allowed the product to accumulate in quantities up to 2.0 micromoles/ml.

NATIONAL INSTITUTE OF ARTHRITIS
AND METABOLIC DISEASES
NATIONAL INSTITUTES OF HEALTH EDITH C. WOLFF[9]
PUBLIC HEALTH SERVICE SIMON BLACK
U. S. DEPARTMENT OF HEALTH, EDUCATION
AND WELFARE, BETHESDA, MD. PHYLLIS F. DOWNEY

RECEIVED SEPTEMBER 13, 1956

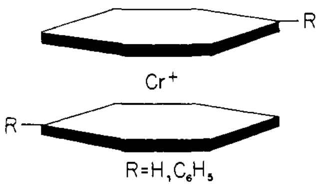
---

[9] Post-doctoral Research Fellow of the National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service.

SUBSTITUTED AROMATIC-CHROMIUM COMPLEXES

Sir:

First in 1954[1] and later in 1955[2] we proposed the general bis-arene structure I for aromatic-chromium compounds on the basis of results obtained with lithium aluminum hydride and deuteride reductions,[3] in explanation of the numerous anomalies reported earlier by Fr. Hein, *et al.*,[3] in the course of their work with these substances, and as a result of other theoretical considerations.[4] As a further step in the development of this chemistry we have succeeded in isolating the *predicted* water-soluble *bis-benzene-chromium* (I) cation, previously unreported from the reaction between phenylmagnesium bromide and chromyl chloride *or* chromic trichloride, as a major product. Reduction of its *tetraphenylboron salt* II [Calcd. for $C_{36}H_{32}BCr$: C, 81.98; H, 6.11. Found: C, 82.06; H, 6.27] or *picrate*, explosion p. 138° [Calcd. for $C_{18}H_{14}O_7N_2Cr$: C, 49.55; H, 3.23; N, 9.63. Found: C, 49.30; H, 3.36; N, 9.36] with hypophosphorous acid yielded *bis-benzenechromium*, m.p. 282–284°, whose physical, chemical and spectral properties[5] are the same as those exhibited by "di-benzol-chrom" prepared from benzene.[6] More fundamentally, we have now discovered the presence of a Grignard reaction intermediate whose usefulness in preparing a wide range of bis-arene-chromium complexes will be apparent.



I

Formation of the bis-arene-chromium cation clearly involves both oxidation–reduction and coordination-complexing steps. The former may be written as

$$2C_6H_5MgBr + CrCl_3 \longrightarrow (C_6H_5)_2 + Cr^ICl + MgBr_2 + MgCl_2$$

and the latter as

$$2C_6H_5MgBr + Cr^ICl \longrightarrow \underset{A}{[C_6H_5MgBr]_2Cr^ICl}$$

or as

$$C_6H_5MgBr + CrCl_3 \longrightarrow C_6H_5CrCl_2 + MgBrCl \quad (a)$$

$$2\ C_6H_5CrCl_2 + Cr^ICl \longrightarrow \underset{B}{[C_6H_5CrCl_2]_2Cr^ICl} \quad (b)$$

A simple test for the presence of an intermediate of either type A or B was made by carbonating the reaction mixture at −10° and then hydrolyzing the product with aqueous alkali. A water-soluble sodium salt of the product complex was then precipitated by tetraphenylboron ion as a less soluble yellow salt whose infrared spectrum was quite similar to that of II but which also contained very strong bands at 6.24 and 7.3 μ (carboxylate ion). This salt was further purified by precipitation from dilute, aqueous solution with barium ion, and this complex salt, likewise yellow, gave the same absorption bands. The introduction of carbon dioxide into the aromatic complex was confirmed by isotopic hydrolysis of the Grignard reaction intermediate with deuterium oxide. The tetraphenylboron salt of this product, after filtration, washing with water and recrystallization from acetone, exhibited the characteristic aromatic C–D band at 4.42 μ.[7] The existence of this intermediate also permits a reasonable explanation for the observed formation of benzene-diphenyl- and bis-diphenylchromium cations in this Grignard reaction.[1–3] Details of this work together with the results of the investigation of the manifold ramifications will be reported shortly.

CENTRAL RESEARCH LABORATORIES
MONSANTO CHEMICAL COMPANY HAROLD H. ZEISS
DAYTON 7, OHIO WALTER HERWIG[8]

RECEIVED OCTOBER 24, 1956

---

[1] Abstr., 126th Meeting, Amer. Chem. Soc., p. 29–0, Sept. 14 1954, New York, N. Y.; *Angew. Chem.*, **67**, 282 (1955).

[2] *Yale Sci. Mag.*, **29**, 14 (1955); *Handbook, XIVth International Congress of Pure and Applied Chemistry*, p. 262, July 23, 1955, Zürich; and in lectures presented at Munich, Heidelberg and Tübingen, June–July, 1955.

[3] *Cf.* F. A. Cotton, *Chem. Rev.*, **55**, 551 (1955).

[4] Professor L. Onsager first proposed this structure during the progress of the original experimental work being done by Dr. M. Tsutsui at Yale University.

[5] Nuclear magnetic resonance studies on this and related complexes are being made by Dr. L. N. Mulay together with Professor E. G. Rochow at Harvard University and will be published separately.

[6] E. O. Fischer and W. Hafner, *Z. anorg. Chem.*, **286**, 146 (1956).

[7] *Cf.* C. R. Bailey, R. R. Gordon, J. B. Hale, N. Herzfeld, C. K. Ingold and H. G. Poole, *J. Chem. Soc.*, 299 (1946).

[8] Monsanto Research Fellow ,1956–57.