

Preliminary communication

SYNTHESIS OF BIS(ARENE)CHROMIUM COMPOUNDS FROM 1,4-DIPHENYLBUTANE AND CHROMIUM VAPOUR

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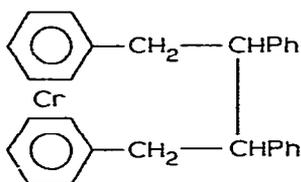
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Summary

Bridged dibenzenechromium 1,1'-tetramethylenedibenzenechromium (I) together with bis(1,4-diphenylbutane)chromium (II) and bis-1,4[1'-(δ -phenylbutano)dibenzenechromo]butane (III) were synthesized from the reaction of 1,4-diphenylbutane with chromium vapour.

A number of ferrocene derivatives with one, two and three bridges of different length are known [1]. At the same time the only obtained bridged dibenzenechromium [2] is

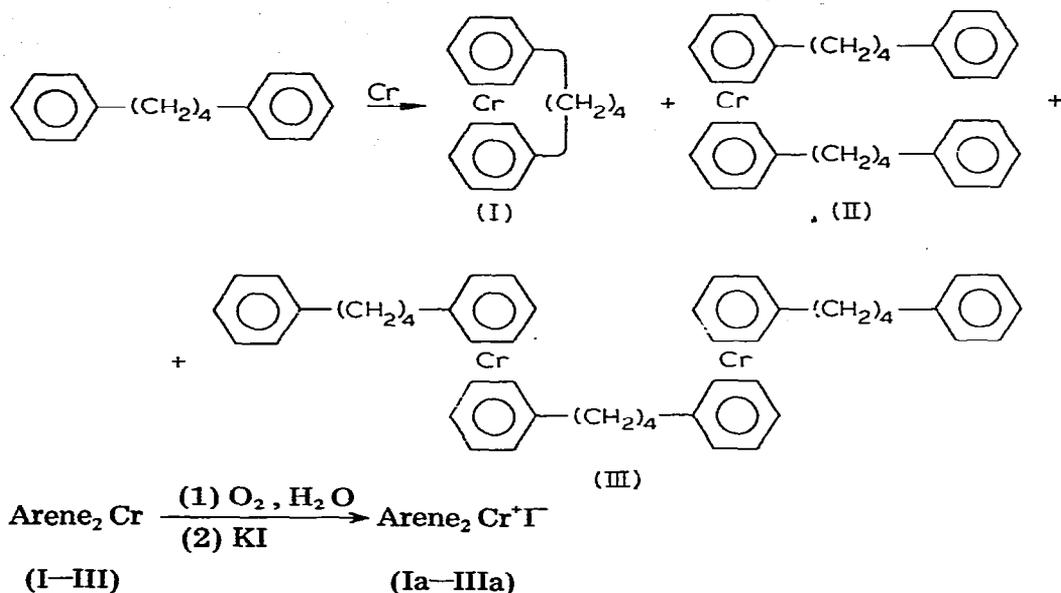


1,1'-trimethylenedibenzenechromium has also been mentioned previously [3].

We now report some preliminary results on the synthesis of bridged dibenzenechromium from 1,4-diphenylbutane (DPB) and chromium vapour. Previously DPB was observed to isomerise under conditions of the reducing Friedel—Crafts synthesis of bis(arene)chromium yielding bis(tetraline)chromium and benzene-(tetraline)chromium [4].

Bis(arene)chromium compounds from DPB and chromium vapour were obtained as described previously [5]. DPB was introduced into the reaction vessel as a solution in decane. Neutral complexes were oxidized with an air current in the presence of water, aqueous solution was treated with KI and iodides were extracted with chloroform. After evaporation 4.3 g of iodide mixture were obtained (from two experiments).

The mixture of bis(arene)chromium iodides was separated by thin layer chromatography (TLC) on alumina in an acetone/ethanol 3:1 system. After repeated chromatography the following compounds were isolated: Ia (0.25 g), IIa (1.26 g) and IIIa (0.66 g), the quantity of compounds in the mixture was found to be 6, 29 and 15% respectively.



After recrystallization from alcohol all compounds were characterized by elemental analysis (Table 1).

Our proof of monomeric bridged structure I for complex (DPB)Cr is based on mass spectral data and molecular weight measurement by ebullioscopy in ethanol. The mass spectrum of I, obtained by the reduction of Ia, showed peaks at m/e 262, corresponding to the molecular ion, m/e 234 ($\text{C}_{14}\text{H}_{14}\text{Cr}$)⁺, m/e 210 (DPB)⁺ and peaks of ligand fragment ions. It is worthwhile to compare the mass spectrum of I with that for II. Both spectra are very similar, differing in the absence of the ($\text{C}_{14}\text{H}_{14}\text{Cr}$)⁺ ion (m/e 234) in the mass spectrum of II. The molecular ion (m/e 472) is absent in the spectrum of II. The minor peak at m/e 262 corresponds to the ion produced by the loss of one ligand from the molecular ion.

The air sensitivity of neutral bis(arene)chromiums makes it difficult to

TABLE 1

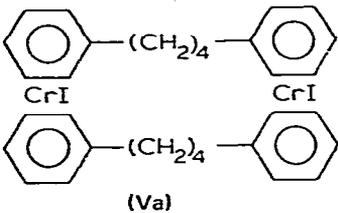
ANALYTICAL DATA OF BIS(ARENE)CHROMIUM COMPOUNDS

Compound	M.p. or decomp. p. (°C)	R_f^a	Analysis found (calcd.) (%)			
			C	H	Cr	I
Ia	decomp. p. 156–160	0.39	49.06 (49.35)	4.57 (4.63)	13.66 (13.37)	30.72 (32.65)
IIa	decomp. p. 154–158	0.53	64.15 (64.11)	6.27 (6.01)	8.64 (8.68)	20.85 (21.20)
IIIa	m.p. 138–140	0.25	58.43 (58.30)	5.83 (5.47)	10.18 (10.53)	24.34 (25.71)

^a Acetone/ethanol = 3:1.

measure their molecular weights by ebullioscopy. That is why molecular weights were determined for bis(arene)chromium iodides, Ia and also IIa and bis(toluene)-chromium iodide (IVa) for comparison. As should be expected the observed values of molecular weights of bis(arene)chromium iodides were much lower in comparison with the calculated ones because of dissociation. In the case of Ia and IVa the experimental values of the molecular weights were close to values \overline{M}_n , calculated by assuming complete dissociation of bis(arene)chromium iodides in alcohol. If the complex (DPB)CrI had the dimeric structure Va or moreover was

TABLE 2
MOLECULAR WEIGHTS OF BIS(ARENE)CHROMIUM COMPLEXES

Compound	Mol. wt. found (calcd.)	\overline{M}_n^a
$(\text{CH}_3\text{C}_6\text{H}_4)_2\text{CrI}$ (IVa)	190 (363)	181.5
Ia	170 (389)	194.5
IIa	420 (599)	299.5
	— (778)	259

\overline{M}_n^a = average molecular weight calculated assuming 100% bis(arene)chromium iodide dissociation:
 $\text{Arene}_2\text{CrI} \rightleftharpoons \text{Arene}_2\text{Cr}^+ + \text{I}^-$ (for IVa, Ia, IIa)
 $\text{Arene}_2\text{Cr}_2\text{I}_2 \rightleftharpoons (\text{Arene}_2\text{Cr}_2)^{2+} + 2\text{I}^-$ (for Va)

oligomeric $[(\text{DPB})\text{CrI}]_n$, one would expect the observed value of the molecular weight to be greater.

Besides iodides Ia, IIa and IIIa, isolated individually, we also, in the system studied, obtained 0.43 g of an iodide mixture with a low R_f value. According to TLC in more polar systems the mixture consists of several compounds, probably oligomers $(\text{LCrI})_n$ which were not studied further.

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