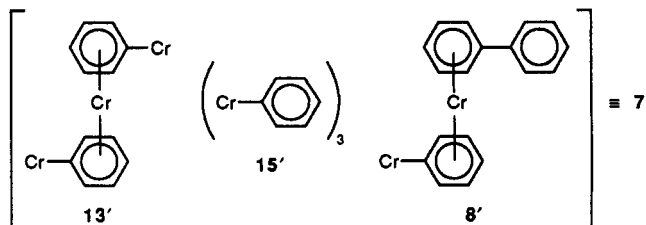$$^1/_2Cr(i\text{-}C_3H_7)_4 + {}^1/_2\text{"}Cr(i\text{-}C_3H_7)_2\text{"} \quad (19)$$

chromium compounds have been prepared in a similar way.[31] Thus, an analogous disproportionation of triphenylchromium is a reasonable possibility (Scheme V, eq 20). Tetramesitylchromium,[32] another σ-aryl compound, is even stable in air. The π-arene complex 6, as an isomer of Cr(C6H5)4 (9), certainly is thermodynamically more stable. It is likely that 6, as a product of the thermal

(30) Müller, J.; Holzinger, W. Angew. Chem. 1975, 87, 781; Angew. Chem., Int. Ed. Engl. 1975, 14, 760.
(31) Kruse, W. J. Organomet. Chem. 1972, 42, C39.
(32) Seidel, W.; Bürger, I. Z. Anorg. Allg. Chem. 1976, 426, 155.

Scheme V

$$2Cr^{III}(C_6H_5)_3 \longrightarrow Cr^{IV}(C_6H_5)_4 + Cr^{II}(C_6H_5)_2 \quad (20)$$
$$\quad\quad\quad\quad\quad\quad\quad 9 \quad\quad\quad\quad\quad 10$$
$$\downarrow \quad\quad\quad\quad\quad\quad \downarrow$$
$$Cr^0(C_6H_5C_6H_5)_2 \quad Cr(C_6H_5C_6H_5)$$
$$\quad 6 \quad\quad\quad\quad\quad\quad 11$$

$$Cr(C_6H_5)_3 \longrightarrow C_6H_5C_6H_5 + \text{"}Cr(C_6H_5)\text{"} \quad (21)$$

14

7 + 13CH₃OH ⟶

$$8 + [Cr(C_6H_6)_2](OCH_3) + 3C_6H_6 + 6Cr^{2+} + 12CH_3O^- + 3^1/_2H_2 \quad (23)$$

13

decomposition of 4 (eqs 17 and 20), is derived from a rearrangement of 9. Essential to such a rearrangement is the mobility of the four aryl groups. This is possible in 9 but not in tetramesitylchromium with its bulky aryl substituents (see the rigid structure of the analogous tetramesitylvanadium[33]). When the temperature is raised, tetramesitylchromium eliminates mesitylene, but no rearrangement occurs. In an analogous rearrangement of intermediate 10, the half-sandwich 11, a possible source of the mixed π-arene complex 8, could be formed. Benzene, the second π-bonded ligand of 8, may be supplied by a second pathway of thermolysis (67%) via the fragment "Cr(C6H5)". This second pathway may involve the reductive elimination of biphenyl (eq 21). "Cr(C6H5)" is the basic unit of the so-called "black product 7", the final product of the thermolysis of (THF)3Cr(C6H5)3. The magnetic moment (1.24 μB per chromium) shows the cluster character of 7, while the products of its methanolysis demonstrate the chemical inhomogeneity and the different functionalities of the phenyl moieties. Hähle[29] discussed $Cr^I(C_6H_5)$, $Cr^0(C_6H_5C_6H_5)$, and Cr^0 in a ratio of 6:1:1 as the main constituents of 7. Therefore, composition and chemical properties of the black product 7 are best expressed by the components 8′, 13′, and 15′ as a whole.

(33) Glowiak, T.; Grobelny, R.; Jezowska-Trzebiatowska, B.; Kreisel, G.; Seidel, W.; Uhlig, E. J. Organomet. Chem. 1978, 155, 39.

The proposed composition of 7 is founded on an important suggestion, i.e., the ability of the phenyl group of the fragment $Cr(C_6H_5)$ in the special role of an intermediate of thermal decomposition of $(THF)_3Cr(C_6H_5)_3$ to π coordinate with chromium(0) or a chromium(0) moiety. This provides an explanation of the formation of 8', the source of 8 in the course of methanolysis (eq 19). Finally, fragment 13' as the source of the cation $[Cr(C_6H_6)_2]^+$ (eq 18) must be attributed to a third pathway of the thermal decomposition. A causal relation between 13' and the benzene eliminated in the course of the thermolysis (eq 18) is outlined by the molar ratio of 0.11:0.33. Possibly a weak π interaction of phenyl groups, for instance, of $Cr(C_6H_5)$ moieties with the central atom of an unchanged triphenylchromium in an intermediate such as 14 accelerates the elimination of benzene and simultaneously opens the way for formation of component 13' of the black product 7 (eq 22). An essential for the elimination of benzene is the presence of the hydrogen-supplying compound RH. THF is one candidate, but the phenyl ligands themselves are candidates as well. The formation of small amounts of *o*-dideuteriobenzene in the deuterolysis of 7 is an indication of this.

The methanolysis of 7 is confined to (σ-phenyl)chromium bonds (eq 23). Final products are hydrogen, benzene, chromium(II), 8, and $Cr(C_6H_6)_2$. The last complex is oxidized by the solvent to the cation $[Cr(C_6H_6)_2]^+$.

The proposed mechanism (eqs 17–24) is speculative, but it provides an explanation of the *main* products of the thermolysis and methanolysis of triphenylchromium. Further studies are needed, first of all as to the third pathway of thermal decomposition (eq 22) and the role and products of RH. Careful studies of the oily, highly air sensitive, dark solids and of the product solutions that contain solutes in different concentrations are indispensable. Such materials, however, are difficult and unpleasant to handle, and a final answer may be long in coming.