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π-Complexes of the Transition Metals. VII. The Reaction of Phenylmagnesium Bromide with Chromium Halides[1]

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The reaction of phenylmagnesium bromide with the chromium halides in diethyl ether followed by hydrolysis under nitrogen leads to a mixture of bis-benzene-chromium(0) and benzene-biphenyl-chromium(0). These π-complexed products are considered to be formed by an internal rearrangement (oxidation–reduction) of σ-bonded phenylchromium intermediates.

The reaction of chromic trichloride with phenylmagnesium bromide was reported initially, in 1914, to give biphenyl in excellent yield according to the equation

$$2CrCl_3 + 2C_6H_5MgBr \longrightarrow C_6H_5C_6H_5 + 2CrCl_2 + MgCl_2 + MgBr_2$$

and was recommended as a preparative method for this compound.[2] Four years later F. Hein submitted his first communication containing the significant report of the isolation of the first organochromium compound, "pentaphenylchromium bromide,"[3] from the same reaction. This note was followed by an extensive series of papers embodying the results of the investigations of this reaction and its products by Hein and his collaborators.[4] Shortly thereafter, Job and Cassal reported the formation of oxygenated organic compounds as well as chromium hexacarbonyl when carbon monoxide was passed into a reacting mixture of phenylmagnesium bromide and chromic trichloride.[5] More recently, Kharasch and co-workers have expended much effort in a study of the effects of metallic halides, including chromic trichloride, on the reactions of aryl Grignard reagents.[6] In the present paper, the mechanistic aspects of this chromium halide–phenylmagnesium bromide reaction are examined.

The specific reaction between chromic trichloride and phenylmagnesium bromide under the experimental conditions described by Hein[4] has been studied independently.[7] This study led to the reformulation of the series of polyphenylchromium compounds isolated by Hein and his students[4] in terms of a single bis-arene chromium(I) cationic structure, *i.e.*, a bis-aromatic chromium π-complex.[8] This proposal has been confirmed in other laboratories[9] and by a different synthesis of the π-complex structure by Fischer and Hafner.[10]

The sequence of chemical events leading to the formation of the π-complexes during the reaction between chromic trichloride and phenylmagnesium bromide clearly requires steps which include oxidation–reduction, formation of π-bonds between the aromatic rings and chromium, and the occurrence of intermediates previously unrecognized. The formation of biphenyl and the reduction of chromium(III) are a demonstration of the first requirement; and the products isolated of course require the second. The observation that a black, pyrophoric solid was deposited from ether as the reaction progressed, decomposing rapidly on hydrolysis,[7] was an indication of the last. The latter requirement now has been substantiated by means of isotopic solvolysis of the reaction mixture in which the existence of π-complexed intermediates is shown by the incorporation of deuterium into the aromatic rings of the π-complexes on quenching the reaction mixture with deuterium oxide.[11]

The first insight into the mechanism of reaction between phenylmagnesium bromide and chromic trichloride was provided by the isolation of triphenylchromium(III),[12] the compound sought in the original investigations.[2,3] The fact that no π-complex was formed when this reaction was per-

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(1) Presented in San Francisco, April 14, 1958; Abstracts, 133rd Meeting, Amer. Chem. Soc., p. 3N; Paper VI, W. Herwig and H. Zeiss, *J. Org. Chem.*, **23**, 1404 (1958).

(2) G. M. Bennett and E. E. Turner, *J. Chem. Soc.*, **105**, 1057 (1914).

(3) F. Hein, *Ber.*, **52**, 195 (1919).

(4) (a) F. Hein, *ibid.*, **54**, 1905 (1921); (b) **54**, 2708 (1921); (c) **54**, 2727 (1921); (d) F. Hein and O. Schwartzkopff, *ibid.*, **57**, 8 (1924); (e) F. Hein and R. Spaete, *ibid.*, **57**, 899 (1924); (f) F. Hein and W. Eissner, *ibid.*, **59**, 362 (1926); (g) F. Hein and R. Spaete, *ibid.*, **59**, 751 (1926); (h) F. Hein, J. Reschke and F. Pintus, *ibid.*, **60**, 679 (1927); (i) **60**, 749 (1927); (j) F. Hein and F. Pintus, *ibid.*, **60**, 2388 (1927); (k) F. Hein with O. Schwartzkopff, K. Hoyer, K. Klar, W. Eissner and W. Clauss, *ibid.*, **61**, 730 (1928); (l) F. Hein and E. Markert, *ibid.*, **61**, 2255 (1928); (m) F. Hein with O. Schwartzkopff, K. Hoyer, K. Klar, W. Eissner, W. Clauss and W. Just, *ibid.*, **62**, 1151 (1929); (n) F. Hein, *J. prakt. Chem.*, **132**, 59 (1931); (o) F. Hein and W. Retter, *Z. physik. Chem.*, **156**, 81 (1931); (p) F. Hein, *Z. anorg. Chem.*, **227**, 272 (1936); (q) F. Hein, *Angew. Chem.*, **51**, 503 (1938); (r) F. Hein and S. Herzog, *Z. anorg. Chem.*, **267**, 337 (1952); (s) F. Hein and H. Pauling, *ibid.*, **273**, 209 (1953); (t) F. Hein and G. Baehr, *Chem. Ber.*, **86**, 1171 (1953).

(5) A. Job and A. Cassal, *Compt. rend.*, **183**, 392 (1926); *Bull. soc. chim.*, **41**, 814 (1927); **41**, 1041 (1927).

(6) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice–Hall, Inc., New York, N. Y., 1954, p. 117.

(7) M. Tsutsui, Dissertation, Yale University, 1954.

(8) (a) H. Zeiss and M. Tsutsui, Abstracts, Amer. Chem. Soc., 126th Meeting, New York, September, 1954, p. 29-O; (b) H. Zeiss, *Yale Sci. Mag.*, **29**, 14 (1955); (c) H. Zeiss, "Handbook," XIVth International Congress of Pure and Applied Chemistry, Zürich, 1955, p. 262; (d) H. Zeiss and M. Tsutsui, THIS JOURNAL, **79**, 3062 (1957); *cf.* also F. A. Cotton, *Chem. Revs.*, **55**, 551 (1955).

(9) (a) E. O. Fischer and D. Seus, *Chem. Ber.*, **89**, 1809 (1956); (b) F. Hein, *ibid.*, **89**, 1816 (1956); (c) F. Hein and H. Mueller, *ibid.*, **89**, 2722 (1956); (d) F. Hein, P. Kleinert and E. Kurras, *Z. anorg. Chem.*, **289**, 229 (1957); (e) F. Hein, *Angew. Chem.*, **69**, 238 (1957); (f) F. Hein and E. Kurras, *Z. anorg. Chem.*, **290**, 179 (1957); (g) G. A. Rasuvayev, Yu. A. Sorokin and G. A. Domrachem, *Doklady Acad. Nauk SSSR*, **111**, 1264 (1956); (h) G. A. Rasuveyev, Yu. A. Sorokin, G. A. Domrachem, G. G. Petrukhov, Yu. D. Tsevetkov and Yu. N. Molin, *ibid.*, **113**, 1293 (1957); (i) F. Hein and K. Eisfeld, *Z. anorg. Chem.*, **292**, 162 (1957).

(10) E. O. Fischer and W. Hafner, *Z. Naturforsch.*, **10b**, 665 (1955); *Z. anorg. Chem.*, **286**, 146 (1956).

(11) H. Zeiss and W. Herwig, *Ann.*, **606**, 209 (1957); THIS JOURNAL, **78**, 5959 (1956).

(12) W. Herwig and H. Zeiss, *ibid.*, **79**, 6561 (1957).

formed in tetrahydrofuran as solvent was the corollary to this result. Also, the aforementioned black solid was not formed; instead, a red-brown solution was obtained which, on hydrolysis, provided the chromium(III) ion but not π-complex. When the concentrations of Grignard reagent and chromic trichloride in tetrahydrofuran were properly adjusted and a mole ratio of 3:1, respectively, was employed, the precipitation of the tetrahydrofuranate of triphenylchromium(III), $(C_6H_5)_3Cr(THF)_3$, was observed to occur. Removal of tetrahydrofuran from this red, crystalline substance resulted in the loss of its red color and conversion into a black, pyrophoric solid closely resembling that noted earlier in the Hein reaction. This solid, as well as that obtained directly from the latter reaction in diethyl ether, yielded both bis-benzene-chromium(0) and benzene-biphenyl-chromium(0) when hydrolyzed under nitrogen with nitrogen-saturated water. If the hydrolysis was performed in air, the corresponding chromium(I) cations were isolated as salts, since the chromium(0) complexes are quite sensitive to oxygen. In either case the amounts of each complex produced were about equal, accompanied by trace amounts (<1%) of bis-biphenyl-chromium, and in no case has more than 30–35% total yield of complex (based on chromium) been obtained. It would appear, therefore, that this limitation is due to mechanistic reasons and not to experimental ones.

The reaction of *chromous* chloride with phenylmagnesium bromide in diethyl ether is another example of this unique rearrangement of a σ-bonded metal–carbon compound into a π-bonded one. Hydrolysis of this reaction mixture under nitrogen gives a 3:2 molar ratio of bis-benzene-chromium(0) and benzene-biphenyl-chromium(0) in 30% total yield. This product ratio is not significantly changed either by an extension of reaction time or by small variations in the reactant ratio. However, if a large excess of Grignard reagent is employed and the reaction allowed to proceed for a long period of time, an increase in benzene-biphenyl-chromium yield occurs at the expense of bis-benzene-chromium, since the total yield remains unchanged (see Table I). The use of excess Grignard reagent in these reactions also promotes the formation of small amounts of bis-biphenyl-chromium.

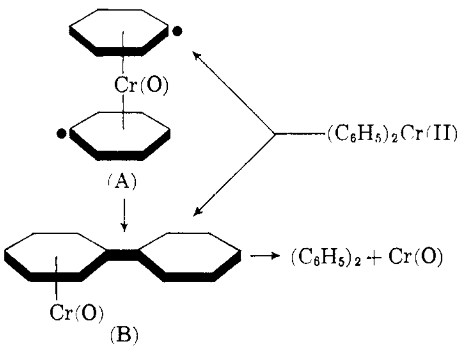
TABLE I

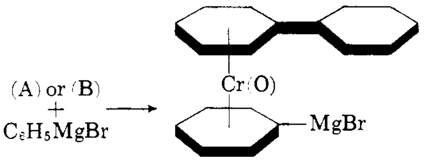
REACTION OF $CrCl_2$ AND C_6H_5MgBr IN DIETHYL ETHER AT −10°

Mole ratio of $CrCl_2$/C_6H_5MgBr	Time	Product ratio of $[C_6H_6]_2Cr(O)$/$[C_6H_6][C_6H_5C_6H_5]Cr(O)$
1:2	2 hr.	3:2
1:2	24 hr.	3:2
1:3	24 hr.	3:2
1:3	4 days	2:3
1:10	4 days	1:9

The formation and existence of triphenylchromium(III) in tetrahydrofuran encouraged us to attempt the isolation of diphenylchromium(III) from the same solvent; but this compound, even in the form of its tetrahydrofuranate, proved to be too unstable. However, the tetrahydrofuranate of dimesitylchromium(II), violet, and that of trimesitylchromium(III), blue, are isolable and do *not* rearrange to π-complexes when their coördinating tetrahydrofuran molecules are removed. This stability undoubtedly accounts for success in this instance.[13] Furthermore, since the products of the chromous chloride–phenylmagnesium bromide reaction in tetrahydrofuran are the same as those from reaction in diethyl ether, the formation of diphenylchromium(II) as a primary intermediate in either solvent is a reasonable assumption.

An internal rearrangement of diphenylchromium(II) is tentatively proposed as the most straightforward way in which to account for the products. According to this proposal, chromium(II) is reduced to its zerovalent state, a π-complexed intermediate is formed by the same process, and biphenyl is produced by decomposition of a "half-complex."[11] Whether the hypothetical di-radical (A) and the "half-sandwich" (B) are formed simultaneously, or whether B is produced from A, reaction of either A or B with phenylmagnesium bromide should provide the benzene-biphenyl-chromium(0) structure (C). The pyrophoric character of the intermediate which is certainly a mixture may be attributed to any of these structures as well as to nascent chromium.[14] It is further noted that this reaction scheme requires that the bis-benzene-chromium intermediate (A) be destroyed by phenylmagnesium bromide in providing the intermediate (C) in agreement with experiment (see Table I).





Hydrolysis of a π-complexed intermediate mixture containing A and C, or its solvolysis with deuterium oxide, must lead, at least in part, to bis-benzene-chromium(0) and benzene-biphenyl-chromium(0), or to the corresponding deuterated complexes previously described.[11] However, there is presently no evidence available regarding the chemical steps involved. The formation of small amounts of bis-biphenyl-chromium(0) when an

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(13) M. Tsutsui and H. Zeiss, unpublished results.

(14) The term "nascent" is used here in its most meaningful sense, *i.e.*, the condition of the element at the moment of liberation from its compound.

excess of phenylmagnesium bromide and long reaction times are employed is considered to be due to a slow coupling reaction between intermediate (C) and phenylmagnesium bromide.[15]

The reaction scheme for the reduction of chromous chloride by phenyl Grignard can be extended by analogy to similar reductions of cobaltous chloride. Whereas Kharasch preferred to write a sequence of free radical steps leading to cobaltous subhalide,[6] the suggestion of Wilds and McCormack[16] is better supported by our work with the chromous salt. The formation of a diarylcobalt compound, which may not be so ephemeral an intermediate as the former author seemed to believe, and of a highly reactive (nascent, not colloidal) form of metallic cobalt as the active reducing agent is consistent with our results whereas the analogous formation of chromous (I) subhalide is not. We have extended our work in this direction.

Experimental

Reaction of Chromous Chloride and Phenylmagnesium Bromide in Diethyl Ether. (a) Mole Ratio 1:2.—Solid chromous chloride (5.00 g., 0.04 mole) was stirred with approximately 100 3-mm. glass beads at a temperature between −10 and −15° while 110 ml. of phenylmagnesium bromide in diethyl ether (0.75 *M*, 0.08 mole) was being added over a period of 4 hours. After an additional 2 hours at the same temperature, the ether was removed from the reaction mixture at the water-pump between 0 and −5°. To the solid residue was now added under a layer of nitrogen (G.E. lamp grade) 100 ml. of benzene and then 100 ml. of oxygen-free, nitrogen-saturated water (5°). Still under nitrogen, the water layer was extracted 5 times with 100-ml. portions of benzene. This aqueous layer was colorless and contained no bis-arene-chromium cation as confirmed by a lack of precipitation when sodium tetraphenylboron was added to it. A portion of the combined brown-colored benzene layers was dried over potassium hydroxide pellets under nitrogen and put aside for the experiment described in the next paragraph. The remainder of the benzene solution was extracted with water *in the presence of air*, the brown color of the benzene layer disappearing with concomitant development of an orange-colored aqueous layer. Complete precipitation of this water layer with sodium tetraphenylboron gave 6.2 g. of yellow salt whose composition was determined by infrared analysis, using characteristic bands at 12.6 and 13.0 μ, to be a 3:2 mixture of bis-benzene-chromium(I) and benzene-biphenyl-chromium(I) tetraphenylborons. The total yield, including salt obtained from the remaining benzene solution used just below, was 7.2 g. (32%).

The solvent was removed *in vacuo* from the dried benzene solution mentioned above, and the black residue was sublimed at 20 mm. between 150–160°. The black, flaky sublimate was shown to be a mixture of bis-benzene-chromium(0) and benzene-biphenyl-chromium(0) by dissolving it in benzene, oxidizing it with air to the water-soluble cations and precipitating with sodium tetraphenylboron. The mixture ratio was the same as above: 3:2.

Changes in the reaction period of the initial reactants when combined in a mole ratio of 1:2, *i.e.*, 2 and 24 hours, produced no significant effect either on the ratio of the bis-arene-chromium complexes formed or on the total complex yield.

(b) **Mole Ratio 1:3.**—The reaction between chromous chloride and phenylmagnesium bromide was carried out under conditions as described in (a). However, at the end of the 6-hour reaction time, an additional 55 ml. of the phenylmagnesium bromide solution in ether was added at −15°, and the reaction mixture was maintained for a total time of 24 hours. However, the products were found to have been formed in the same chromium(0) valency, in the same ratio as before (3:2), and in the same yield (31%).

Another run in which the mole ratio of chromous chloride and phenylmagnesium bromide in ether was reached (1:3) during the first 4 hours of reaction and then maintained for 2 hours longer gave the same ratio and yield (31%).

(c) **Mole Ratio 1:10.**—A drastic change in product ratio was obtained by carrying out the reaction between chromous chloride and phenylmagnesium bromide in diethyl ether as described in (a) and (b) but employing a ratio of 1:10 and a reaction time of 4 days. The yield of total product remained the same (30%), but the ratio of bis-benzene-chromium(0) and benzene-biphenyl-chromium(0) was changed from 3:2 to 1:9.

Reaction of Chromous Chloride and Phenylmagnesium Bromide in Tetrahydrofuran.—Phenylmagnesium bromide, 19 ml. of an 0.96 *M* solution in THF (0.018 mole), was added to 1.12 g. (0.01 mole) of chromous chloride suspended in 20 ml. of THF over a period of 2 hours between −25 and −30° with good agitation. The reaction mixture slowly turned at first to a light brown color and then to black. After 6 hours, the mixture was hydrolyzed in air with water from which 340 mg. (7%) of the tetraphenylboron salts of bis-benzene-chromium(I) and benzene-biphenyl-chromium(I) were precipitated in a ratio of 3:2 with sodium tetraphenylboron. In another run under similar conditions the hydrolysis step was performed under nitrogen. As with diethyl ether as solvent, the products were formed exclusively as the chromium(0) complexes in the 3:2 ratio.

Reaction of Phenylmagnesium Bromide and Chromic Trichloride in Diethyl Ether.—To 1.58 g. (0.01 mole) of chromic trichloride, 46 ml. of 0.65 *M* phenylmagnesium bromide in ether was added in the space of one hour at −10 to −15°. The reaction mixture was magnetically stirred for a total reaction time of 24 hours, and then the solvent was removed under reduced pressure. The residue was now treated with 100 ml. of benzene and 100 ml. of oxygen-free, nitrogen-saturated water under an atmosphere of nitrogen in an ice-bath (0°). The water layer was extracted 6 times with 100-ml. portions of fresh benzene and was then found to be colorless and free of bis-arene-chromium cation by sodium tetraphenylboron precipitation test (negative). The combined benzene layers were now extracted with water in air. From the orange-colored aqueous extracts was precipitated 1.92 g. of a salt which proved to be a 1:1 mixture of the tetraphenylboron salts of bis-benzene-chromium(I) and benzene-biphenyl-chromium(I), a total yield of 34%, by the addition of a concentrated aqueous solution of sodium tetraphenylboron.

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[15] The same *initial* reaction scheme described in the above paragraphs may be applied to the reaction between chromic trichloride and phenylmagnesium bromide. However, additional steps are required to arrive at the same products, since the over-all oxidation-reduction step, Cr(III) → Cr(0), involves a three-electron transfer: H. Zeiss and W. Herwig (paper in preparation).

[16] A. L. Wilds and W. B. McCormack, *J. Org. Chem.*, **14**, 45 (1949).