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Cover Essay

Bis(benzene)chromium. 2. Its Discovery by E. O. Fischer and W. Hafner and Subsequent Work by the Research Groups of E. O. Fischer, H. H. Zeiss, F. Hein, C. Elschenbroich, and Others[†]

IV. Discovery of Bis(benzene)chromium. Ernst Otto Fischer and Walter Hafner at the Technische Hochschule München, 1954−1956

After he had the inspired idea that bis(cyclopentadienyl)iron (ferrocene) had the sandwich structure rather than the structure with η^1-bonded C_5H_5 groups proposed by Peter Pauson and had proved it, together with Wolfgang Pfab, by means of an X-ray crystallographic study,[1] E. O. Fischer had another idea, a most daring one at the time: that similar transition-metal sandwich complexes with two *neutral* benzene molecules π-bonded to a *neutral*, *zerovalent* metal atom might be capable of existence, specifically *bis(benzene)chromium*. He reasoned that if each benzene molecule would donate its 6 π electrons into the appropriate vacant chromium atomic orbitals, then a stable 18-electron noble-gas (krypton) configuration (the same as in ferrocene) would be achieved and a stable, sandwich-type molecule, **1**, might result. This thought was mentioned in passing to Walter Hafner (Figure 1), a chemistry student at the Technische Hochschule München (THM), when he began work in the advanced inorganic chemistry laboratory during the spring/summer semester of 1952, by Fischer and Pfab, the *Assistent* in charge of the laboratory, in a discussion concerning Hafner's initial experimental work.[2] This started Hafner thinking: how could such a molecule, a most unusual one, to say the least, be prepared? Hein's Grignard synthesis did not seem to be suitable, but Hafner thought that a reaction of benzene with in situ generated Cr(0) (via reduction of a chromium halide by a reactive metal, perhaps aluminum powder) in the presence of aluminum chloride might be a possibility. Although he thought that the chances of success were not great, he kept this idea in mind.

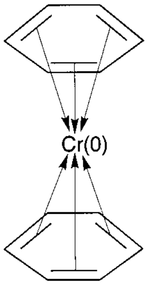

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Figure 1. Walter Hafner in his student days (reproduced courtesy of Walter Hafner).

In March 1953 Hafner began his *Diplom* (i.e., Masters) research under the guidance of E. O. Fischer. His first project was in organochromium chemistry: not the synthesis of bis(benzene)chromium but, rather, of bis(cyclopentadienyl)chromium. This was successfully accomplished,[3] and during the course of his *Diplom* and Ph.D. research, Hafner prepared many other new η^5-cyclopentadienyl−metal complexes: $[Cp_2Cr][CpCr(CO)_3]$, $CpCr(CO)_3H$, $[CpCr(CO)_3]_2$, $CpCr(CO)_2NO$, Cp_2V, $CpV(CO)_4$, and others. This development of the chemistry of η^5-C_5H_5−metal complexes was important and urgent: first of all, it was an entirely new, virgin field of organometallic chemistry and, then, the small Fischer group was engaged in a vigorous competition with the research group of Geoffrey Wilkinson at Harvard University in the development of this field.[1,4] However, Hafner had not forgotten his idea for a bis(benzene)chromium synthesis, and in January 1954 he carried out a "bootleg" experiment to test it out: a reaction at reflux under nitrogen of $AlCl_3$, Al powder, $CrCl_3$, and *m*-xylene.

[†] Dedicated to Professor Dr. Ernst Otto Fischer, an admired and esteemed friend of many years.

(1) Fischer, E. O.; Jira, R. *J. Organomet. Chem.* **2001**, *637−639*, 7 (a retrospective account).

(2) Hafner, W. "Die Entwicklung der Dibenzolchrom−Synthese an der Technischen Hochschule München", an unpublished retrospective account (Walter Hafner, born December 1927, in Lauterbach, Bavaria; studies at the Technische Hochschule München, 1948−1956; at the Consortium für Elektrochemische Industrie, a research subsidiary of Wacker-Chemie GmbH in Munich, 1956 until his retirement in 1992).

(3) Fischer, E. O.; Hafner, W. *Z. Naturforsch.* **1953**, *8b*, 444.

(4) (a) Wilkinson, G. *J. Organomet. Chem.* **1975**, *100*, 273. (b) Cotton, F. A. *J. Organomet. Chem.* **2001**, *637−639*, 18 (both retrospective accounts).

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Figure 2. Some inorganic chemists at the Technische Hochschule München, summer 1955. Front row, left to right: E. O. Fischer, D. Seyferth, Gottfried Brendel (a Hieber student, discoverer of (μ-S_2)$Fe_2(CO)_6$), Walter Hafner. Rear row, left to right: R. Breu (a Hieber student), Erwin Weiss (a Hieber student who carried out X-ray structure determinations and dipole moment measurements for the Fischer group; later Professor at the University of Hamburg, well-known for his X-ray powder diffraction structure determinations of organometallic compounds of the alkali and alkaline earth metals), Robert Werner (a Hieber student) (reproduced courtesy of the Archives, Institute of Inorganic Chemistry, Technical University of Munich, Professor Dr. H. Schmidbaur, Director).

A yellow chromium-containing solution resulted. Evaporation under vacuum left a yellow water-soluble solid that was not sublimable—not properties expected for a neutral bis(arene)chromium complex. Fischer was interested but became more interested when repetition of this reaction under a pressure of carbon monoxide gave $Cr(CO)_6$ in high yield.[5] Reaction of $Cr(CO)_6$ with an alkali-metal cyclopentadienide, followed by careful acidification, formed the novel hydride $CpCr(CO)_3H$, which returned Hafner to (η^5-Cp)Cr chemistry.[6] The investigation of the yellow solid was put on the back burner, but an experiment with benzene under autogenous pressure at ~150 °C showed that it reacted in the same way as *m*-xylene had done.

In the latter part of July 1955, Harold Zeiss visited the University of Munich and gave a seminar, which the members of the THM Inorganic Chemistry Institute (Figure 2) attended, about Tsutsui's doctoral research and their conclusions concerning the nature of Hein's phenylchromium compounds. The fact that the Hein compounds appeared to be η^6 sandwich complexes of biphenyl and benzene with Cr(I) activated Hafner. A few days later, when the summer vacation began, he carried out the first experiments to reduce the yellow solid from the benzene reaction, which obviously was a salt (eq 1; an excess of $AlCl_3$ was needed in order to obtain a soluble product) to the neutral compound. Zinc dust in aqueous HCl had no effect, but aqueous alkaline hydroxylamine or sodium dithionite in dilute aqueous NaOH (eq 2) was effective. The product was a dark brown crystalline, benzene-soluble, and sublimable solid. Bis(benzene)chromium, our cover molecule, had been prepared![7]

$$6C_6H_6 + 3CrCl_3 + 2Al + xAlCl_3 \rightarrow 3[(C_6H_6)_2Cr][AlCl_4]\cdot(x-1)AlCl_3 \quad (1)$$

$$2[(C_6H_6)_2Cr]^+ + S_2O_4^{2-} + 4OH^- \rightarrow 2(C_6H_6)_2Cr + 2SO_3^{2-} + 2H_2O \quad (2)$$

Bis(benzene)chromium was found to be surprisingly thermally stable in the absence of air: it melted at 284−285 °C and decomposed only at around 300 °C to leave a metallic mirror. In air it was oxidized relatively rapidly. As expected, if Cr had attained the krypton configuration, it was diamagnetic. Its dipole moment was zero. A preliminary X-ray crystal structure determination[8] by Erwin Weiss showed $(C_6H_6)_2Cr$ to have cubic symmetry; the molecule was centrosymmetric as required for the sandwich structure **1**.

The preparation of Cr(I) salts from bis(benzene)chromium was best effected by air oxidation in the presence of water followed by treatment of the aqueous solution of the resulting base with the appropriate anion source. Insoluble salts (Reineckate, picrate, tetraphenylborate, perchlorate, and iodide) could be readily prepared by adding the respective alkali-metal salt to the hydrolyzed reaction mixture. Most of the $(C_6H_6)_2Cr^+$ salts were light-sensitive and unstable in air and in acidic solution but stable in neutral and basic solution.

With bis(benzene)chromium now secured, there arose the question as to the relation of this and other $(arene)_2Cr$ products of the reductive Friedel−Crafts synthesis and of the derived $(arene)_2Cr(I)$ salts to the penta-, tetra-, and triphenylchromium compounds of Hein. Of course, Zeiss and Tsutsui had carried out experiments the results of which could be interpreted in terms of (η^6-arene)$_2$Cr(I) structures rather than η^1-C_6H_5Cr species, but universally accepted proof still was lacking (as Zeiss and Tsutsui's difficulties in getting their results published showed). Another student of Fischer's, Dietlinde Seus, who had been studying η^5-indenyl and η^5-dihydroindenyl complexes of iron and cobalt, looked into this question. This study, Fischer and Seus said,[9] was carried out in close collaboration with Hein. Application of the new synthetic procedure used for bis(benzene)chromium(0) and -(I) to the reaction of biphenyl, $AlCl_3$, Al powder, and $CrCl_3$ in the melt at 140 °C gave, after methanolysis, the $(biphenyl)_2Cr^+$ base, which was converted to the poorly soluble iodide in aqueous medium. This product was identical in all respects (orange color, magnetism ($1.75\mu_B$), UV/vis absorption spectrum, IR spectrum, and X-ray absorption edges) with a sample of "$(C_6H_5)_4CrI$" provided by Hein. Thus, conclusive evidence was in hand that one of Hein's compounds indeed was an $(arene)_2Cr$ sandwich complex. Reduction of the iodide with formamidinesulfinic acid or with diaminomethanedisulfinic acid gave the neutral $(C_6H_5C_6H_5)_2Cr$ as dark orange sublimable (170−180 °C under vacuum) crystals. Insoluble salts (Reineckate, picrate, perchlorate, tetraphenylborate) were prepared

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(5) (a) Fischer, E. O.; Hafner, W.; Öfele, K. *Chem. Ber.* **1959**, *92*, 3050. (b) An alternate route to $Cr(CO)_6$, the treatment at higher temperatures of Cp_2Cr with CO under pressure, also was developed at this time: Fischer, E. O.; Hafner, W. *Z. Naturforsch.* **1954**, *9b*, 503.

(6) Fischer, E. O.; Hafner, W. *Z. Naturforsch.* **1955**, *10b*, 140.

(7) (a) Fischer, E. O.; Hafner, W. *Z. Naturforsch.* **1955**, *10b*, 665. (b) *Z. Anorg. Allg. Chem.* **1956**, *286*, 146.

(8) Weiss, E.; Fischer, E. O. *Z. Anorg. Allg. Chem.* **1956**, *286*, 142.

(9) Fischer, E. O.; Seus, D. *Chem. Ber.* **1956**, *89*, 1809 (with a gracious dedication to Hein).

from the original (hydrolyzed) reaction mixture. Also prepared was the phenoxide.

Hein was informed of these findings and, in a paper published immediately following that of Fischer and Seus, said he found the results rather surprising in that this synthesis was carried out at such high temperature in the presence of $AlCl_3$.[10] Returning to his Grignard synthesis, he speculated that phenylmagnesium bromide could have acted as a reducing agent (eqs 3 and 4) and that the biphenyl thus generated could have been

$$C_6H_5MgX + CrX_3 \rightarrow {}^1/_2C_6H_5C_6H_5 + CrX_2 + MgX_2 \tag{3}$$

$$2C_6H_5MgX + CrX_3 \rightarrow C_6H_5C_6H_5 + CrX + 2MgX_2 \tag{4}$$

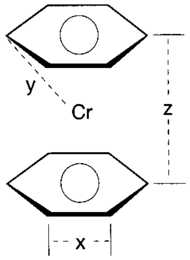
$$2C_6H_5C_6H_5 + CrX \rightarrow [(C_6H_5C_6H_5)_2Cr]X \tag{5}$$

complexed by the Cr(I) intermediate formed in eq 4. However, the action of ethylmagnesium bromide, also a potential reducing agent, on $CrCl_3$ in diethyl ether in the presence of biphenyl did not produce any $(C_6H_5\text{-}C_6H_5)_2Cr^+$ salt; therefore, the mechanism of the Grignard synthesis of the bis(arene)chromium compounds remained a mystery.

At this point, Walter Hafner leaves our story. Despite the urgings of Fischer and Professor Walter Hieber, Director of the Inorganic Chemistry Institute of the Technische Hochschule, to stay and undertake his *Habilitation* and follow a career in academe, he chose a career in industry. He joined the Consortium für Electrochemische Industrie, a research subsidiary of Wacker-Chemie in Munich, in 1956, where he made another outstanding and industrially important contribution as the inventor of the well-known Wacker reaction, the regiospecific, Pd-catalyzed oxidation of an olefinic double bond to give a carbonyl compound which found worldwide industrial application in the conversion of ethylene to acetaldehyde (the Wacker process).

After the synthesis of bis(benzene)chromium and the unambiguous identification of one of the Hein phenylchromium compounds as a bis(arene)chromium(I) salt, everybody involved in this aspect of organochromium chemistry, Fischer, Hein, Zeiss, and Tsutsui, pursued research in this area with renewed vigor. Most of this work was directly relevant to bis(benzene)chromium and other bis(arene)chromium compounds and related bis(arene) compounds of other transition metals, and we shall deal with these aspects in the following sections. However, a brief discussion of the structure and bonding of bis(arene)chromium compounds, which involves the work of others, is appropriate at this point.

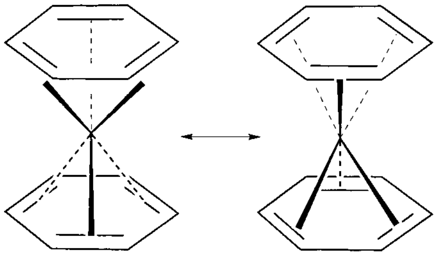
The first years after the discovery of bis(benzene)chromium were fraught with controversy, which revolved around the questions of whether the molecule has D_{6h} (all six C−C bonds of the benzene ligands equivalent) or D_{3d} symmetry (alternating C−C bonds of different length, i.e., a "fixed" Kekulé structure for the benzene ligands) and the nature of the bonding. Eventually, it was the D_{6h} structure which prevailed. A low-temperature X-ray crystal structure determination at 100 K by Keulen and Jellinek finally confirmed that the $(C_6H_6)_2Cr$ molecule has D_{6h} symmetry in the solid state with planar benzene rings and the molecular dimensions shown in formula **2**.[11] An electron diffraction study of bis(benzene)chromium in the gas phase by Arne Haaland gave essentially the same results.[12] Further proof for D_{6h} symmetry was provided by an IR and Raman spectroscopic study of $(C_6H_6)_2Cr$ in the vapor state[13] and a normal coordinate analysis of molecular vibrations and calculations of mean C−C vibrational amplitudes,[14] as well as by thermodynamic evidence.[15]



x = 1.417(3) Å
y = 2.142(3) Å
z = 3,22 Å

2

The currently accepted molecular orbital representation of bis(benzene)chromium of D_{6h} symmetry is shown in Figure 3.[16] There are six strong bonding interactions between the metal and the two benzene molecules: hence, the high thermal stability of bis(benzene)chromium. A localized valence-bond description involving six equivalent Cr d^2sp^3 hybrid orbitals that point in an octahedral orientation toward six benzene π bonds as shown in the resonance hybrids **3′** and **3″** also is possible.[17]



3' **3"**

The heat of combustion of bis(benzene)chromium has been measured calorimetrically, and the value determined has been used in the calculation of its heat of formation in the gas phase ($2C_6H_6(g) + Cr(g) = (C_6H_6)_2Cr(g)$) as −56.6 kcal/mol.[18] This value is decidedly smaller than the comparable heat of formation of ferrocene, −147 kcal/mol. Ionization potentials and

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

(11) Keulen, E.; Jellinek, F. *J. Organomet. Chem.* **1966**, *5*, 490. A neutron diffraction study of bis(benzene)chromium also has been reported: Förster, E.; Albrecht, G.; Dürselen, W.; Kurras, E. *J. Organomet. Chem.* **1969**, *19*, 215.

(12) Haaland, A. *Acta Chem. Scand.* **1965**, *19*, 41.

(13) Ngai, L. H.; Stafford, F. E.; Schäfer, L. *J. Am. Chem. Soc.* **1969**, *91*, 48.

(14) (a) Brunvoll, J.; Cyvin, S. J.; Schäfer, L. *J. Organomet. Chem.* **1971**, *27*, 69. (b) Schäfer, L.; Southern, J. F.; Cyvin, S. J.; Brunvoll, J. *J. Organomet. Chem.* **1970**, *24*, C13.

(15) Andrews, J. T. S.; Westrum, E. F., Jr.; Bjerrum, N. *J. Organomet. Chem.* **1969**, *17*, 293.

(16) Elschenbroich, C.; Salzer, A. *Organometallics—A Concise Introduction*, 2nd ed.; VCH: Weinheim, Germany, 1992; pp 346, 347. See also: Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499.

(17) (a) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960. (b) Hoffmann, R. *Science* **1981**, *211*, 995. (c) Hsu, C.-Y.; Orchin, M. *J. Chem. Educ.* **1973**, *50*, 114.

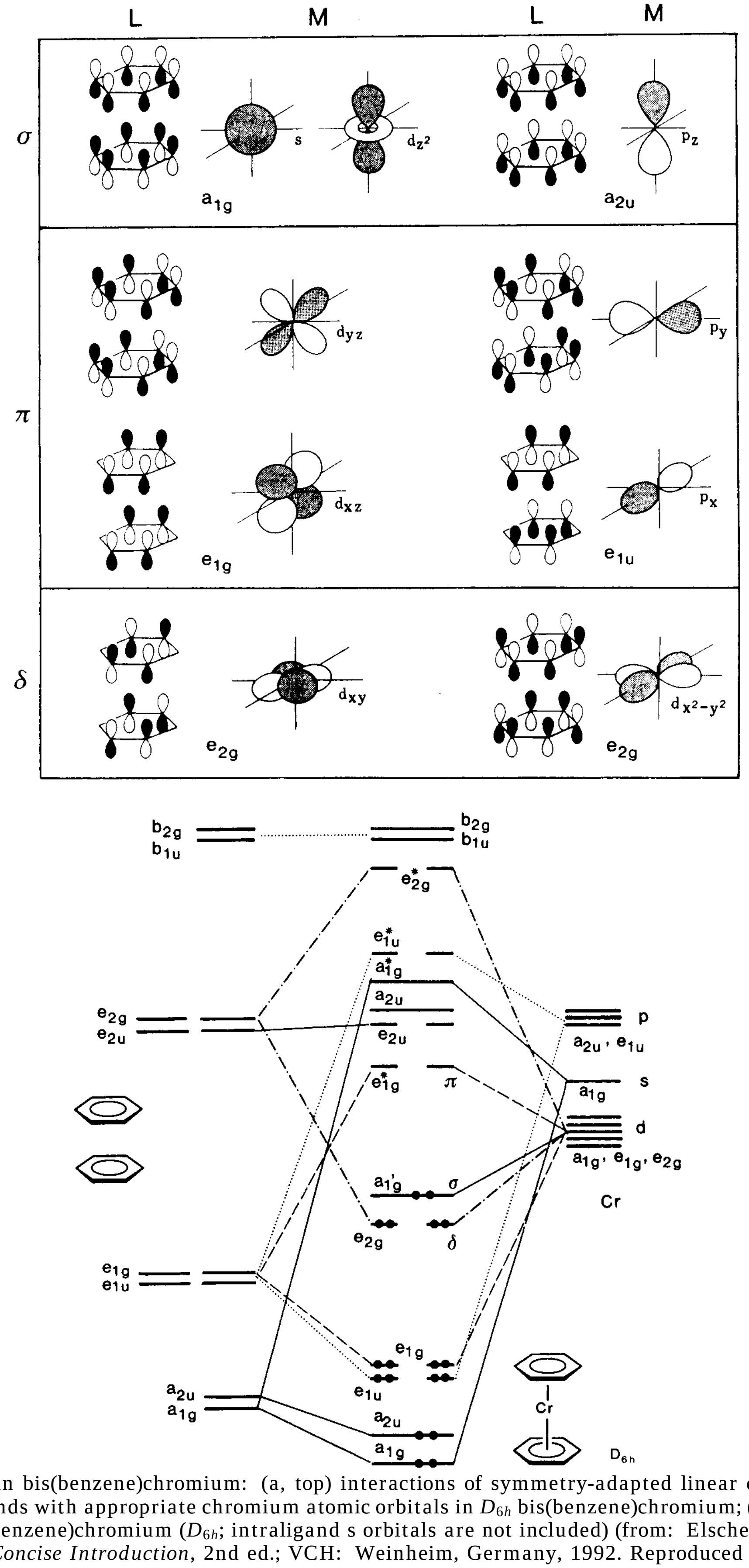


Figure 3. Bonding in bis(benzene)chromium: (a, top) interactions of symmetry-adapted linear combinations of the π MOs of two C_6H_6 ligands with appropriate chromium atomic orbitals in D_{6h} bis(benzene)chromium; (b, bottom) qualitative MO diagram for bis(benzene)chromium (D_{6h}; intraligand s orbitals are not included) (from: Elschenbroich, C.; Salzer, A. *Organometallics—A Concise Introduction*, 2nd ed.; VCH: Weinheim, Germany, 1992. Reproduced by permission of B.G. Teubner GmbH).

appearance potentials were measured by mass spectrometry for bis(benzene)chromium and some other bis(arene)chromium complexes.[19] The fragmentation of $Cr(arene)_2$ complexes occurs almost exclusively by suc-

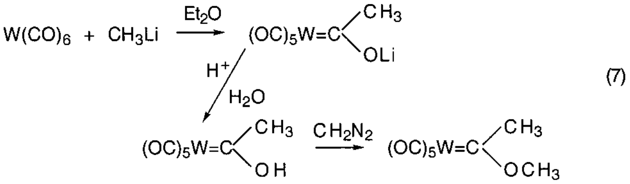
Figure 4. Ernst Otto Fischer (1959) (reproduced courtesy of the Gesellschaft Deutscher Chemiker E.V.).

cessive loss of the arene ligands. The stability sequence $C_6(CH_3)_6 \gg C_6H_5{-}C_6H_5 \geq C_6H_3(CH_3)_3 > C_6H_6$ was established for the Cr−arene ligand bond strengths in the neutral complexes.

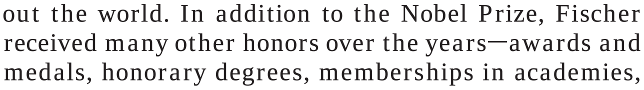
V. After Bis(benzene)chromium: E. O. Fischer and Co-Workers at the Technische Hochschule München Develop Bis(arene)metal Chemistry, 1956−1965.

Ernst Otto Fischer (Figure 4) is well-known to most of our readers. He was one of the most outstanding players on the organometallic chemistry field; a heavy hitter, with four home runs: ferrocene and cyclopentadienylmetal compounds, bis(benzene)chromium and other arene−metal complexes, transition-metal−carbene complexes ("Fischer carbenes"), and transition-metal−carbyne complexes, in addition to many other hits.[20] For ferrocene and the development of cyclopentadienylmetal chemistry, he shared the Nobel Prize in Chemistry with Geoffrey Wilkinson in 1973.[20a] E. O. Fischer was born on November 10, 1918. His father, Karl T. Fischer, was a professor of physics at the Technische Hochschule München. Fischer's studies got off to a late start. He was just about to complete his obligatory two-year military service when World War II started on September 1, 1939. Military service in Poland, France, and Russia followed. His active service ended when he was wounded in Russia. He began his chemistry studies during a semester of study leave in 1941 and returned to the Technische Hochschule München (THM) in 1946. He chose as his research area metal carbonyl chemistry under the supervision of Professor Walter Hieber, Director of the Inorganic Chemistry Institute, the pioneer of modern metal carbonyl chemistry. For his Ph.D. research he carried out a study of the synthesis of $Ni(CO)_4$ by reduction of Ni(II) salts with aqueous dithionite in the presence of carbon monoxide (eq 6). Fischer obtained his Ph.D. in March 1952. Although he had already accepted a position at Wacker-Chemie, at Hieber's urging he stayed at THM to work on his *Habilitation* (on ferrocene and other metal cyclopentadienyl complexes), completing it in 1954. He stayed at THM as *Privatdozent* (equivalent to assistant professor). In 1957 he moved down the street to the University of München, where he became full professor in 1959. Fischer returned to THM in 1964 as successor to Professor Hieber, who had reached retirement age. It was in 1964 that Fischer and Maasböl reported the preparation of $(OC)_5W{=}C(OCH_3)CH_3$, the first "Fischer carbene complex" (eq 7).[21a] The versatile chemistry of such complexes has been developed very broadly throughout the world in the succeeding years. Notable are their extensive applications as important reagents in organic synthesis, pioneered by his students K.-H. Dötz (Bonn) and R. Aumann (Münster). In 1973 followed another exciting contribution to transition-metal−organic chemistry: the discovery of transition-metal−carbyne complexes (eq 8) by Fischer and Kreis.[21b]

$$Ni^{2+} + S_2O_4^{\ 2-} + 4CO \rightarrow Ni(CO)_4 + 2SO_3^{\ 2-} + 2H_2O \qquad (6)$$



(7)



$$(OC)_5MC\begin{matrix}R\\OCH_3\end{matrix} + BX_3 \xrightarrow[\text{low T}]{\text{pentane}} (OC)_4\underset{X}{\underset{|}{M}}{\equiv}CR + BX_2(OCH_3) \qquad (8)$$

This class of complexes, with a metal−carbon triple bond, was an entirely new one, and it aroused great interest in the organometallic community. During the following years, Fischer and his students studied the carbene and carbyne complexes in great detail, and they were joined in this endeavor by other chemists throughout the world. In addition to the Nobel Prize, Fischer received many other honors over the years—awards and medals, honorary degrees, memberships in academies, and name lectureships. Many of his students have had distinguished careers in German universities and have themselves made notable contributions to organometallic chemistry. His contributions and influence have extended beyond the laboratory to science, university, and education policy in Bavaria and in Germany. In 1984 he retired. As Professor Emeritus, he has main-

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[18] (a) Fischer, E. O.; Schreiner, S. *Chem. Ber.* **1958**, *91*, 2213. (b) Fischer, E. O.; Schreiner, S.; Reckziegel, A. *Chem. Ber.* **1961**, *94*, 258.

[19] Herberich, G. E.; Müller, J. *J. Organomet. Chem.* **1969**, *16*, 111.

[20] (a) Seyferth, D.; Davison, A. *Science* **1973**, *182*, 699. (b) Herrmann, W. A. *Naturwiss. Rundsch.* **1988**, *41*, 442.

[21] (a) Fischer, E. O.; Maasböl, A. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 580. (b) Fischer, E. O.; Kreis, G.; Kreiter, C. G.; Müller, J.; Huttner, G.; Lorenz, H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 564. See also: (c) Fischer, E. O. *Angew. Chem.* **1974**, *86*, 651 (Fischer's Nobel Lecture, a review of his transition metal−carbene and the early stages of transition metal−carbyne research). (d) Fischer, E. O.; Schubert, U. *J. Organomet. Chem.* **1975**, *100*, 59 (carbyne complexes: a review).

tained contact with chemistry and with former students and colleagues worldwide. We still see him at chemical conferences, still actively interested in organometallic chemistry.

Now we return to the THM in 1956. Bis(benzene)chromium has been discovered. It has been established, by comparison of the respective products, that Hein's "tetraphenylchromium iodide" is, in fact, the π complex bis(biphenyl)chromium iodide. Now the chemistry of arene−metal complexes had to be explored in breadth and depth.[22] Fischer and Seeholzer studied the "reductive Friedel−Crafts synthesis" of bis(arene)chromium compounds in great detail.[23] It was found that in sealed-tube reactions (eq 1) the use of a large (8-fold) excess of $AlCl_3$ was decidedly beneficial. The reaction started at 90 °C, was complete in 3 h at 140 °C, and gave an almost quantitative yield of product. Furthermore, under these conditions, methyl-substituted benzenes reacted satisfactorily. In particular, mesitylene gave a 95% yield of the bis(mesitylene)chromium cation within a few hours at 65 °C. This led to the important finding that mesitylene could catalyze the formation of bis(benzene)chromium. Its synthesis now could be carried out at atmospheric pressure in refluxing benzene in high yield when a small amount of mesitylene was present. Obviously, $AlCl_3$ catalyzes the exchange equilibrium shown in eq 9. It was found that the $[(C_6H_6)_2Cr]^+$ cation undergoes a valence disproportionation in aqueous alkaline medium to form $(C_6H_6)_2Cr$, but at the expense of half of the original $[(C_6H_6)_2Cr]^+$ (eq 10). To avoid this waste of product, methanolysis of the reaction mixture followed by reduction prior to hydrolysis is preferred.

$$[(C_6H_3(CH_3)_3)]_2Cr^+ + 2C_6H_6 \overset{AlCl_3}{\rightleftharpoons} [(C_6H_6)_2Cr]^+ + 2C_6H_3(CH_3)_3 \quad (9)$$

$$2[(C_6H_6)_2Cr]^+ \xrightarrow{OH^-} (C_6H_6)_2Cr + Cr^{2+} + 2C_6H_6 \quad (10)$$

Long reaction times at higher temperatures, it was found, can lead to problems with methyl-substituted benzenes. Thus, a reaction of mesitylene with the usual $CrCl_3/AlCl_3/Al$ reagent at 80 °C for 14 h followed by dithionite reduction gave a mixture of bis(arene)chromium products, the arene ligands of which were 90% mesitylene, 9% xylenes, and 1% tetramethylbenzene.[24] Such Friedel−Crafts isomerization reactions could be avoided by carrying out the reaction at room temperature for 10 h using instead the $CrBr_3/AlBr_3/Al$ system. Isomerically pure bis(mesitylene)chromium was obtained in this way.

Studies of the reactivity of bis(benzene)chromium with the aim of introducing functional groups on the aromatic ligands were of limited success. A Friedel−Crafts reaction with $CH_3C(O)Cl/AlCl_3$ resulted in acylation of the benzene rings but destroyed the complex.[25] Attempted mercuration, nitration, and sulfonation, as well as arylation with a phenyldiazonium salt, also led to decomposition. Arene ligand metalation could, however, be effected with a strong base (eq 11).[26] The metalation reaction, however, was not very selective. When n-amylsodium was generated in the presence of bis(benzene)chromium by reaction of n-amyl chloride with finely divided sodium in hexane at 0 °C (1:1 molar ratio of $n\text{-}C_5H_{11}Na$ to $(C_6H_6)_2Cr$) and the resulting mixture then was heated at reflux, metalation of $(C_6H_6)_2Cr$ did occur. Alkylation of the metalated bis(benzene)chromium with methyl iodide and conversion of the product to the cation followed. Finally, oxidation with aqueous dichromate released the free arene ligands of the product. The 1:1 reaction was unsatisfactory, giving mostly benzene (i.e., most of the $(C_6H_6)_2Cr$ had not reacted), some toluene (the expected arene from the monometalation product), and m- and p-xylene (derived from dimetalation). Increasing the $n\text{-}C_5H_{11}Na{:}(C_6H_6)_2Cr$ ratio to 5 increased the extent of metalation: with similar workups, the yields of toluene and m- and p-xylene were increased, and now small amounts of o-xylene, methylethylbenzene (from CH_3 group metalation), and mesitylene also were detected. Treatment of the metalation reaction mixture with CO_2 and subsequently with dimethyl sulfate gave red-brown $(C_6H_6)Cr(C_6H_5CO_2CH_3)$ and a mixture of isomeric disubstituted ester Cr complexes in low yield. Nevertheless, Fischer and Brunner utilized the 5:1 n-amylsodium metalation procedure for preparative purposes, quenching the metalation product mixture not only with carbon dioxide but also with formaldehyde, acetaldehyde, benzaldehyde, and benzophenone.[27] The monosubstitution products could be isolated from the product mixture in each case. This required an initial air oxidation of the product mixture in the presence of water, which formed the water-soluble cations of the functionalized bis(benzene)chromium complexes and left the organic impurities in the organic phase. Subsequent reduction of the cations in water/benzene medium led to formation of the Cr(0) complexes. The pure monosubstituted Cr(0) complexes were isolated by column chromatography on Al_2O_3 in the absence of air. Prepared in this manner were $(C_6H_6)Cr(C_6H_5CH_2OH)$, $(C_6H_6)Cr(C_6H_5CH(OH)C_6H_5)$, $(C_6H_6)Cr(C_6H_5C(OH)(C_6H_5)_2)$, and $(C_6H_6)Cr(C_6H_5CH(OH)CH_3)$. The carbonyl-containing complexes $(C_6H_6)Cr(C_6H_5C(O)C_6H_5)$ and $(C_6H_6)Cr(C_6H_5C(O)OCH_3)$ could be reduced with $LiAlH_4$ and phenylated with C_6H_5MgBr without destroying the Cr(0) complex.

$$(C_6H_6)_2Cr + \text{excess } n\text{-}C_5H_{11}Na \rightarrow (C_6H_5Na)_2Cr + \text{higher metalated products} \quad (11)$$

This functionalization of bis(benzene)chromium was not very practical, and a few years later a more useful metalation procedure was developed by Elschenbroich using $n\text{-}C_4H_9Li/Me_2NCH_2CH_2NMe_2$ in cyclohexane solution at 70 °C.[28] It was found that coordination of benzene to chromium increases its kinetic C−H acidity and, furthermore, that the rate of lithiation of $(C_6H_6)(C_6H_5Li)Cr$ is greater than that of the unlithiated complex. Reaction of $(C_6H_5Li)_2Cr$ with $(CH_3)_3SiCl$ gave

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[22] For a review covering the period 1955−1961, see: Fischer, E. O.; Fritz, H. P. *Angew. Chem.* **1961**, *73*, 353.

[23] Fischer, E. O.; Seeholzer, J. *Z. Anorg. Allg. Chem.* **1961**, *312*, 244.

[24] Huttner, G.; Fischer, E. O.; Elschenbroich, C. *J. Organomet. Chem.* **1965**, *3*, 330.

[25] Fritz, H. P.; Fischer, E. O. *Z. Naturforsch.* **1957**, *12b*, 67.

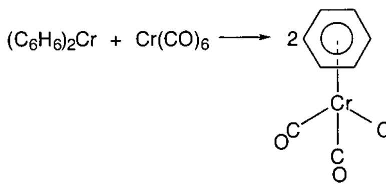
[26] (a) Fischer, E. O.; Brunner, H. *Z. Naturforsch.* **1961**, *16b*, 406. (b) *Chem. Ber.* **1962**, *95*, 1999.

[27] Fischer, E. O.; Brunner, H. *Chem. Ber.* **1965**, *98*, 175.

[28] (a) Elschenbroich, C. *J. Organomet. Chem.* **1968**, *14*, 157. (b) *J. Organomet. Chem.* **1970**, *22*, 677.

$(C_6H_5Si(CH_3)_3)_2Cr$ in the form of brown, very air-sensitive needles which decomposed rapidly in polar solvents, even in the absence of air.[28b]

Some chromium complexes that contained only one π-coordinated arene ring also were prepared. Thus, the reaction of $CrCl_3$ with a THF solution containing equimolar amounts of C_5H_5MgBr and C_6H_5MgBr gave orange, air-sensitive, paramagnetic (molar susceptibility 1.70 μ_B; i.e., one unpaired electron) $(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)Cr$.[29] Of much greater interest and much greater practical utility were the (arene)chromium tricarbonyl complexes. The original synthesis of (benzene)chromium tricarbonyl of Fischer and Öfele[30] is of limited applicability, requiring a sealed-tube reaction at 220 °C of bis(benzene)chromium and chromium hexacarbonyl (eq 12). The product is a lemon yellow, readily sublimable, crystalline, diamagnetic solid. At almost the same time, three different research groups reported a more practical, more generally applicable synthesis of the (arene)chromium tricarbonyl complexes by direct reaction of the arene with chromium hexacarbonyl, either in an autoclave or in a refluxing, high-boiling solvent.[31−33] This procedure is much more versatile, being applicable to (arene)$Cr(CO)_3$ syntheses using many different functionally substituted arenes such as chlorobenzene, aniline, methyl benzoate, phenol, etc. These complexes, in contrast to the bis(arene)chromium complexes, have a broad, well-developed chemistry of their own and have become valuable reagents and/or intermediates in organic synthesis.[34] The arene + $Cr(CO)_6$ procedure also was found to be applicable to polynuclear hydrocarbons[35] and to aromatic heterocycles such as thiophene[36] and 2-methylpyridine (via reaction of *N*-methylpyridinium iodide with $Cr(CO)_6$ and pyrolysis of the resulting $[CH_3NC_5H_5][Cr(CO)_5I]$).[37]



(12)

Considerable effort was devoted by Fischer and his students to the preparation of bis(arene) complexes of other metals. Green bis(benzene)molybdenum[38] and bis(benzene)tungsten[39] were prepared, as were $C_6H_6Mo(CO)_3$ and $C_6H_6W(CO)_3$.[39] Outside of group 6, neutral and cationic bis(arene) complexes of vanadium, iron, ruthenium, osmium, rhenium, technicium, cobalt, rhodium, and iridium were prepared.[22]

As noted earlier, in 1964 Maasböl prepared the first Fischer-type transition-metal carbene complex and this led to a change in the research focus of the Fischer group, away from π-arene−metal chemistry. Fischer's contributions in this area had been outstanding: in only 10 years he had opened up and very significantly developed this completely new field of organometallic chemistry, one that still is being pursued vigorously throughout the world today.

VI. Zeiss at Monsanto: Dayton and Zürich, 1955−1975. Focus on Organochromium Chemistry

In 1955, Harold Zeiss left Yale for the Monsanto Chemical Co.'s Central Research Laboratory in Dayton, OH. There, as a research associate, he was able to pursue independent research with a small group of co-workers. Tsutsui's doctoral research at Yale had opened the door to a new and potentially interesting field of organometallic chemistry, and Zeiss decided to follow up on Tsutsui's results.

In his consideration of the published results of Hein's $C_6H_5MgBr + CrCl_3$ reaction (and of Tsutsui's repetition of this work), Zeiss was puzzled by the failure to find any "diphenylchromium" salts: i.e., what he now believed would be a bis(benzene)chromium(I) salt. This question was investigated with his co-worker Walter Herwig. Zeiss had assumed that the $(C_6H_6)_2Cr^+$ hydroxide had been missed by Hein because of its high water solubility, and it was in the aqueous mother liquors (after isolation of the $(C_6H_5C_6H_5)_2Cr^+$ and $(C_6H_5C_6H_5)(C_6H_6)Cr^+$ products) that Herwig looked.[40] Addition of sodium tetraphenylborate did indeed precipitate the yellow $(C_6H_6)_2Cr[B(C_6H_5)_4]$. Reduction of the latter with hypophosphorous acid or aqueous alkaline dithionite gave bis(benzene)chromium that was identical in all respects with the bis(benzene)chromium of Fischer and Hafner. Therefore, it turned out that Hein had the $(C_6H_6)_2Cr^+$ ion right from the start!

Anhydrous, sublimed chromium trichloride has the drawback that it is essentially insoluble in diethyl ether and THF. An improvement on this situation was made by Herwig and Zeiss[41] when they prepared $CrCl_3{\cdot}3THF$, which is soluble in THF (2.8 g/100 mL of hot THF). This facilitated its reactions with organometallic reagents. Using this $CrCl_3$ adduct, an exciting breakthrough was made by Herwig and Zeiss in 1957: the synthesis of the *σ-bonded triphenylchromium*, the compound that had been sought unsuccessfully by Bennett and Turner and by Hein, as its tris-THF adduct.[42] When a dilute, violet solution of $CrCl_3{\cdot}3THF$ at −30 °C *under oxygen-free nitrogen* was treated with exactly 3 molar equiv of

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(29) Fischer, E. O.; Kögler, H. P. *Z. Naturforsch.* **1958**, *13b*, 197.

(30) Fischer, E. O.; Öfele, K. *Chem. Ber.* **1957**, *90*, 2532.

(31) (a) Fischer, E. O.; Öfele, K.; Essler, H.; Fröhlich, W.; Mortensen, J. P.; Semmlinger, W. *Z. Naturforsch.* **1958**, *13b*, 458. (b) *Chem. Ber.* **1958**, *91*, 2763.

(32) Natta, G.; Ercoli, R.; Calderazzo, F. *Chim. Ind. (Milano)* **1958**, *40*, 287.

(33) (a) Nicholls, B.; Whiting, M. C. *Proc. Chem. Soc.* **1958**, 152. (b) *J. Chem. Soc.* **1959**, 551.

(34) (a) Semmelhack, M. F. In *Comprehensive Organic Synthesis*; Trost, B., Ed.; Pergamon: Oxford, U.K., 1991; Vol. 4, pp 517−549. (b) Black, D. St. C.; Jackson, W. R.; Swan, J. M. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon: Oxford, U.K., 1979; Vol. 3, pp 306−322. (c) Pape, A. R.; Kaliappan, K. P.; Kündig, E. P. *Chem. Rev.* **2000**, *100*, 2917. (d) Rose-Munch, F.; Rose, E. *Curr. Org. Chem.* **1999**, *3*, 445. (e) Merlic, C. A.; Miller, M. M.; Hietbrink, B. N.; Houk, K. N. *J. Am. Chem. Soc.* **2001**, *123*, 4904.

(35) (a) Fischer, E. O.; Kriebitzsch, N.; Fischer, R. D. *Chem. Ber.* **1959**, *92*, 3214. (b) Willeford, B. R.; Fischer, E. O. *J. Organomet. Chem.* **1965**, *4*, 109.

(36) Fischer, E. O.; Öfele, K. *Chem. Ber.* **1958**, *91*, 2395.

(37) (a) Fischer, E. O.; Öfele, K. *Z. Naturforsch.* **1959**, *14b*, 736. (b) *Chem. Ber.* **1960**, *93*, 1156.

(38) Fischer, E. O.; Stahl, H.-O. *Chem. Ber.* **1956**, *89*, 1805.

(39) Fischer, E. O.; Scherer, F.; Stahl, H. O. *Chem. Ber.* **1960**, *93*, 2065.

(40) Zeiss, H. H.; Herwig, W. (a) *J. Am. Chem. Soc.* **1956**, *78*, 5959. (b) *Justus Liebigs Ann. Chem.* **1957**, *606*, 209.

(41) Herwig, W.; Zeiss, H. H. *J. Org. Chem.* **1958**, *23*, 1404.

(42) (a) Herwig, W.; Zeiss, H. H. *J. Am. Chem. Soc.* **1957**, *79*, 6561. (b) *J. Am. Chem. Soc.* **1959**, *81*, 4798. (c) Khan, S. I.; Bau, R. *Organometallics* **1983**, *2*, 1896.

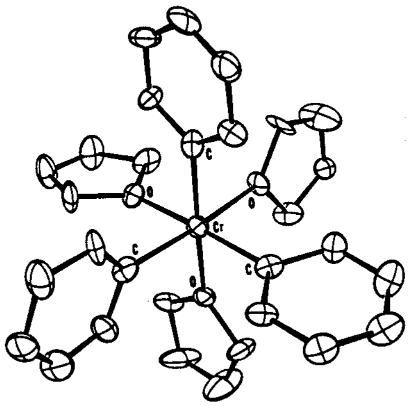
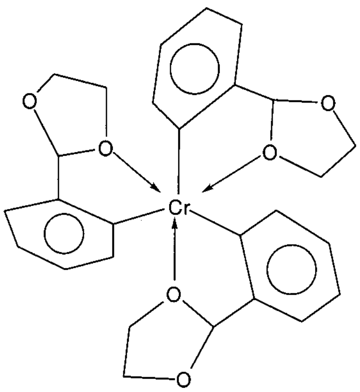


Figure 5. Molecular structure of $(C_6H_5)_3Cr{\cdot}3THF$ (from ref 42c).

C_6H_5MgBr in THF, a dark red precipitate and a red-brown solution were formed. Addition of more THF gave a clear, dark red-brown solution of $(C_6H_5)_3Cr{\cdot}3THF$. Further dilution with THF and stirring resulted in crystallization of blood red needles of $(C_6H_5)_3Cr{\cdot}3THF$ in low yield. Most of the $(C_6H_5)_3Cr{\cdot}3THF$ could not be separated from the magnesium halides by fractional crystallization, their solubilities being too similar, and a combined solid, $(C_6H_5)_3Cr{\cdot}3MgBrCl{\cdot}6THF$, was isolated. Triphenylchromium–tris(tetrahydrofuran) could, however, be isolated as the pure compound by addition of an equal volume of diethyl ether to a THF solution of $(C_6H_5)_3Cr{\cdot}3THF$ and Mg salts. It is extremely air- and moisture-sensitive and is hydrolyzed to $Cr(H_2O)_6^{3+}$ (but no π complexes are formed). Its magnetic moment of 3.89 μ_B is indicative of the presence of three unpaired electrons, as is expected for Cr(III). Twenty-six years later, Khan and Bau reported an X-ray diffraction study of $(C_6H_5)_3Cr{\cdot}3THF$.[42c] The Cr atom, as expected, is octahedrally coordinated by the six ligands; the molecule is in a cis(facial) configuration (Figure 5). Thes authors also improved the synthesis of $(C_6H_5)_3Cr{\cdot}3THF$. By carrying out the $C_6H_5MgBr/CrCl_3{\cdot}3THF$ reaction for longer times (24–30 h rather than 4 h) at −30 °C, they obtained a product that was magnesium halide free.

Removal of solvent from $(C_6H_5)_3Cr{\cdot}3THF$ or $(C_6H_5)_3Cr{\cdot}3MgBrCl{\cdot}6THF$ by mild heating (20–40 °C) at 0.05 mmHg for 2–4 h produced a black, pyrophoric, paramagnetic solid which was soluble in THF but insoluble in Et_2O. Hydrolysis of the black solid in oxygen-free water, followed by benzene extraction, gave neutral bis(arene)chromium complexes. These were quantified by air oxidation in aqueous medium and precipitation of the bis(arene)chromium cations as the tetraphenylborates. A roughly 1:1 mixture of $(C_6H_6)_2Cr^+$ and $(C_6H_6)(C_6H_5C_6H_5)Cr^+$, together with a trace amount of $(C_6H_5C_6H_5)_2Cr^+$, was obtained in about 20–22% yield. The same black solid was obtained when either solid $(C_6H_5)_3Cr{\cdot}3THF$ or its mixture with magnesium halides was added to a large volume of diethyl ether or when $(C_6H_5)_3Cr{\cdot}3THF$ was heated to 85 °C under nitrogen at atmospheric pressure. The nature and structure of the black solid were (and still are) unknown. Interestingly, its treatment under nitrogen with D_2O gave $(C_6H_5D)_2Cr$ and $(C_6H_5D)(C_6H_5C_6H_5)Cr$, while it (as the product of the reaction of $CrCl_3$ with C_6H_5MgBr in diethyl ether) reacted with carbon dioxide to produce red-orange $(C_6H_5C_6H_5)Cr(C_6H_5CO_2H)$.[43] Triphenylchromium–tris(tetrahydrofuran) was important not only in its own right as a long-sought molecule but also as the now recognized initial intermediate on the way to Hein's bis(π-arene)chromium complexes. Herwig and Zeiss explained the σ-to-π rearrangement in terms of a radical process with π-bonded radical intermediates of the type $(C_6H_5^{\bullet})_2Cr$ and $(C_6H_5^{\bullet})(C_6H_5C_6H_5)Cr$. However, this explanation was only a tentative one, and later work (vide infra) led to an alternate mechanism. The reaction of *p*-tolylmagnesium bromide with $CrCl_3$ in diethyl ether provided an answer to the question as to whether the biphenyl ligand in $(C_6H_6)(C_6H_5C_6H_5)Cr^+$ and $(C_6H_5C_6H_5)_2Cr^+$ in Hein's synthesis was formed by ortho or by para coupling of two phenyl groups within the organochromium intermediate.[44] The products were toluene, *p,p′*-bitolyl, and a mixture of bis(arene) π complexes from which $(CH_3C_6H_5)_2Cr^+$ (as the $B(C_6H_5)_4^-$ salt) could be isolated. In a separate experiment, the bis(arene)chromium tetraphenylborates were pyrolyzed, giving toluene and *p,p′*-bitolyl in addition to benzene and biphenyl from the tetraphenylborate anion. Thus, it is para coupling which occurs.

A remarkably unreactive triarylchromium compound, **4**, was prepared by the Grignard procedure and structurally characterized by X-ray cyrstallography.[45] It was found to be inert to oxygen, water, methanol, ketones, nitriles, and ethylene oxide, in contrast to the high reactivity of $(C_6H_5)_3Cr{\cdot}3THF$. The dioxolano ligands apparently shield the Cr atom from attack by these reagents.



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The reaction of C_6H_5MgBr with chromium(II) chloride, $CrCl_2$, in diethyl ether, carried out by Tsutsui while he was with Zeiss in the Monsanto laboratories in Dayton,[46] gave results very similar to those obtained with $CrCl_3$. Hydrolysis of the reaction mixture under nitrogen led to the formation of a 3:2 mixture of $(C_6H_6)_2Cr$ and $(C_6H_6)(C_6H_5C_6H_5)Cr$. In this case, $(C_6H_5)_2Cr$ was suggested to be the initial intermediate.

Triarylchromium compounds were found by Zeiss and co-workers to be useful reagents for the synthesis of mono- and polynuclear aromatic hydrocarbons.[47] A rapid reaction occurred when 2-butyne was added to solid $(C_6H_5)_3Cr{\cdot}3THF$. The nature of the products was found

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(43) Burger, T. F.; Zeiss, H. *Chem. Ind. (London)* **1962**, 183.

(44) Sneeden, R. P. A.; Zeiss, H. H.; Anderes, A. *J. Organomet. Chem.* **1965**, *4*, 355.

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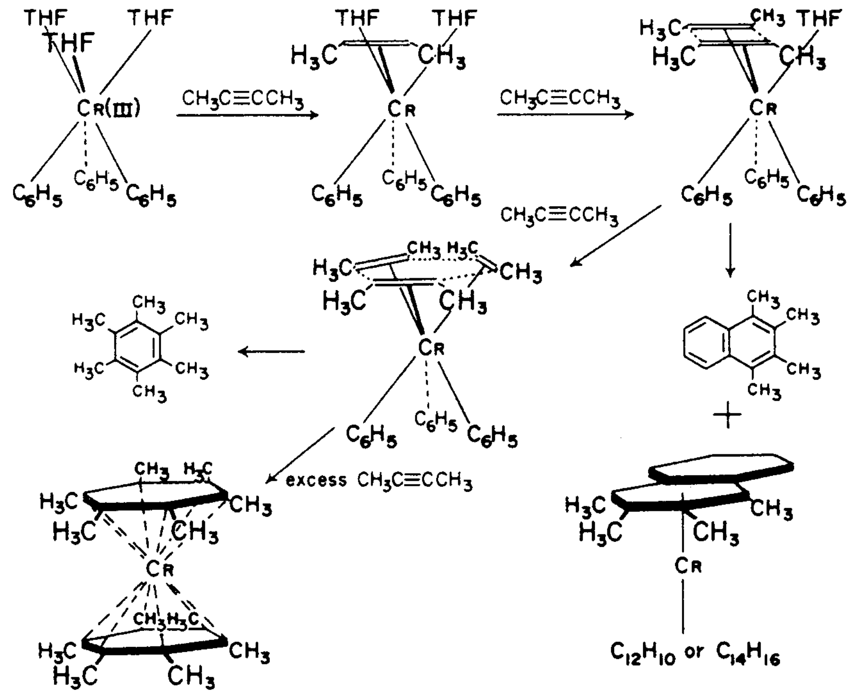
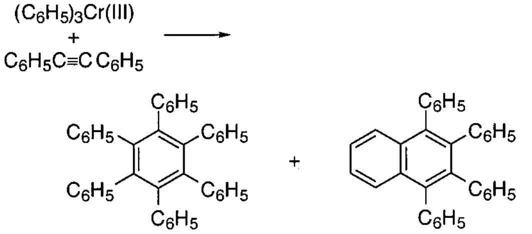
Scheme 1[a]



[a] From ref 47.

to depend on the stoichiometry used. When 4 molar equiv of the acetylene with respect to 1 equiv of the chromium compound was used, the products were 1,2,3,4-tetramethylnaphthalene and its Cr π complex.[47c] When 6 molar equiv of 2-butyne was used, hexamethylbenzene (50−55%) and 1,2,3,4-tetramethylnaphthalene (38−40%) were obtained. With a still larger excess (~20 molar equiv) of the acetylene, the π-complexes of the last two products were produced as well. The suggested reaction course is shown in Scheme 1. The reaction that occurred when diphenylacetylene was used is shown in eq 13. Tri-α- and tri-β-naphthylchromium reacted with 2-butyne as shown in eq 14. It was found that prior isolation of the triarylchromium compound was not necessary. Thus, 2-butyne was cyclized in a rapid reaction when it was added to a mixture of Mg powder, bromobenzene, and $CrCl_3 \cdot 3THF$. Cyclization of diphenylacetylene also could be effected with diphenylchromium.[48] A similar reaction which gave bis(hexamethylbenzene)chromium was reported by Wilke and Kröner.[49] A heterogeneous 1,3-butadiene cyclooligomerization catalyst, prepared by the action of triethylaluminum on chromyl chloride in benzene, reacted with 2-butyne in benzene at room temperature. Treatment of the reaction mixture with 2 N HCl in the absence of air and subsequent reduction with Al/Mg alloy resulted in formation of orange-brown $(C_6(CH_3)_6)_2Cr$.

Triphenylchromium−tris(tetrahydrofuran) also reacted with olefins that were capable of complexing with chromium in the sense of a phenylation reaction.[50] For instance, its reaction at room temperature with bicyclo[2.2.1]heptadiene-2,5 resulted in formation of the mono- and diphenylated bicyclo[2.2.1]heptene-2, while a reaction with maleic anhydride proceeded as shown in eq 15. As was expected, triphenylchromium•3THF reacted with ketones in THF at room temperature.[51] With diethyl ketone, nearly equal amounts of phenyldiethylcarbinol and 5-ethyl-4-methyl-3-phenyl-3,5-heptanediol were obtained. With cyclohexanone, the products were 1-phenylcyclohexanol, a diol believed to be 1-phenyl-2-(1-hydroxycyclohexyl)cyclohexanol, and 2-cyclohexenylcyclohexanone. All of the phenyl groups of $(C_6H_5)_3Cr$ were accounted for in the first two products. Thus, it



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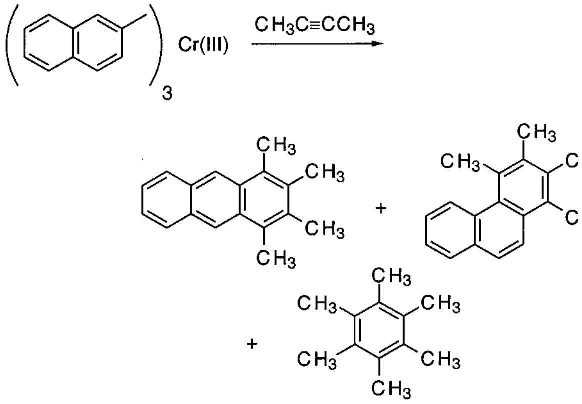

(14)

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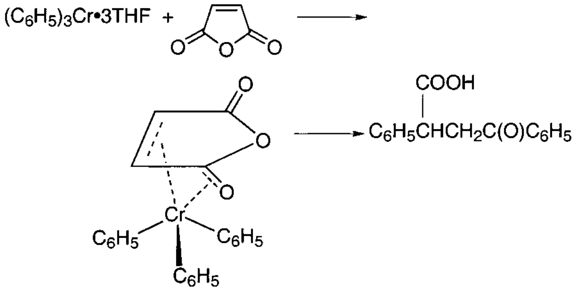
(47) (a) Zeiss, H. H.; Herwig, W. *J. Am. Chem. Soc.* **1958**, *80*, 2913. (b) Metlesics, W.; Zeiss, H. *J. Am. Chem. Soc.* **1959**, *81*, 4117. (c) Herwig, W.; Metlesics, W.; Zeiss, H. *J. Am. Chem. Soc.* **1959**, *81*, 6203. (d) Sneeden, R. P. A.; Zeiss, H. *J. Organomet. Chem.* **1969**, *20*, 153. (e) Sneeden, R. P. A.; Zeiss, H. H. *J. Organomet. Chem.* **1972**, *40*, 163.

(48) Tsutsui, M.; Zeiss, H. *J. Am. Chem. Soc.* **1960**, *82*, 6255.

(49) Wilke, G.; Kröner, M. *Angew. Chem.* **1959**, *71*, 574.

(50) Metlesics, W.; Wheatley, P. J.; Zeiss, H. *J. Am. Chem. Soc.* **1962**, *84*, 2327.

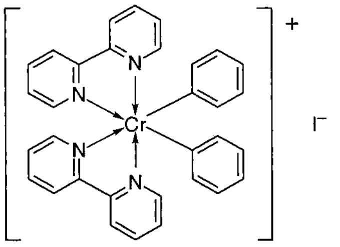
(51) Sneeden, R. P. A.; Burger, T. F.; Zeiss, H. H.; Anderes, A. *J. Organomet. Chem.* **1965**, *4*, 397.



(15)

appears that the $(C_6H_5)_3Cr$/ketone reactions proceed differently from those of the phenyl Grignard reagent. When carbon monoxide was bubbled into a THF solution of $(C_6H_5)_3Cr{\cdot}3THF$ at room temperature, a mildly exothermic reaction occurred. After hydrolysis of the reaction mixture, benzopinacol, $(C_6H_5)_2C(OH)C(OH)(C_6H_5)_2$, was isolated in essentially quantitative yield. It was suggested that CO had inserted into the C_6H_5-Cr bond, giving intermediates of the type $[C_6H_5C(O)]_n(C_6H_5)_{3-n}Cr$.[51]

Once it was known that triarylchromium compounds were stable when coordinated with THF, a good Lewis base, it seemed reasonable to prepare other, even more stable σ-bonded organochromium compounds using stronger Lewis bases. Particularly effective in this regard was 2,2′-bipyridyl. Among the stable mono- and diarylchromium halide complexes prepared in Zeiss' laboratory were p-$CH_3C_6H_4CrCl_2{\cdot}3THF$,[52] [*cis*-$(C_6H_5)_2Cr(2,2'\text{-bipy})_2]I$[53] (**5**), [*cis*-$Ar_2Cr(2,2'\text{-bipy})_2]I$ (Ar = 2-, 3-, 4-$CH_3OC_6H_4$, 4-$CH_3C_6H_4$, C_6H_5),[54] and [*cis*-$(2\text{-}CH_3OC_6H_4)_2Cr(2,2'\text{-bipy})_2]I{\cdot}H_2O$,[55] as well as the benzyl derivatives $C_6H_5CH_2Cr(py)_3Cl_2$ and 2- and 4-$ClC_6H_4CH_2Cr(py)_3Cl_2$[56] and the dialkyl compound $[(Me_3SiCH_2)_2Cr(2,2'\text{-bipy})_2]I$.[57] For some of these the structures were determined by X-ray crystallography.[52,53,55,57]



5

Trialkylchromium compounds were found to be much less stable than the triaryl analogues. For example, tri-n-decylchromium is only moderately stable in THF at −40 °C. n-Decylchromium dichloride, on the other hand, is moderately stable at 0 °C.[58] Alkylchromium systems, their preparation, their fragmentation upon thermal decomposition, their reactions with dienes and acetylenes, etc. were studied extensively in the Zürich laboratories by Zeiss and co-workers, but this aspect of Zeiss' research is outside the scope of this essay. Some reviews[59−61] and two books[62,63] provide more details of Zeiss' work in organochromium chemistry.

As we come to the end of our account of Zeiss' work in organochromium chemistry, we take special note again of two of his contributions that stand out as ones of great importance in the history of organometallic chemistry: providing the solution to the mystery of Hein's "polyphenylchromium complexes", that they are bis(η^6-arene) complexes of chromium, and the preparation of the long-sought triphenylchromium (as the tris-THF adduct) and the demonstration that it is the initial intermediate on the way to the bis(η^6-arene)chromium complexes.

VII. Hein and His Students at the University of Jena Revisit Old and Develop New Organochromium Chemistry. 1956−1970s

It must have been a great disappointment for Franz Hein that others solved the mystery of the constitution and structure of the chromium compounds on which he had worked so long. He was gracious in his remarks about the Fischer/Seus synthesis of bis(biphenyl)chromium and the derived cation[10] and then, with his students at the University of Jena, in 1956 returned to organochromium chemistry in a vigorous research program (Figure 6).

Fischer and Seus had demonstrated that the bis(biphenyl)chromium(I) iodide obtained from bis(biphenyl)chromium prepared by the reductive Friedel−Crafts procedure was identical with Hein's "$(C_6H_5)_4CrI$". Hein did the same for "$(C_6H_5)_3CrI$".[64] The reaction of $CrCl_3$, $AlCl_3$, and Al powder with a mixture (6:5 by weight) of biphenyl and benzene at atmospheric pressure at 140 °C (using a cold condenser to retain the benzene in the reaction system) gave (as expected) a mixture of all three possible products (isolated as the iodides): $[(C_6H_6)_2Cr]I$, $[(C_6H_6)(C_6H_5C_6H_5)Cr]I$, and $[(C_6H_5C_6H_5)_2Cr]I$. The mixed (benzene)(biphenyl)chromium iodide was indeed identical with the "$(C_6H_5)_3CrI$" first reported in 1921. An improved Grignard procedure was developed which gave better yields of $[(C_6H_6)(C_6H_5C_6H_5)Cr]I$, which, it was found, could be reduced to $(C_6H_6)(C_6H_5C_6H_5)Cr$ not only with dithionite but also with $H_2Fe(CO)_4$.[65] In contrast, $Fe(CO)_5$ acted as an oxidizing agent on reaction with $(C_6H_5C_6H_5)_2Cr$, giving $[(C_6H_5C_6H_5)_2Cr][Fe_4(CO)_{13}]$.[66]

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(52) (a) Daly, J. J.; Sneeden, R. P. A.; Zeiss, H. H. *J. Am. Chem. Soc.* **1966**, *88*, 4287. (b) Daly, J. J.; Sneeden, R. P. A. *J. Chem. Soc. A* **1967**, 736.

(53) Daly, J. J.; Sanz, F.; Sneeden, R. P. A.; Zeiss, H. H. *J. Chem. Soc., Dalton Trans.* **1973**, 73.

(54) Sneeden, R. P. A.; Zeiss, H. H. *J. Organomet. Chem.* **1973**, *47*, 125.

(55) Daly, J. J.; Sanz, F. *J. Chem. Soc., Dalton Trans.* **1972**, 2584.

(56) (a) Sneeden, R. P. A.; Throndsen, H. P. *Chem. Commun.* **1965**, 509. (b) *J. Organomet. Chem.* **1966**, *6*, 542.

(57) (a) Daly, J. J.; Sanz, F.; Sneeden, R. P. A.; Zeiss, H. H. *Helv. Chim. Acta* **1973**, *56*, 503. (b) *J. Chem. Soc., Dalton Trans.* **1973**, 1497.

(58) Sneeden, R. P. A.; Zeiss, H. H. *J. Organomet. Chem.* **1968**, *13*, 369.

(59) Zeiss, H. Arene Complexes of the Transition Metals. In *Organometallic Chemistry*; Zeiss, H., Ed.; ACS Monograph Series 147; Reinhold: New York, 1960; pp 380−425.

(60) Zeiss, H. H. *Bull. Soc. Chim. Fr.* **1963**, *7*, 1500.

(61) Zeiss, H. H.; Sneeden, R. P. A. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 435.

(62) Zeiss, H.; Wheatley, P. J.; Winkler, H. J. S. *Benzenoid-Metal Complexes*; Ronald Press: New York, 1966.

(63) Sneeden, R. P. A. *Organochromium Compounds*; Academic Press: New York, 1975. (Raymond Sneeden (1927−2001) was the main organochromium researcher in the Zürich laboratory. He studied chemistry at the University of Glasgow and received his Ph.D. from the University of Oxford in 1959. He joined the Monsanto Research Laboratory in Zürich in the same year. After the Monsanto Laboratory closed in 1975, he was last employed in the Institut de Recherches sur la Catalyse in France.)

(64) Hein, F.; Eisfeld, K. *Z. Anorg. Allg. Chem.* **1957**, *292*, 162.

Figure 6. Franz Hein (1955) (reproduced courtesy of the Archives, Deutsche Akademie der Naturforscher Leopoldina, Erna Lämmel, Director).

Both paper chromatography[67] and column chromatography[68] were found to be effective in the analysis and separation of bis(arene)chromium salts. Column chromatography was used in the analysis of Hein's original "crude bromide".[69]

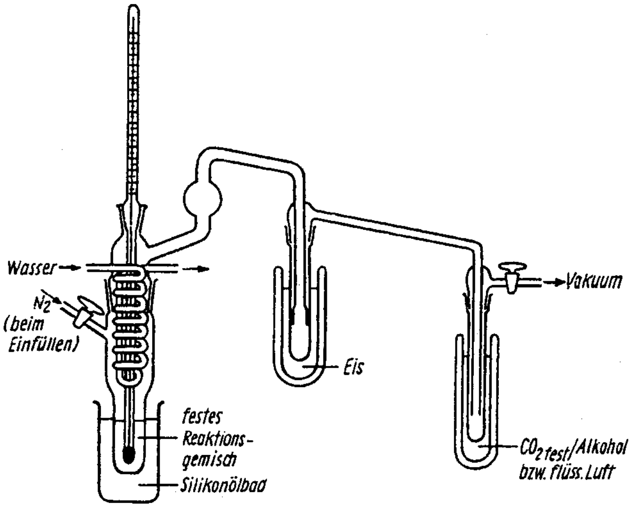

Figure 7. Kartte's apparatus for his study of the arene displacement reactions of bis(arene)chromium complexes (from ref 70, reproduced by permission of Wiley-VCH).

In view of the presence of $AlCl_3$ in the reductive Friedel−Crafts synthesis of bis(arene)chromium complexes, the studies of Hein and Kartte of the action of $AlCl_3$ on such complexes were of interest. The $AlCl_3$-catalyzed arene ligand exchange reactions between a bis(arene)chromium and a free arene, e.g., eqs 16 and 17, were examined in detail by Kartte using the ap-

$$(C_6H_6)(C_6H_5C_6H_5)Cr + C_6H_5C_6H_5 \underset{115\ °C}{\overset{AlCl_3}{\rightleftharpoons}} (C_6H_5C_6H_5)_2Cr + C_6H_6 \quad (16)$$

$$(C_6H_6)(C_6H_5C_6H_5)Cr + C_6H_6 \underset{80\ °C}{\overset{AlCl_3}{\rightleftharpoons}} (C_6H_6)_2Cr + C_6H_5C_6H_5 \quad (17)$$

paratus shown in Figure 7 and were found to be equilibrium processes.[70] This arene displacement reaction worked well with tetralin, mesitylene, and *p,p′*-ditolyl but was not generally applicable. Such reactions were unsuccessful with fluorene, phenylcyclohexane, diphenylmethane, dibenzyl, and stilbene, possibly due to steric problems. Polynuclear aromatic hydrocarbons and halogenated aromatic hydrocarbons also did not react with $(C_6H_6)(C_6H_5C_6H_5)Cr$ in the presence of $AlCl_3$. It was found that the bis(arene)chromium complexes that contain two different arene ligands can disproportionate in the presence of $AlCl_3$ (eq 18). This also is an

$$2(C_6H_6)(C_6H_5C_6H_5)Cr \overset{AlCl_3}{\rightleftharpoons} (C_6H_6)_2Cr + (C_6H_5C_6H_5)_2Cr \quad (18)$$

equilibrium reaction, and as expected, a mixture of bis(benzene)chromium and bis(biphenyl)chromium underwent $AlCl_3$-induced thermal equilibration to give some $(C_6H_6)(C_6H_5C_6H_5)Cr$. The reaction course and the intermediates involved are unclear. The action of $AlCl_3$ on $(C_6H_5C_6H_5)_2Cr$ in benzene resulted in formation of a solid that Hein and Kartte wrote as $[(C_6H_5C_6H_5)_2Cr][AlCl_4]$ (i.e., a Cr(I) complex) on the basis of elemental analysis. However, further investigation of this product gave ambiguous results, some indicating that it was a Cr(0) complex and others that it was a mixture of Cr(0) and Cr(I) complexes, with the latter predominating. Hein and Kartte concluded that $AlCl_3$ oxidized the Cr(0) complex with formation of metallic aluminum (eq 19).

$$3(\text{arene})_2Cr + 4AlCl_3 \rightarrow 3[(\text{arene})_2Cr][AlCl_4] + Al \quad (19)$$

It was found that the $[(C_6H_5C_6H_5)_2Cr][AlCl_4]$ complex undergoes arene ligand exchange only in the presence of an excess of $AlCl_3$ (at least 1 molar equiv). Thus, the $(\text{arene})_2Cr$ + arene′ displacement reaction is more complicated than had been expected.[71] Boron trifluoride and phosphorus trichloride also oxidized $(C_6H_5C_6H_5)_2Cr$, giving $[(C_6H_5C_6H_5)_2Cr][BF_4]$ and $[(C_6H_5C_6H_5)_2Cr]Cl$, respectively.[72]

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(65) Hein, F.; Kleinert, P.; Kurras, E. *Z. Anorg. Allg. Chem.* **1957**, *289*, 229.
(66) Hein, F.; Reinert, H. *Chem. Ber.* **1960**, *93*, 2089.
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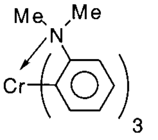
(68) Hein, F.; Fischer, K. W. *Z. Anorg. Allg. Chem.* **1956**, *288*, 279.
(69) Hein, F. *Ber. Dtsch. Chem. Ges.* **1921**, *54*, 1908.
(70) Hein, F.; Kartte, K. *Z. Anorg. Allg. Chem.* **1960**, *307*, 22.
(71) Hein, F.; Kartte, K. *Z. Anorg. Allg. Chem.* **1960**, *307*, 52.
(72) Hein, F.; Kartte, K. *Z. Anorg. Allg. Chem.* **1960**, *307*, 89.

In aqueous solution, under an inert atmosphere, $[(C_6H_5C_6H_5)_2Cr]Cl$ was found to undergo a slow, UV-induced valence disproportionation (eq 20). A complication was the chemical reduction of the as yet unreacted Cr(I) complex by the Cr^{2+} formed in the initial reaction.[73]

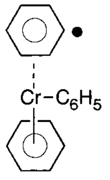
$$[(C_6H_5C_6H_5)_2Cr]Cl \xrightarrow{UV} (C_6H_5C_6H_5)_2Cr + CrCl_2 + 2C_6H_5C_6H_5 \quad (20)$$

Two of Hein's students, Günter Stolze and Johannes Hähle, carried out an extensive study of the preparation of σ-bonded triarylchromium compounds and their conversion to the respective bis(π-arene) complexes. The following $Ar_3Cr{\cdot}n$THF compounds were reported: $(p\text{-}FC_6H_4)_3Cr{\cdot}3THF$, $(p\text{-}ClC_6H_4)_3Cr{\cdot}3.5THF$, $(m\text{-}ClC_6H_4)_3Cr{\cdot}3THF$, $(p\text{-}C_6H_5C_6H_4)_3Cr{\cdot}3THF$, $(p\text{-}BrC_6H_4)_3Cr{\cdot}3THF$, $(p\text{-}CH_3C_6H_4)_3Cr{\cdot}4THF$, $(m\text{-}CH_3C_6H_4)_3Cr{\cdot}3THF$, and $(2\text{-}C_4H_3S)_3Cr{\cdot}3THF$.[74] All, like $(C_6H_5)_3Cr{\cdot}3THF$, are air- and moisture-sensitive, red, crystalline solids with magnetic susceptibilities indicative of the presence of three unpaired electrons. The *p*- and *m*-tolyl and the biphenylyl compounds were found to undergo the solvent-induced (Et_2O, dioxane, C_6H_6) σ-to-π conversion more readily than $(C_6H_5)_3Cr{\cdot}3THF$, while the halophenyl compounds and tris(2-thienyl)Cr·3THF merely dissolved in these solvents without reaction, very likely because their Cr–C bonds are stronger. In the successful solvent-induced reactions, the organochromium products were the respective bis(arylarene)chromium and, in each case, a black product of the type observed by Herwig and Zeiss with $(C_6H_5)_3Cr{\cdot}3THF$. Hydrolysis of these solids gave the respective bis(arene)chromium and (arene)(arylarene)chromium complexes. Hein and Tille prepared an interesting triarylchromium compound, the red, crystalline **6**.[75] This compound did not form a THF adduct. Apparently, the dimethylamino groups donated their lone electron pairs to the Cr atom. As a result compound **6** was much more stable toward ambient air and was solvolyzed only slowly by alcohol. Trimesitylchromium–tetrahydrofuran in the form of dark blue crystals was prepared by the Grignard procedure.[76] The tris-THF adduct is sterically impossible, and Tsutsui's claim to have prepared it[77] is incorrect. $(2,4,6\text{-}(CH_3)_3C_6H_2)_3Cr{\cdot}THF$ is extremely air- and moisture-sensitive in solution. Removal of the THF at 80 °C in vacuo resulted in complete decomposition. In benzene and dioxane solution, THF dissociation occurred according to cryoscopic measurements. A σ-to-π conversion was not observed. Also prepared was dimesitylchromium–tris(tetrahydrofuran) by the action of mesitylmagnesium bromide on $CrCl_2$ in THF.[78] Isolated as air- and moisture-sensitive violet crystals, the compound lost two of its THF ligands on addition of hexane. Redistribution occurred on reaction with $CrCl_2$ in THF to give light blue crystals of $(2,4,6\text{-}(CH_3)_3C_6H_2)CrCl{\cdot}2THF$.

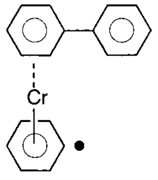


6

The question of the mechanism of the σ-to-π conversion of a triarylchromium compound to the three possible (π-arene)chromium complexes, $(arene)_2Cr$, (arene)(arylarene)Cr, and $(arylarene)_2Cr$, has been one that engaged all of the early workers in the field. Zeiss considered the possibility of radical intermediates in the case of triphenylchromium–tris(tetrahydrofuran), **7a** and **7b**.[59] Tsutsui also favored radical intermediates, talking about "π-radical hybridization"[77,79] and "proximity effects in arene π-complex formation."[80] Hähle and Stolze[81] showed that the first step in the σ-to-π conversion of $(C_6H_5)_3Cr{\cdot}3THF$ is the reversible loss of a THF ligand to give the green, crystalline $(C_6H_5)_3Cr{\cdot}2THF$. The latter, as the solid, slowly decomposed to a black solid with concurrent decrease in the magnetic susceptibility. Treatment of $(C_6H_5)_3Cr{\cdot}3THF$ with diethyl ether under an inert atmosphere ultimately led to decomposition with formation of $(C_6H_5C_6H_5)_2Cr$, biphenyl, and benzene, as well as the "black solid". Hydrolysis or methanolysis of the latter in the absence of air then gave $(C_6H_6)_2Cr$ and $(C_6H_6)(C_6H_5C_6H_5)Cr$, benzene, H_2, THF, and $Cr(OH)_3$. Treatment of the "black solid" with D_2O gave D_2 and monodeuterated products, $(C_6H_6)(C_6H_5D)Cr$ and $(C_6H_5D)(C_6H_5C_6H_5)Cr$, as Zeiss and Herwig[42] had found. The "black solid" had a magnetic moment of 1.15 μ_B, indicating the presence of low-valent Cr. Hähle and Stolze wrote the "mechanism" shown in Scheme 2 for the conversion of $(C_6H_5)_3Cr{\cdot}3THF$ to the π-arene products. A more detailed (and complicated) discussion of the σ-to-π conversion, based on the 1965 Ph.D. dissertations of Hähle and Stolze, was given by Uhlig in his excellent review "Seventy-five Years of π-Complexes of Chromium(I)."[82] This is probably the last word on the subject of the mechanism of the $(C_6H_5)_3Cr{\cdot}3THF$ to (π-arene)chromium conversion, unless new experimental results become available. As Uhlig noted,[82] "the oily, highly air-sensitive, dark solids" and the product solutions "are difficult and unpleasant to handle, and a final answer may be long in coming." However, the work by Zeiss and co-workers at Monsanto and by Hähle and Stolze in Jena was carried out without the benefit of mass spectroscopy, ESR, liquid chromatography, and other more modern techniques, so perhaps there still is opportunity to probe more deeply.



7a



7b

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(73) Hein, F.; Scheel, H. *Z. Anorg. Allg. Chem.* **1961**, *312*, 264.

(74) (a) Hein, F.; Hähle, J.; Stolze, G. *Monatsber. Dtsch. Akad. Wiss. Berlin* **1963**, *5*, 528. (b) Stolze, G.; Hähle, J. *J. Organomet. Chem.* **1966**, *5*, 545.

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(76) Stolze, G. *J. Organomet. Chem.* **1966**, *6*, 383.

(77) Tsutsui, M. *Z. Chem.* **1963**, *3*, 215.

(78) Stolze, G.; Hähle, J. *J. Organomet. Chem.* **1967**, *7*, 301.

(79) (a) Tsutsui, M.; Chang, G. *Can. J. Chem.* **1963**, *41*, 1255. (b) Tsutsui, M.; Hancock, M.; Ariyoshi, J.; Levy, M. N. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 410. (c) Hancock, M.; Levy, M. N.; Tsutsui, M. *Organomet. React.* **1972**, *4*, 1.

(80) Tsutsui, M.; Levy, M. N. *Z. Naturforsch.* **1966**, *21b*, 823.

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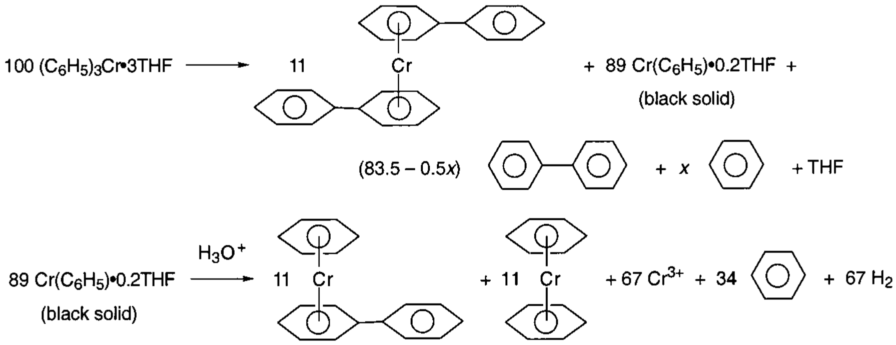
Scheme 2



Hein's original purpose when he started his organochromium research in 1918 was to prepare σ-bonded organic derivatives of Cr(III). As was found by Herwig and Zeiss, such compounds are stable enough to permit their isolation when they are bonded to 3 mol of a Lewis base: e.g., $(C_6H_5)_3Cr{\cdot}3THF$. Other such $(C_6H_5)_3Cr$/Lewis base adducts were prepared later in Jena: $(C_6H_5)_3Cr(THF)(bipy)$,[83] $(C_6H_5)_3Cr(THF)(o\text{-}phen)$,[83] $(C_6H_5)_3Cr[P(C_6H_5)R_2]_2$ ($R = C_2H_5$, $n\text{-}C_4H_9$),[84] $(C_6H_5)_3Cr(P(C_2H_5)_3)_2$,[84] and $(C_6H_5)_3Cr{\cdot}1.75CH_3OCH_2CH_2OCH_3$.[85]

In view of the existence of the neutral $(C_6H_5)_3Cr{\cdot}3THF$ adduct, it should have been expected that analogous stable adducts of $(C_6H_5)_3Cr$ with negatively charged Lewis bases could be prepared, and indeed, this turned out to be the case. The reaction of phenyllithium in diethyl ether with anhydrous $CrCl_3$, with scrupulous exclusion of air and moisture during all operations, was reported by Hein and Weiss to give a red-yellow, crystalline solid whose elemental analysis indicated a formulation that they wrote as $3C_6H_5Li{\cdot}Cr(C_6H_5)_3{\cdot}2.5(C_2H_5)_2O$.[86] The product was extremely air- and moisture-sensitive. Its hydrolysis gave only benzene, but curiously, its oxidation with air or iodine gave biphenyl (eq 21). Measurement of its magnetic susceptibility

$$Li_3Cr(C_6H_5)_6 + {}^9/_2I_2 \rightarrow 3C_6H_5I + {}^3/_2C_6H_5C_6H_5 + 3LiI + CrI_3 \quad (21)$$

indicated the presence of Cr(III). Its solubility in diethyl ether and benzene led Hein to suggest that the product was not particularly salt-like. In any case, the compound contained at least three Cr–C σ bonds, and Hein called it a "genuine" organochromium compound (the title of the paper[86] was "Zur Existenz echter Organochromverbindungen").

The discovery of $Li_3Cr(C_6H_5)_6{\cdot}2.5(C_2H_5)_2O$ (as Hein subsequently wrote it) opened up a fertile new area of organochromium chemistry, that of the polyphenyl- and polyalkylchromates in which the valence state of chromium usually is III but can be II. Like the neutral $(C_6H_5)_3Cr{\cdot}3THF$, some of these anionic (σ-phenyl)chromium compounds can be converted to bis(arene)chromium complexes. A crystal structure of $Li_3Cr(C_6H_5)_6$ was not available at that time, but the analogous methyl derivative, $Li_3Cr(CH_3)_6{\cdot}3(dioxane)$,[87a,b] was shown in an X-ray diffraction study to have octahedral coordination of the six CH_3 groups about the Cr atom with the CH_3 groups bridging to the three Li atoms (Figure 8).[87c] The structure of $Li_3Cr(C_6H_5)_6{\cdot}3Et_2O$ was reported by Olmstead, Power, and Shoner in 1988.[88] The Cr atom is octahedrally coordinated by the six phenyl substituents, and all Cr–C bonds are bridging to the three Li atoms (Figure 9). This explains the observed solubility of the hexaphenyl complex. The analogous $Na_3Cr(C_6H_5)_6{\cdot}n(C_2H_5)_2O$ also has been prepared.[89] This yellow compound, however, was found to be unstable; it readily lost 1 mol of C_6H_5Na to give the stable, but pyrophoric, blue-green $Na_2Cr(C_6H_5)_5{\cdot}3(C_2H_5)_2O$. The instability of $Na_3Cr(C_6H_5)_6$ vs the stability of $Li_3Cr(C_6H_5)_6$ is surprising. It may be that the greater stability of $Li_3Cr(C_6H_5)_6$ is due

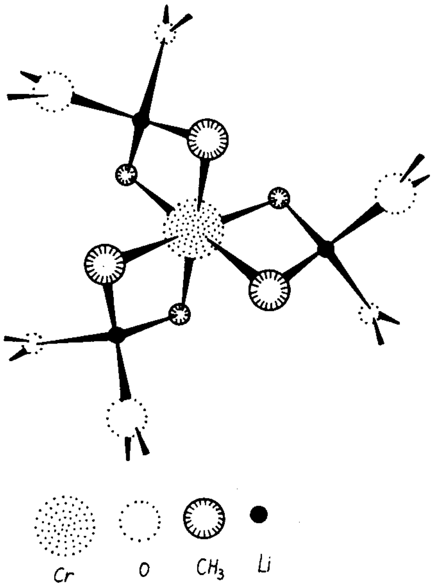


Figure 8. Molecular structure of $Li_3Cr(CH_3)_6{\cdot}3(dioxane)$ (from ref 87c, reproduced by permission of Elsevier Science).

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[83] Müller, H. *Z. Chem.* **1968**, *8*, 67.

[84] Schmiedeknecht, K.; Reichardt, W.; Seidel, W. *Z. Chem.* **1971**, *11*, 432.

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[87] (a) Kurras, E.; Otto, J. *Monatsber. Dtsch. Acad. Wiss. Berlin* **1963**, *5*, 705. (b) *J. Organomet. Chem.* **1965**, *4*, 114. (c) Krausse, J.; Marx, G.; Schödl, G. *J. Organomet. Chem.* **1970**, *21*, 159. (d) Krausse, J.; Marx, G. *J. Organomet. Chem.* **1974**, *65*, 215. See, however: Hao, S.; Gambarotta, S.; Bensimon, C. *J. Am. Chem. Soc.* **1992**, *114*, 3556. Hao, S.; Song, J.-I.; Berno, P.; Gambarotta, S. *Organometallics* **1994**, *13*, 1326.

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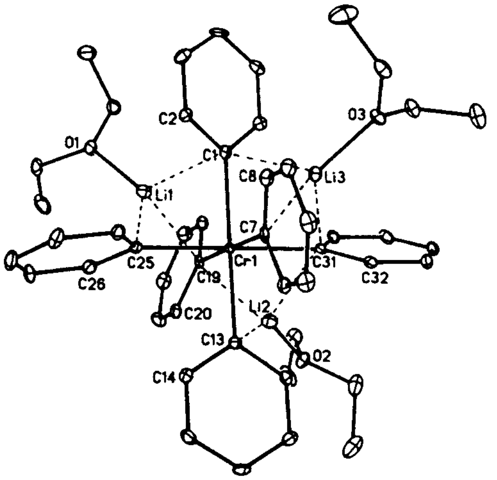

Figure 9. Molecular structure of $Li_3Cr(C_6H_5)_6{\cdot}3Et_2O$ (from ref 88).

to stronger Li···C···Cr three-center–two-electron bonds (vs Na···C···Cr). $Na_2Cr(C_6H_5)_5$ also reacted with iodine to produce not only iodobenzene but also biphenyl. An X-ray crystallographic structure determination of $Na_2Cr(C_6H_5)_5{\cdot}3(C_2H_5)_2O{\cdot}THF$ (Figure 10) showed that the five phenyl groups are bonded to Cr in a distorted-trigonal-bipyramidal configuration, with each of the Na atoms surrounded by two oxygen atoms and two phenyl groups.[89b] The phenyl groups appear to bridge the Na and Cr atoms.

Sodium and lithium tetraphenylchromates, cherry-red crystalline solids, were prepared by the reactions shown in eqs 22 and 23.[90] A change in reactant stoichiometry allowed preparation of $(C_6H_5)_3Cr{\cdot}3THF$ (eqs 24 and 25) (DME = $CH_3OCH_2CH_2OCH_3$). Also prepared was $(C_6H_5)_3Cr{\cdot}1.75DME$, which was more stable than the tris-THF adduct; it dissolved in diethyl ether without decomposition to the black solid.

$$4Na_2Cr(C_6H_5)_5 + CrCl_3 \xrightarrow{DME} 5NaCr(C_6H_5)_4{\cdot}4DME + 3NaCl \quad (22)$$

$$2Li_3Cr(C_6H_5)_6 + CrCl_3 \xrightarrow{DME} 3LiCr(C_6H_5)_4{\cdot}4DME + 3LiCl \quad (23)$$

$$3Na_2Cr(C_6H_5)_5 + 2CrCl_3 \xrightarrow{THF} (C_6H_5)_3Cr{\cdot}3THF + 6NaCl \quad (24)$$

$$Li_3Cr(C_6H_5)_6 + CrCl_3 \xrightarrow{THF} 2(C_6H_5)_3Cr{\cdot}3THF + 3LiCl \quad (25)$$

When the quantity of $CrCl_3$ used in reactions with the sodium and lithium polyphenylchromates was increased, phenylchromium chlorides were formed: e.g., eqs 26 and 27.[91]

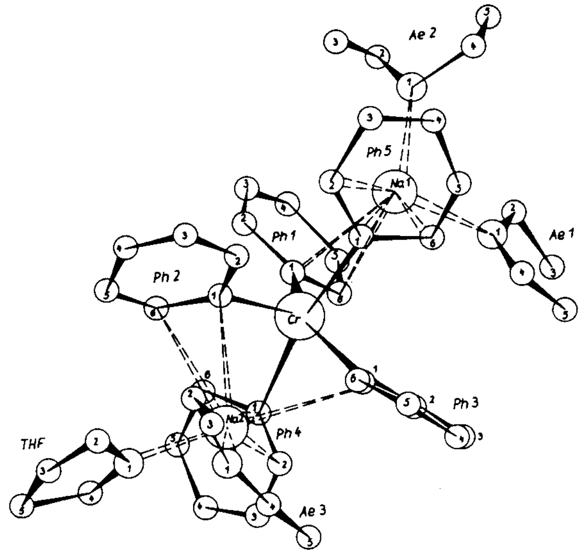

Figure 10. Molecular structure of $Na_2Cr(C_6H_5)_5{\cdot}3(C_2H_5)_2O$ (from ref 89b, reproduced by permission of Elsevier Science).

$$Li_3Cr(C_6H_5)_6 + 5CrCl_3 \xrightarrow{THF} 6C_6H_5CrCl_2{\cdot}3THF + 3LiCl \quad (26)$$

$$2Na_2Cr(C_6H_5)_5 + 3CrCl_3 \xrightarrow{DME} 5(C_6H_5)_2CrCl{\cdot}1.5DME + 3NaCl \quad (27)$$

The reaction of $CrCl_2{\cdot}2THF$ with 4 molar equiv of C_6H_5Li in THF/$(C_2H_5)_2O$ gave the yellow, crystalline Cr(II) compound $Li_2Cr(C_6H_5)_4$, whose magnetic moment of 4.73 μ_B indicated a high-spin configuration. The compound was stable in the absence of air.[92] An X-ray diffraction study, reported in 1990, of $Li_2Cr(C_6H_5)_4{\cdot}4THF$ showed a square-planar coordination of the four phenyl groups about the Cr atom. [92b] The ipso phenyl carbon atoms bridge the Cr atom and the two Li atoms, and two THF oxygen atoms are bonded to each Li atom. Interestingly, the analogous methyl compound $Li_2Cr(CH_3)_4{\cdot}2THF$ differs from $Li_2Cr(C_6H_5)_4$ in that its magnetic moment was only 0.57 μ_B and that it was shown to be a dimer by cryoscopy.[87b] X-ray crystallography confirmed that it is a dimeric complex, $Li_4Cr_2(CH_3)_8{\cdot}4THF$ (Figure 11) with a short (1.980(5) Å) Cr–Cr distance. The presence of a quadruple ($\sigma^2\pi^4\delta^2$) Cr–Cr bond was discussed.[87d] That $Li_2Cr(C_6H_5)_4$ is a monomer apparently is due to steric factors.

Added to these various sodium and lithium polyphenylchromates were the very interesting Cr(II) compounds $NaCr(C_6H_5)_3{\cdot}1.5(C_2H_5)_2O$ and the analogous lithium compound.[93] Both were prepared using a Cr(III) starting material; therefore, a redox process must have produced the Cr(II) products. The suggested reaction course for the formation of $LiCr(C_6H_5)_3$ in diethyl ether is shown in eq 28.

$$4C_6H_5Li + CrCl_3 \rightarrow [LiCr(C_6H_5)_4] + 3LiCl \quad (28a)$$

$$[LiCr(C_6H_5)_4] \rightarrow LiCr(C_6H_5)_3 + 0.5C_6H_5C_6H_5 \quad (28b)$$

The $MCr(C_6H_5)_3$ compounds were isolated as pyrophoric,

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(90) Hein, F.; Schmiedeknecht, K. *J. Organomet. Chem.* **1967**, *8*, 503.

(91) Hein, F.; Schmiedeknecht, K. *Z. Anorg. Allg. Chem.* **1967**, *352*, 138.

(92) (a) Seidel, W.; Fischer, K.; Schmiedeknecht, K. *Z. Anorg. Allg. Chem.* **1972**, *390*, 273. (b) Edema, J. J. H.; Gambarotta, S.; van Bolhuis, F.; Smeets, W. J. J.; Spek, A. L.; Chiang, M. Y. *J. Organomet. Chem.* **1990**, *389*, 47.

(93) Hein, F.; Schmiedeknecht, K. *J. Organomet. Chem.* **1966**, *6*, 45.

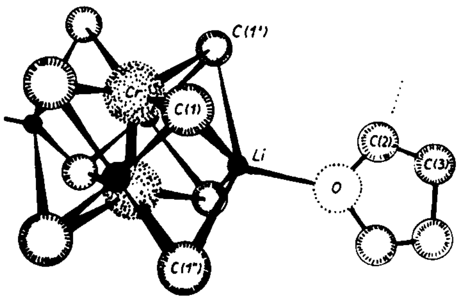


Figure 11. Molecular structure of $Li_4Cr_2(CH_3)_8{\cdot}4THF$ (from ref 87d, reproduced by permission of Elsevier Science).

brown-black solids that dissolved readily in ethereal solvents. Their magnetic moments (0.70 μ_B for the Na compound; 0.62 μ_B for the Li compound) suggested that they were dimeric or possibly polymeric.

The Cr(III) compounds $Na_2Cr(C_6H_5)_5{\cdot}3(C_2H_5)_2O$ and $Li_3Cr(C_6H_5)_6{\cdot}2.5(C_2H_5)_2O$ on reaction with $CrCl_3{\cdot}3THF$ in diethyl ether (3:2 and 1:1 ratios, respectively) gave a brown-black solution whose hydrolysis (in air) resulted in formation of bis(arene)chromium complexes, $(C_6H_6)(C_6H_5C_6H_5)Cr$ and $(C_6H_5C_6H_5)_2Cr$.[93] The suggested process is shown in Scheme 3 with nicely balanced equatios: i.e., a reaction sequence that involves a redox process giving a Cr(II) intermediate. Thus, we have here another example of the conversion of σ-bonded phenylchromium compounds to bis(π-arene)chromium complexes.

Scheme 3

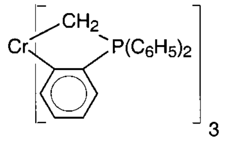
$$\begin{array}{lcll}
20\ Li_3Cr(C_6H_5)_6 + 4\ CrCl_3 & \longrightarrow & 24\ Li_2Cr(C_6H_5)_5 & + 12\ LiCl \\
24\ Li_2Cr(C_6H_5)_5 + 6\ CrCl_3 & \longrightarrow & 30\ [LiCr(C_6H_5)_4] & + 18\ LiCl \\
30\ [LiCr(C_6H_5)_4] & \longrightarrow & 30\ LiCr(C_6H_5)_3 & + 15\ C_6H_5C_6H_5 \\
30\ LiCr(C_6H_5)_3 + 10\ CrCl_3 & \longrightarrow & 40\ [Cr(C_6H_5)_2] & + 5\ C_6H_5C_6H_5 + 30\ LiCl \\
\hline
Li_3Cr(C_6H_5)_6 + CrCl_3 & \longrightarrow & 2\ [Cr(C_6H_5)_2] & + C_6H_5C_6H_5 + 3\ LiCl
\end{array}$$

and finally:

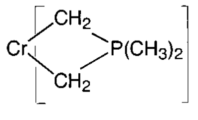
$$[Cr(C_6H_5)_2] \xrightarrow{\text{hydrolysis}} \text{bis(arene)Cr complexes}$$

Erhard Kurras, one of Hein's students, continued research on organochromium chemistry after he left Jena for the DDR Academy of Sciences laboratories in Rostock, and some very interesting transformations that he and co-workers reported are worth a final mention. $Li_3Cr(C_6H_5)_6$ was found to react with methyltriphenylphosphonium halides in THF in the absence of air as shown in eq 29. An analogous reaction with $[(CH_3)_4P]Cl$ gave **8**, which was isolated in the form of extremely air- and moisture-sensitive red needles.[94a] The same products were formed also in reactions of $(C_6H_5)_3Cr{\cdot}3THF$ with $(C_6H_5)_3P{=}CH_2$ and $(CH_3)_3P{=}CH_2$, respectively. Since it was known that $Na_3Cr(C_6H_5)_6$ readily loses 1 mol of C_6H_5Na, similar loss of C_6H_5Li from $Li_3Cr(C_6H_5)_6$ may be possible, and thus the initial step in reaction 29 and in that of $[(CH_3)_4P]Cl$ was suggested to be deprotonation by released C_6H_5Li to give the respective methylenephosphorane,[94b] leaving $Li_2Cr(C_6H_5)_5$. The sequential reactions given in Scheme 4 then may occur to give the final product. Isolation of an intermediate, **8a**, provided evidence in favor of such a reaction course.

$$Li_3Cr(C_6H_5)_6 + 3\ [(C_6H_5)_3PCH_3]Cl \longrightarrow$$



$$+\ 6\ C_6H_6 + 3\ LiCl \qquad (29)$$



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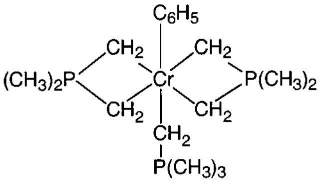
Scheme 4

$$\begin{array}{l}
Li_2Cr(C_6H_5)_5 + (CH_3)_3P{=}CH_2 \longrightarrow (C_6H_5)_5Cr[CH_2P(CH_3)_3]Li_2 \\
(C_6H_5)_5Cr[CH_2P(CH_3)_3]Li_2 \longrightarrow C_6H_6 + (C_6H_5)_4Cr[(CH_2)_2P(CH_3)_2]Li_2 \\
(C_6H_5)_4Cr[(CH_2)_2P(CH_3)_2]Li_2 \rightleftharpoons (C_6H_5)_3Cr[(CH_2)_2P(CH_3)_2]Li + C_6H_5Li \\
\qquad\qquad \text{etc.}
\end{array}$$



8a

With this, the account of the investigations of Franz Hein and his students in organochromium chemistry in the years after the discovery of our cover molecule is at its end. In the period covered in this section (1956–1975), their research at the University of Jena resulted in some very interesting new organochromium chemistry: (1) contributions which led to a better understanding of the conversion of $(C_6H_5)_3Cr$ to the three π-bonded sandwich complexes $(C_6H_6)_2Cr$, $(C_6H_6)(C_6H_5C_6H_5)Cr$, and $(C_6H_5C_6H_5)_2Cr$, (2) the discovery of a completely new class of anionic, σ-bonded phenylchromium(III) and -(II) complexes and the study of their reactivity, which uncovered an alternate σ-to-π rearrangement, and (3) the discovery and the development of the chemistry of new types of neutral and anionic chromium alkyl and allyl derivatives. That this large volume of first-rate work was carried out successfully under difficult conditions—both professional and often personal—during the days of the German Democratic Republic is to the great credit of Franz Hein and his students. Not all of the work carried out at the University of Jena, especially the work of Kurras on alkylchromium systems, has been covered, but the reader will find a good review of organochromium chemistry up to 1972 in Sneeden's book[63] and later work is covered in the appropriate chapters of the first and second editions of *Comprehensive Organometallic Chemistry*.

VIII. A New Synthesis of Bis(arene)chromium Complexes and the Bis(arene)chromium Chemistry Research of Christoph Elschenbroich at the University of Marburg, 1975–.

The metal atom (or metal vapor)/ligand vapor cocondensation procedure is a powerful and versatile method

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(94) (a) Kurras, E.; Rosenthal, U.; Mennenga, H.; Oehme, G. *Angew. Chem.* **1973**, *85*, 913. (b) Kurras, E.; Rosenthal, U. *J. Organomet. Chem.* **1978**, *160*, 35.

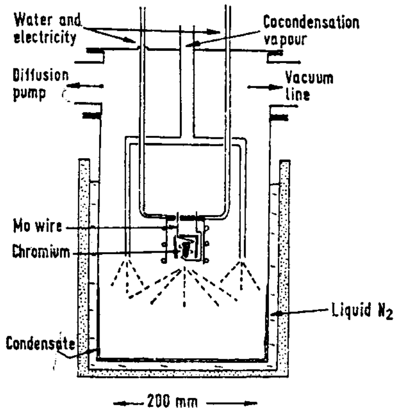

Figure 12. Timms' apparatus for carrying out Cr atom/ligand vapor condensation reactions (from ref 97, reproduced by permission of the Royal Society of Chemistry).

for the preparation of inorganic and organic compounds of the main-group elements and the transition metals.[95] In 1969 Peter Timms (University of Bristol) reported that this procedure could be applied with good success to the preparation of bis(benzene)chromium in 60% yield by the low-temperature reaction of chromium atoms with benzene.[96] In this procedure, metallic chromium was vaporized (as Cr atoms) at 1450 °C in high vacuum from a resistance-heated Mo-wire-wound alumina crucible which was mounted in the center of a stainless steel chamber. The walls of the latter were cooled to −196 °C. During vaporization of the Cr an excess of benzene vapor was sprayed into the steel chamber, where it immediately condensed on the walls, on which the Cr atoms also condensed. During this process the pressure did not exceed 10^{-4} Torr; therefore, there was little in the way of gas-phase reactions. The benzene/Cr atom cocondensate reacted as the chamber was warmed slowly to room temperature. Figure 12 shows a schematic diagram of Timms' apparatus. This new procedure, although using equipment not usually found in a synthetically oriented laboratory and requiring special conditions, had an important advantage over the reductive Friedel−Crafts and Hein Grignard procedures: it could be used to prepare bis(arene)metal complexes of all kinds of functionally substituted arenes, polynuclear aromatic hydrocarbons, and heteroarenes, most of which could not be obtained by the earlier procedures. Once it was known that bis(benzene)chromium could be prepared in good yield by the metal atom/ligand vapor cocondensation procedure, rapid and broad development of the bis(arene)metal complex field followed.

Timms extended the Cr atom/arene vapor cocondensation synthesis to the preparation of bis(cumene)- and bis(*m*-diisopropylbenzene)chromium and, by using a mixture of two different ligands, an arene and PF_3, prepared (arene)$Cr(PF_3)_3$ complexes, where arene = benzene, cumene, mesitylene, hexafluorobenzene.[97] Philip Skell, at Penn State, who was a pioneer in the area of carbon, silicon, and metal atom/ligand vapor cocondensation reactions,[98] prepared $(C_6H_6)_2Cr$ and also $(C_6H_5CH_3)_2Cr$, $(C_6H_5C_2H_5)_2Cr$, $(C_6H_5Cl)_2Cr$, $(C_6H_5F)_2Cr$, and $(p\text{-}F_2C_6H_4)_2Cr$,[99] as well as $(C_6H_6)_2Mo$, $(C_6H_5CH_3)_2Mo$, $(C_6H_5F)_2Mo$, $(C_6H_5Cl)_2Mo$, $(C_6H_5NMe_2)_2Mo$, $(C_6H_5CO_2CH_3)_2Mo$, $(C_6H_6)_2W$, $(C_6H_5CH_3)_2W$, $(1,2\text{-}(CH_3)_2C_6H_4)_2W$, and $(C_6H_5OCH_3)_2W$,[100] preparations which very nicely illustrate the functional group tolerance of the metal atom/substituted arene cocondensation procedure.

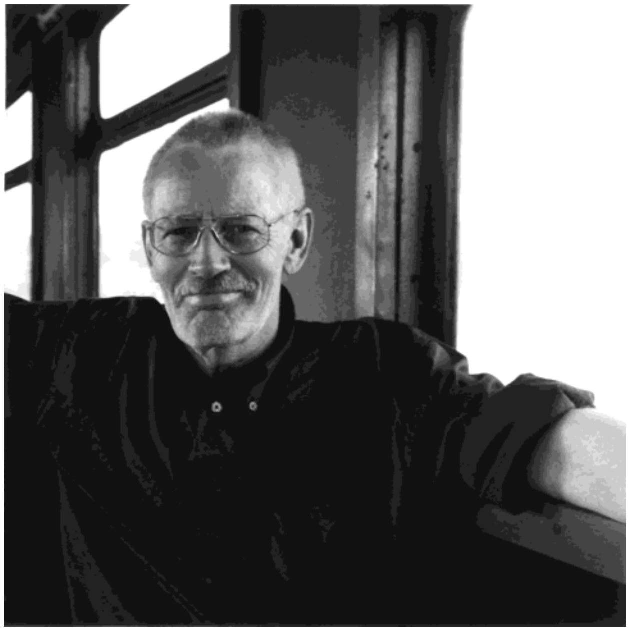

Figure 13. Christoph Elschenbroich (reproduced courtesy of C. Elschenbroich).

Other workers also were active in this area. McGlinchey and Tan[101] prepared a series of substituted bis(fluorobenzene)Cr complexes, $(C_6H_4FX)_2Cr$ (X = H, *o*-, *m*-, *p*-F, Cl, CH_3, *m*-CF_3), and studied their ^{19}F NMR spectra. On the basis of the observed ^{19}F chemical shifts, they concluded "that the overall electron-withdrawing effect of a π-bonded Cr on each ring is similar to the effect of 4 ring fluorine substituents as in C_6F_5X." For ^{13}C NMR spectroscopic studies, Graves and Lagowski prepared a large number of (variously substituted arene)$_2$Cr complexes, some known and some new, by Cr atom/arene cocondensation.[102] Brunner and Koch prepared mixtures of $(C_6H_6)_2Cr$, $(C_6H_6)(C_6H_5Y)Cr$, and $(C_6H_5Y)_2Cr$ (Y = CO_2R, CH_2CO_2R, $CH_2CH_2CO_2R$; R = Me, Et) and $N(CH_3)_2$, as well as $(C_6H_6)_2Cr$, $(C_6H_4Y_2)_2Cr$ (Y = *o*-, *m*-, *p*-CO_2M), and the respective paramagnetic Cr(I) cationic complexes. The former were prepared by Cr atom/mixed C_6H_6/C_6H_5Y vapor or $C_6H_4Y_2$ vapor cocondensation and the latter by iodine oxidation of the

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(95) For reviews see: (a) Timms, P. L. *Adv. Inorg. Chem. Radiochem.* **1972**, *14*, 121. (b) Blackborow, J. R.; Young, D. *Metal Vapor Synthesis in Organometallic Chemistry*; Springer-Verlag: Berlin, 1979. (c) Klabunde, K. J. *Chemistry of Free Atoms and Particles*; Academic Press: New York, 1980. (d) Green, M. L. H. *J. Organomet. Chem.* **1988**, *200*, 119. (e) Timms, P. L. *Angew. Chem.* **1975**, *87*, 295. (f) Skell, P. S.; McGlinchey, M. J. *Angew. Chem.* **1975**, *87*, 215. (g) Klabunde, K. J. *Acc. Chem. Res.* **1975**, *8*, 393.

(96) Timms, P. L. *J. Chem. Soc. D* **1969**, 1033.

(97) Middleton, R.; Hull, J. R.; Simpson, S. R.; Tomlinson, C. H.; Timms, P. L. *J. Chem. Soc., Dalton Trans.* **1973**, 120.

(98) For example, synthesis of the bis(cyclopentadienyl)metal complexes of Cr, Fe, Co, and Ni by reaction of the respective metal atoms with cyclopentadiene: Skell, P. S.; Engel, R. R. *J. Am. Chem. Soc.* **1966**, *88*, 3749.

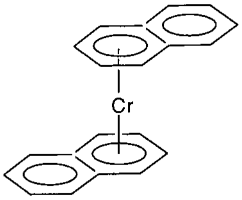
(99) Skell, P. S.; Williams-Smith, D. L.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1973**, *95*, 3337.

(100) Silvon, M. P.; Van Dam, E. M.; Skell, P. S. *J. Am. Chem. Soc.* **1974**, *96*, 1945.

(101) McGlinchey, M. J.; Tan, T.-S. *Can. J. Chem.* **1974**, *52*, 2439.

(102) Graves, V.; Lagowski, J. J. *Inorg. Chem.* **1976**, *15*, 577.

Chart 1



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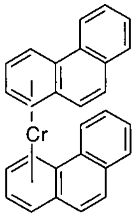

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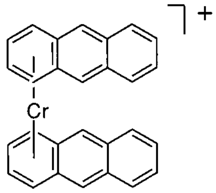

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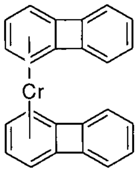

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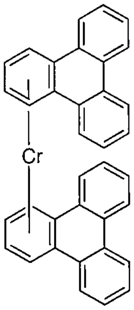

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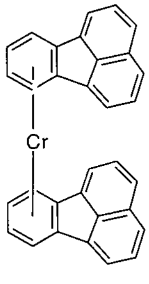

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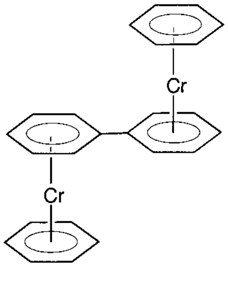

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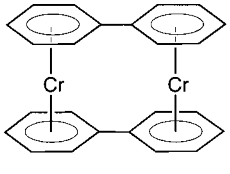

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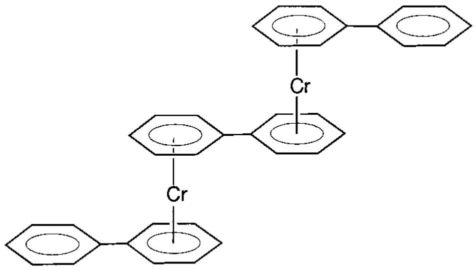

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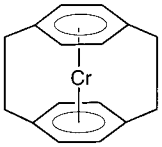

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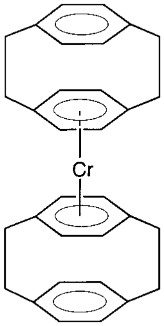

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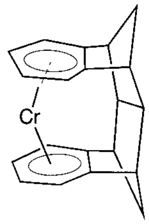

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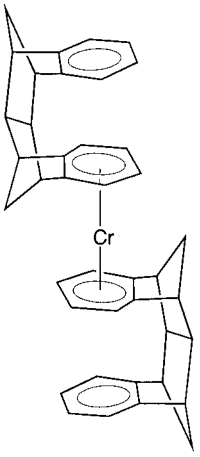

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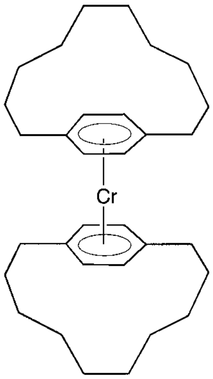

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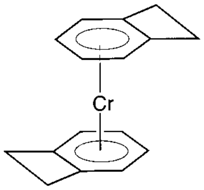

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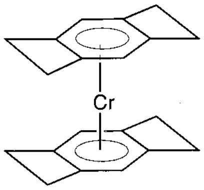

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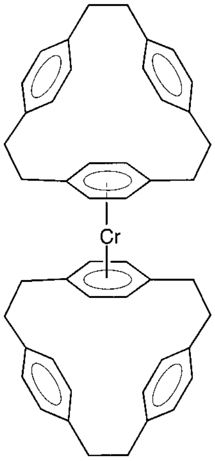

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neutral complexes,[103] and they were used in ^1H NMR and cyclic voltammetry studies. The metal atom/ligand vapor cocondensation procedure has been used to prepare bis(arene) complexes of metals other than those of group 6: Ti, Zr, Hf, Nb, Ta, V, Y, Gd, etc. (e.g., ref 104).

The research of Christoph Elschenbroich and his students at the University of Marburg, however, stands out, having been devoted to the study of π-arene−metal (mostly π-arene−chromium and −vanadium) chemistry for the last 26 years, and to conclude Part 2 of this essay, some highlights of this work are summarized. Elschenbroich (Figure 13) (b. 1939) carried out his *Diplom* research under the guidance of E. O. Fischer at the University of Munich (1964) and followed Fischer to the Technische Hochschule München in 1964, where he obtained his Ph.D. in 1966 with thesis research on arene−metal π-complexes of Nb, Cr, Ru, and Os with

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[103] Brunner, H.; Koch, H. *Chem. Ber.* **1982**, *115*, 65.

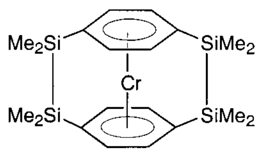
[104] Cloke, F. G. N.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1981**, 1938 (Zr, Hf, Nb, Ta).

mono- and polycyclic aromatic ligands, thus beginning his longstanding interest in arene−metal π-complexes. After some years spent at the Technion in Haifa, Israel, in industry, and at the University of Basel (*Habilitation* in 1975), he joined the chemistry department of the University of Marburg in 1975. His textbook *Organometallics—A Concise Introduction*, with Albrecht Salzer (with the third edition in preparation), is indeed a concise and excellent introduction to the subject.

Elschenbroich and his students have used the chromium atom/arene co-condensation procedure creatively to good advantage. Among the many bis(arene)chromium compounds prepared in his laboratories were **9**,;[105] **10**,[106] **11**,[107] **12**,[108] **13** and **14**,[109] **15**,[110] **16** and **17**,[111] the cyclophanes **18** and **19**,;[112] **20** and **21**,[113] **22**,[114] **23** and **24**,[115] and **25**[116] (Chart 1). This is by no means the complete list of Cr atom/aromatic hydrocarbon cocondensation-derived bis(arene)chromium complexes, but it serves to illustrate the versatility of this procedure.

Some other examples of the preparation of functionally substituted bis(arene)chromium complexes by the Cr atom/ligand vapor condensation route are of interest. Although bis(*N*,*N*-dimethylaniline)chromium could be prepared by metal atom/ligand cocondensation,[102,103] this procedure was unsuccessful with aniline itself. However, when the N−H functions were silylated to $[(CH_3)_3Si]_2NC_6H_5$, the bis(arene)chromium complex $\{[(CH_3)_3Si]_2NC_6H_5\}_2Cr$ could be prepared. Its desilylation with $[Bu_4N]F{\cdot}3H_2O$ gave the desired $[(H_2NC_6H_5)_2]Cr$ as a red-brown, microcrystalline solid.[117] It was found that the basicity of the complexed aniline was 1000 times greater than that of free aniline.

A boron-substituted bis(benzene)chromium complex was prepared. Reaction of $C_6H_5B(OPr^i)_2$ with Cr atoms in a metal atom reactor at 77 K gave the $[(Pr^iO)_2BC_6H_5]_2Cr$ π-arene complex.[118] Also prepared by the Cr atom route have been the trimethylsilyl-substituted bis(benzene)chromium complexes $(Me_3SiC_6H_5)_2Cr$, (1,4-$(Me_3Si)_2C_6H_4)_2Cr$, and (1,3,5-$(Me_3Si)_3C_6H_3)_2Cr$. These were very readily desilylated, anhydrous methanol at room temperature sufficing to accomplish this. Treatment of these complexes with pyridine-4-carboxaldehyde gave the radical cations, while a potassium mirror reduced them to the radical anions.[119] (In contrast to earlier workers, Elschenbroich calls the $[(arene)_2Cr]^+$ cations "radical cations" in order to emphasize the presence of their one unpaired electron.) Also prepared in this manner were (1,4-$(ClMe_2Si)_2C_6H_4)_2Cr$ and $(ClMe_2SiC_6H_5)_2Si$. Treatment of these complexed arylchlorosilanes with lithium naphthalenide in DME formed the novel tetrasila- and disila-η^{12}-paracyclophanes **26** and **27**, respectively.[120] Chromium atom/ligand cocondensation also served in the preparation of $(Me_3GeC_6H_5)_2Cr$ and $(BrMe_2GeC_6H_5)_2Cr$.[121] Sodium naphthalenide in DME converted the latter to the germachromocyclophane **28**. The cocondensation procedure also was used to prepare $(Me_3SnC_6H_5)_2Cr$.[122]



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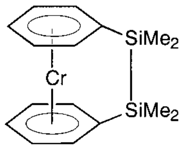

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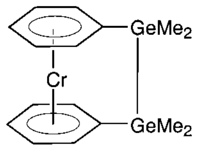
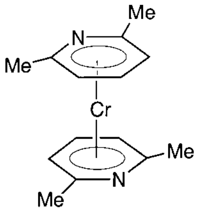


28

Of particular interest are bis(heteroarene)metal complexes. As noted earlier, (2-methylpyridine)chromium tricarbonyl had been prepared by Fischer and Öfele,[37] but a bis(η^6-pyridine)chromium(0) complex could not be prepared by the then available procedures. J. J. Lagowski and co-workers prepared bis(η^6-2,6-dimethylpyridine)chromium (**29**) by the metal atom/ligand co-condensation procedure,[123] but an attempted synthesis of bis(η^6-pyridine)chromium by this procedure by Elschenbroich was unsuccessful. However, cocondensation of a 5:2 mixture of benzene and pyridine with Cr atoms gave $(C_6H_6)(C_5H_5N)Cr$ in low yield.[124] The synthesis of bis(η^6-pyridine)chromium was accomplished in a clever manner (Scheme 5):[124] first, 2,6-bis(trimethylsilyl)pyridine was cocondensed with Cr atoms to give **30** in a reaction that was successful because the silyl groups, like the 2,6-methyl substituents, would sterically hinder N→Cr



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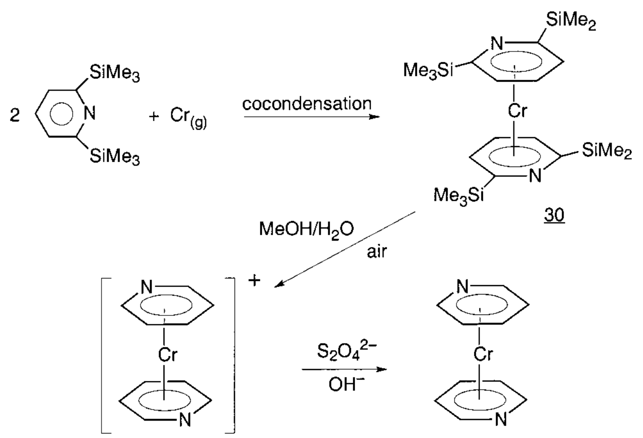
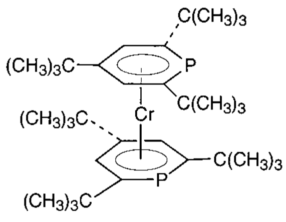
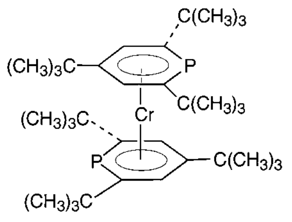
Scheme 5



coordination (the problem in the case of pyridine itself). Subsequent treatment of **30** with aqueous methanol in air resulted in hydrolytic desilylation and oxidation to the Cr(I) cation, which in a final step was reduced with alkaline dithionite to the neutral (η^6-$C_5H_5N)_2Cr$. An analogous substituted bis(η^6-phosphabenzene)chromium complex, (η^6-2,4,6-t-$Bu_3C_5H_2P)_2Cr$, present as the two rotamers **31a** and **31b**, was prepared by Cr atom/ligand cocondensation,[125] but the procedure did not work with phosphabenzene (phosphinine) itself. Instead, P-bonded (η^1-$C_5H_5P)_6Cr(0)$ was produced.[126] It would appear that, as in the case of pyridine, phosphinine must be sterically blocked from forming the hexakis η^1 complex of chromium. In contrast to what was observed with Cr atoms, phosphinine in cocondensation with vanadium atoms did give the thermally stable but air-sensitive reddish brown (η^6-$C_5H_5P)_2V$.[127a]

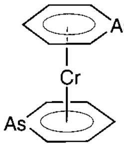


31a



31b

Arsenine (arsabenzene) reacted with chromium and with vanadium atoms to give (η^6-$C_5H_5As)_2Cr$ (**32**) and (η^6-$C_5H_5As)_2V$, respectively.[127b,c] While almost all such bis(heteroarene) complexes of chromium have involved the group 15 heteroarenes, Gerhard Herberich of the Technische Hochschule Aachen, also a Fischer Ph.D. student, has devoted the past 32 years to a broad investigation of borabenzene derivatives.[128] Among the many borabenzene−metal π complexes prepared were $Cr(C_5H_5BR)_2$ (**33**; R = CH_3, C_6H_5), with planar C_5B rings.[129] These complexes were prepared by reaction of the potassium boratabenzenes $K[C_5H_5B-R]$ with $CrCl_2\cdot THF$ in THF and were isolated as light red (R = CH_3) and wine red (R = C_6H_5) crystals that were air-stable in the solid state but extremely air-sensitive in solution. The analogy of the $Cr(C_5H_5BR)_2$ complexes is not with $(C_6H_6)_2Cr$ but with chromocene, $Cr(C_5H_5)_2$. They are paramagnetic, with magnetic moments of 3.0 μ_B (R = CH_3) and 3.3 μ_B (R = C_6H_5), compared with 3.1 μ_B for $Cr(C_5H_5)_2$. Thus, they are compounds of Cr(II), not Cr(0), and the C_5H_5BR ligands are −1 anions.



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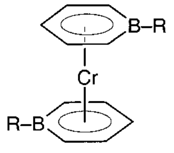

33

Elschenbroich's lithiation of bis(benzene)chromium using *n*-butyllithium/tetramethylethylenediamine in cyclohexane[28] has been mentioned earlier in this essay. Here, as in the case of metalation with *n*-$C_5H_{11}Na$, a mixture of mono- and dimetalated bis(benzene)chromium is obtained. However, the monolithio and 1,1′-dilithio bis(benzene)chromium compounds can be separated very easily by decanting the red cyclohexane reaction solution (which contains the monolithiated complex) from the reaction solids, which contain the insoluble dilithiated product.[130] These reagents were used to prepare the carbonyl and carboxyl derivatives $(C_6H_6)(C_6H_5C(O)Ar)Cr$ and $(C_6H_5C(O)Ar)_2Cr$[131a] and $(C_6H_5CO_2H)_2Cr$.[131b] The monolithiated bis(benzene)chromium underwent lithium−bromine exchange with 2-bromoanisole. Coupling of the resulting (bromobenzene)chromium complex with monolithiated bis(benzene)chromium (present in excess) allowed preparation of **15** in a one-pot reaction, albeit in only 5% yield.[132]

Organometallic and organometalloidal derivatives of bis(benzene)chromium have been prepared using $(C_6H_6)(C_6H_5Li)Cr$ and $(C_6H_5Li)_2Cr$. The reaction of the latter with dimesitylboron fluoride gave red-violet $[(2,4,6\text{-}Me_3C_6H_2)_2BC_6H_5]_2Cr$.[130] This complex was not readily oxidized, probably, as in the long-known case of trimesitylborane, due to steric reasons. The silylene-bridged **34a**[133] and **35**,[134] prepared by reaction of $(C_6H_5Li)_2Cr$ with the respective chlorosilanes, were of special interest. Lithium naphthalenide in DME at −50 °C coupled **35** to give the novel disilane **36**. A carbon-bridged analogue of **36**, complex **37**, also was prepared (Scheme 6),[135a] and **34b**, prepared by Manners and co-workers, underwent ring-opening copolymerization with the analogous $(CH_3)_2Si$-bridged [1]ferrocenophane at 170 °C or by initiation with *n*-BuLi/TMEDA.[135b]

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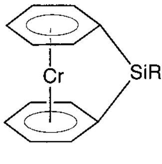
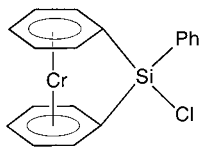


34 a, R = Ph
b, R = CH_3



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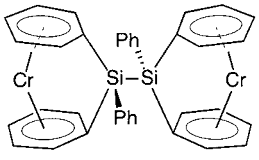

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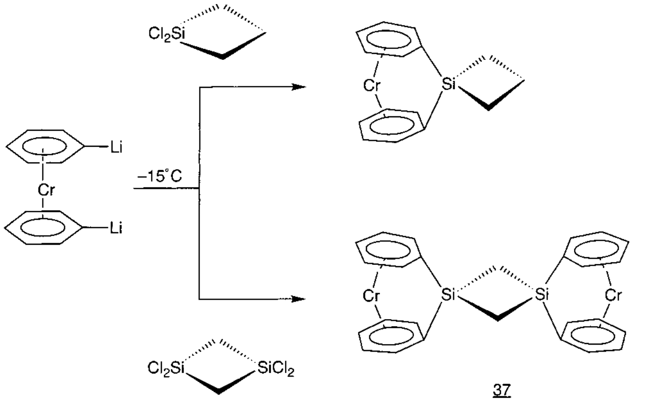
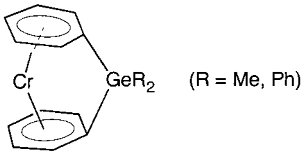
Scheme 6



37

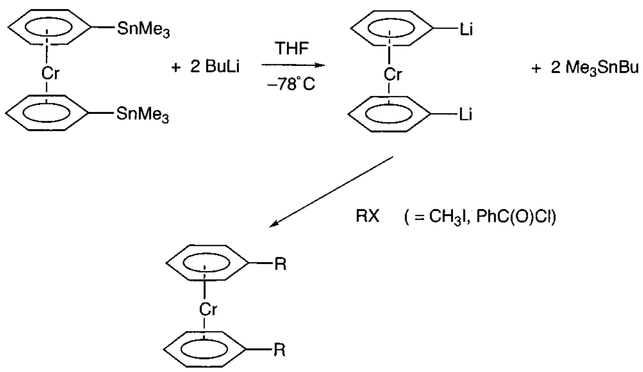
The organolithium route also was used in the synthesis of the germyl−bis(benzene)chromium complexes $(R_3GeC_6H_5)_2Cr$ (R = Me, Ph) and the germylene-bridged compounds **38**.[121] The organotin-substituted complex $(Me_3SnC_6H_5)_2Cr$, prepared by the Cr atom procedure, provided a route, via transmetalation with *n*-BuLi in THF at −78 °C, to $(C_6H_5Li)_2Cr$ free of the monolithiated species (Scheme 7).[122] Organotin derivatives could also be prepared by the action of R_3SnLi (R = Me, Ph) on $(C_6H_5Cl)_2Cr$ and $(p\text{-}CH_3OC_6H_4Cl)_2Cr$.[122]

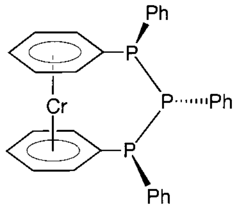


38

Of particular interest are phosphino derivatives of the type $(R_2PC_6H_5)_2Cr$, since they can function as simple or as chelating donor molecules. Both $(Me_2PC_6H_5)_2Cr$[136] and $(Ph_2PC_6H_5)_2Cr$[137] were prepared by reaction of $(C_6H_5Li)_2Cr$ with the respective R_2PCl compound. Attempts to prepare the PhP intramolecularly bridged bis(benzene)chromium were unsuccessful; the P_3-bridged complex **39** was obtained instead. Also prepared by reaction of Ph_2PLi with $(1,4\text{-}Cl_2C_6H_4)_2Cr$ was the bis-chelating $(1,4\text{-}(Ph_2P)_2C_6H_4)_2Cr$.[139] These diphosphines were found to be excellent chelating donors, and they have been used to prepare many transition-metal complexes.

Scheme 7

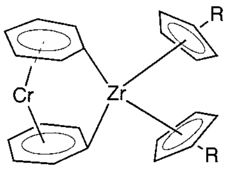




39

Organosulfur and organoselenium derivatives of bis(benzene)chromium, $(CH_3SC_6H_5)_2Cr$[140] and $(RSeC_6H_5)_2Cr$ (R = Me, Ph),[141] were prepared by the reaction of $(C_6H_5Li)_2Cr$ with R_2S_2 and R_2Se_2, respectively, or, in the case of $(CH_3SeC_6H_5)_2Cr$, by reaction of $(C_6H_5Li)_2Cr$ with Se_8 followed by alkylation of the resulting $(C_6H_5SeLi)_2Cr$ with CH_3I.

The highly air-sensitive zircona[1]chromacyclophanes **40** were prepared by the organolithium route from the respective zirconocene dichloride.[142] Although chemically very reactive, these complexes are very stable thermally. It is readily apparent that $(C_6H_5Li)_2Cr$ and $(C_6H_6)(C_6H_5Li)Cr$ are very useful reagents that will allow the preparation of many more new organic and organometallic derivatives of bis(benzene)chromium.



40 (R = H, t-Bu)

In this survey of Elschenbroich's (arene)chromium work, the focus has been on synthesis and reactivity. However, Elschenbroich has covered much more ground. Many of his complexes were oxidized to the radical cation, and some were reduced to the radical anion, either chemically or electrochemically, with extensive and detailed ESR studies of the resulting paramagnetic species. Cyclic voltammetry studies of the redox processes also were carried out. The structures of many complexes were determined by X-ray crystallography.

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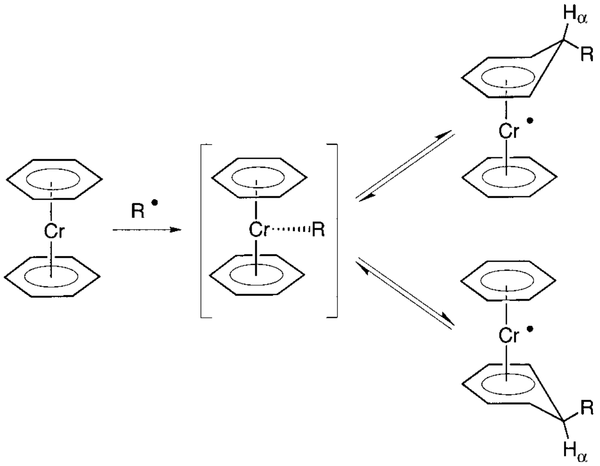
NMR (^{1}H, ^{13}C, heteroatom) studies were used to shed light on conformation, the presence of rotamers in the case of hindered arene ligands, electronic effects, etc.

Some uses of bis(benzene)chromium complexes have begun to emerge. Bis(benzene)chromium was found, in an ENSC Paris/Marburg collaboration, to be an efficient spin trap, trapping H$^\bullet$ and D$^\bullet$ atoms (from $PhSiH_3$ and $PhSiD_3$) and $(CH_3)_2(CN)C^\bullet$ radicals from AIBN to form paramagnetic 17e$^-$ adducts (eq 30).[143] In further studies, bis(benzene)chromium was revealed to be a useful precatalyst for the hydrosilylation of aryl ketones in the presence of air and for the dehydrocoupling between primary alcohols and triphenylsilane to give $Ph_3Si\text{-}OCH_2R$.[144]



(30)

Elschenbroich continues to be active in π-arene–metal research, and now that he has completed the third edition of his organometallic chemistry textbook, we can expect to see more publications in this area from Marburg.

Epilogue

We have come a long way since the days of Hein's "crude bromide". After 35 years of mystery and confusion, Zeiss and Tsutsui, with Onsager's help, solved the mystery. A year later the Fischer/Hafner synthesis of bis(benzene)chromium put the bis(arene)chromium complexes on firm ground and led to many other bis- and mono(arene)metal complexes at a rapid pace. Subsequent synthesis of σ-bonded $(C_6H_5)_3Cr{\cdot}3THF$ by Herwig and Zeiss and a study of its decomposition provided the beginnings of an understanding of Hein's chemistry. The preparation of diverse polyphenylchromates(III) and -(II) by Hein and his students furnished interesting new σ-bonded anionic phenylchromium compounds. An important advance in bis(arene)chromium chemistry was provided by Peter Timms' preparation of bis(benzene)chromium by the metal atom/ligand vapor condensation procedure in 1969, a procedure that was found to be tolerant of most (but not all) functional groups. This allowed Elschenbroich to develop bis(arene)chromium chemistry in great breadth and depth. The preparation of still more functionally substituted bis(benzene)chromium complexes has been further facilitated by the nucleophilic reactivity of $(C_6H_6)(C_6H_5Li)Cr$ and $(C_6H_5Li)_2Cr$, so that by now the number of known substituted bis(benzene)chromium complexes, while by no means rivaling that of substituted ferrocenes, is respectably large.

The arene–metal area has now reached a state of maturity. Especially the mono(arene) derivatives (in particular, those of chromium, ruthenium, and iron) have been developed broadly and have found useful application in synthesis, both stoichiometrically and catalytically.

Bis(benzene)chromium and ferrocene are the two molecules that caught the interest and sparked the imagination of organometallic chemists as well as of many inorganic and organic chemists whose research had never before involved organometallic compounds (except perhaps Grignard and organolithium reagents). As a result of their discovery, organotransition-metal chemistry underwent an explosive growth that led to many new types of organometallic compounds and to their many applications in organic, inorganic, and polymer synthesis, both as stoichiometric reagents and as catalysts or catalyst precursors. Not just iron and chromium, but all other transition metals, the lanthanides, and the actinides have become involved in the 50-odd years since these molecules made their debut.

This essay has gotten to be rather long. Even so, much other literature on bis(arene)chromium chemistry has not been covered, since a comprehensive review was not intended. The interested reader is referred to two comprehensive summaries[145,146] and to the reviews in ref 34.

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