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Abstract

Full Text

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ON THE STRUCTURE OF ORGANOCHROMIUM COMPOUNDS

(Presented by Academician N. N. Semenov, March 8, 1957)

In a recently published work by Fischer ([1]), the synthesis of neutral dibenzenechromium and of its salts was described, and a brief report was given on certain other aromatic derivatives of chromium-(0). On the basis of X-ray structural ([2]), magnetochemical and spectral data ([3]), as well as measurements of dipole moments ([4]), the author assumes that dibenzenechromium-(0) has structure A, analogous to ferrocene.

Recently a number of communications have appeared ([5,6]), in which the isolation from the reaction products of C_6H_5MgBr with anhydrous chromic chloride of, along with "pentaphenylchromium hydroxide" and "tetra- and triphenylchromium iodides" of Hein ([7]), dibenzenechromium iodide has been described.

According to the bold, but not rigorously proven, supposition of Zeiss ([8]), polyphenyl derivatives of chromium have the general bis-arene structure B. Thus, for a number of the indicated compounds it is expedient to adopt a unified nomenclature ([9]), according to which they should be called salts of di-(π-arene)-chromium. Hein, incidentally, also agrees with this ([6]).

Fig. 1. I $R = R' = H,\ X = J$. II $R = H,\ R' = C_6H_5,\ X = J$. III $R = R' = C_6H_5,\ X = J$. IV $R = R' = C_6H_5,\ X = C_6H_5O$. V $R = R' = C_3H_7$-iso $X = J$. VI $R = R$-cyclohexyl, $X = J$

As his own experimental proofs, Zeiss used data obtained by him in the reduction of Hein' s organochromium compounds in ether medium with $LiAlH_4$, and also $LiAlD_4$. However, in both cases these data are not very convincing. Thus, in the reduction with $LiAlD_4$ of 0.107 mmole of III, he isolated only 0.054 mmole of diphenyl (instead of 0.214 mmole by calculation) with a content of 5% D. From 0.70 mmole of II, 0.58 mmole of diphenyl was obtained with a content of 6.6–6.7% D.

If it is assumed that in the iodides of (π-benzene, π-diphenyl)-chromium and di-(π-diphenyl)-chromium the diphenyl groups are bound covalently ([10]), then

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Fig. 2. Absorption spectrum of an aqueous solution of III; concentration 10^{-2} mol/l

Figure 1: Fig. 2. Absorption spectrum of an aqueous solution of III; concentration 10^{-2} mol/l

in the diphenyl isolated after reaction with $LiAlD_4$ one would expect 10% D; but if they have structure B II and III, then the diphenyl should not contain deuterium.

The composition and yield of the organic products of the photodecomposition of organochromium compounds in chloroform ([11]) are in good agreement with structures B. For more complete proof we carried out the photolysis of III and IV in deuterochloroform (58.2% D). After irradiation with ultraviolet light (PRK-2 lamp) of 1.258 g of tetrahydrate IV in 29.05 g of $CDCl_4$ for 111 hours, diphenyl was obtained in 73.3% yield and with a D content of $< 0.1\%$. As a result of photodecomposition (64 hours) of 0.610 g of III in 26.18 g of $CDCl_3$, diphenyl was isolated with a deuterium content of $\sim 0.3\%$ (the error in determination of D is 0.2%); the yield was quantitative. For the latter reaction we propose the following overall scheme:

$$\text{III} + CDCl_3 \xrightarrow{h} 2C_6H_5{-}C_6H_5 + CrCl_3 + J_2.$$

It is known [3,12] that the compounds of series B (I–IV) are paramagnetic and have a magnetic moment of 1.7 Bohr magnetons, which corresponds to the presence in the molecule of each of them of one unpaired electron. In this connection it was of interest to record the spectra of paramagnetic electron resonance of such compounds in order to obtain data on the localization of the free electron. The absorption spectrum of an aqueous solution of III is shown in Fig. 2. The presence of hyperfine structure and qualitative analysis of the distribution of intensities indicate that the unpaired electron interacts with the hydrogen nuclei of the aromatic rings.

Fig. 2. Absorption spectrum of an aqueous solution of III; concentration 10^{-2} mol/l

A detailed consideration of these data, as well as data from the investigation of the spectra of paramagnetic electron resonance of other compounds of this type, will be published in the near future.

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REFERENCES CITED

[1] E. O. Fischer, W. Hafner, *Zs. anorg. allgem. Chem.*, **286**, 146 (1956).
[2] E. Weiss, E. O. Fischer, *Zs. anorg. allgem. Chem.*, **286**, 142 (1956).
[3] E. O. Fischer, W. Hafner, *Zs. Naturforsch.*, **10B**, 665 (1955).
[4] E. Weiss, *Zs. anorg. allgem. Chem.*, **287**, 236 (1956).
[5] H. H. Zeiss, W. Herwig, *J. Am. Chem. Soc.*, **78**, 5959 (1956).
[6] F. Hein, H. Müller, *Ber.*, **89**, 2722 (1956).
[7] F. Hein, *J. Prakt. Chem.*, **132**, 59 (1931).
[8] H. H. Zeiss, *Yale Sci. Mag.*, **29**, 14 (1955).
[9] A. K. Fischer, G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 149 (1956).
[10] F. A. Cotton, *Chem. Rev.*, **55**, 566 (1955).
[11] G. A. Razuvaev, Yu. A. Sorokin, G. A. Domrachev, *DAN*, **111**, No. 6, 1264 (1956).
[12] W. Klemm, A. Nellber, *Zs. anorg. allgem. Chem.*, **227**, 261 (1936).

Note: Figure translations are in progress. See original paper for figures.

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