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INTERACTION OF DIPHENYLACETYLENE WITH CHROMIUM ATOMS

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Summary

The reaction of diphenylacetylene with chromium atoms results in the formation of bisarenechromium π-complexes containing diphenylacetylene and its cyclotrimer as ligands, viz., bis(η^6-diphenylacetylene)chromium, (η^6-diphenylacetylene)(η^6-hexaphenylbenzene)chromium and bis(η^6-hexaphenylbenzene)chromium. The other reaction products were found to be uncomplexed hexaphenylbenzene and 1,2,3,4-tetraphenylbutadiene-1,3.

The reaction of acetylenes with chromium atoms has been studied for 1-butyne, 2-butyne, 1-pentyne [1] and 1,7-cyclododecadiyne [2]. Chromium vapour causes cyclotrimerization of alkylsubstituted acetylenes into the corresponding substituted benzenes but in no case were arene-chromium coordination products detected. However, reaction of 2-butyne with triphenylchromium(III) tris-tetrahydrofuranate, $(C_6H_5)_3Cr \cdot 3THF$ gives rise to cyclooligomerization products (hexamethylbenzene and tetramethylnaphthalene) which are formed both in the free state and in the form of π-complexes with chromium [3]. Replacement of 2-butyne by diphenylacetylene results in the formation of free hexaphenylbenzene only.

In our previous paper [4] we have shown that the reaction of benzonitrile with chromium atoms gives, along with 2,4,6-triphenyltriazine (a product of benzonitrile cyclotrimerization), an arene π-complex of benzonitrile with chromium: bis(benzonitrile) chromium. By analogy with this reaction, one would also expect the formation of bisarenechromium complexes with a triple bond in a side chain from arylacetylenes. Until now no such derivatives of dibenzenechromium are known.

Results and discussion

In this paper we have studied the interaction of diphenylacetylene with atomic chromium in high vacuum upon cooling with liquid nitrogen. The reaction proceeds

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with the formation of a mixture of organochromium and organic products.

$$\begin{aligned} C_6H_5C{\equiv}CC_6H_5 + Cr \rightarrow {} & \underset{(I)}{(\eta^6\text{-}C_6H_5C{\equiv}CC_6H_5)_2Cr} \\ & + \underset{(II)}{(\eta^6\text{-}C_6H_5C{\equiv}CC_6H_5)Cr[\eta^6\text{-}(C_6H_5)_6C_6]} \\ & + \underset{(III)}{[\eta^6\text{-}(C_6H_5)_6C_6]_2Cr} \\ & + \underset{(IV)}{(C_6H_5)_6C_6} + \underset{(V)}{C_6H_5CH{=}C(C_6H_5){-}C(C_6H_5){=}CHC_6H_5} \end{aligned} \tag{1}$$

The bisarenechromium complexes I–III were separated from the organic compounds by oxidation to hydroxides of the corresponding cations (Ia–IIIa), which are insoluble in non-polar solvents. The separation of the tolane complexes (I and II) from bis(hexaphenylbenzene)chromium (III) was based on the fact that hydroxides of cations of Ia and IIa are soluble in water whereas the hydroxide of IIIa is insoluble in water but soluble in methanol. The mixture of cations of tolane complexes was reduced and I and II were separated by chromatography on alumina.

$$\underset{(I\text{–}III)}{Arene_2Cr} \xrightarrow{O_2,H_2O} \underset{(Ia\text{–}IIIa)}{Arene_2Cr^+OH^-} \xrightarrow{KI} \underset{(Ib\text{–}IIIb)}{Arene_2Cr^+I^-} \tag{2}$$

$$\underset{(Ib\text{–}IIIb)}{Arene_2Cr^+I^-} \xrightarrow{Na_2S_2O_4,\ KOH} \underset{(I\text{–}III)}{Arene_2Cr} \tag{3}$$

Complexes I–III are formed by reaction 1 in low yields (0.7, 0.5, and 2%, respectively, based on chromium vapour).

Bis(η^6-diphenylacetylene)chromium I was isolated as the iodide of the corresponding cation Ib and characterized by elemental analysis. In the products of photochemical cleavage of Ib in CH_2Cl_2 only diphenylacetylene was detected (by GLC). The mass spectrum of I contained peaks corresponding to the molecular ion, to the ion of the fragment $(C_6H_5C_2C_6H_5Cr)^+$, and to the ligand $(C_6H_5C_2C_6H_5)^+$ and chromium ions.

Unlike free diphenylacetylene, which reacts readily with dicobalt octacarbonyl forming a complex of the π-acetylene type, $(C_6H_5C{\equiv}CC_6H_5)Co_2(CO)_6$ [5], diphenylacetylene η^6-coordinated in complex I does not form the corresponding acetylene π-complex with $Co_2(CO)_8$ under similar conditions. Dicobalt octacarbonyl oxidizes bisarenechromium complex I to the corresponding cation which was isolated from an aqueous extract and identified as the iodide Ib by TLC:

$$\begin{aligned} & \underset{(I)}{(\eta^6\text{-}C_6H_5C{\equiv}CC_6H_5)_2Cr} + Co_2(CO)_8 \rightarrow \\ & \quad [(\eta^6\text{-}C_6H_5C{\equiv}CC_6H_5)_2Cr]^+[Co(CO)_4]^- + Co_4(CO)_{12} \end{aligned} \tag{4}$$

Tetracobalt dodecacarbonyl, $Co_4(CO)_{12}$ (identified by IR and mass spectrometry), is another reaction product. Its mass spectrum contains a peak corresponding to the molecular ion (m/e 572) and peaks corresponding to the ions formed by successive loss of carbonyl groups. The complex was also identified by comparison with an authentic sample [6] by TLC ($R_f = 0.58$ on Silufol in petroleum ether).

The mixed complex (η^6-diphenylacetylene)(η^6-hexaphenylbenzene)chromium (II) was not obtained in an analytically pure form and was identified by physico-chemical methods. The IR spectrum of II contains an absorption band (2210 cm^{-1}) corresponding to stretching vibrations of the C≡C triple bond and bands characteristic of stretching vibrations of phenyl rings. In products of the photochemical decomposition of II, diphenylacetylene and hexaphenylbenzene were detected by GLC and TLC, respectively. In the mass spectrum of II the fragment $[(C_6H_5)_6C_6Cr]^+$ is the heaviest ion and the peak of $[(C_6H_5)_6C_6]^+$ is the most intensive. No peaks of the molecular ion and of the fragment $[C_6H_5C_2C_6H_5Cr]^+$ are present in the mass spectrum. The presence in the spectrum, however, of the intense peak of $(C_6H_5C_2C_6H_5)^+$ (60% relative to $[(C_6H_5)_6C_6]^+$) points to the presence of this fragment in the initial molecule of the complex. Had the ion $(C_6H_5C_2C_6H_5)^+$ been the product of decomposition of $[(C_6H_5)_6C_6]^+$, the peak corresponding to $(C_6H_5C_2C_6H_5)^+$ would have been much less intense: in the mass spectrum of hexaphenylbenzene recorded under similar conditions the intensity of the peak of $(C_6H_5C_2C_6H_5)^+$ is only 7.59% of that of the molecular ion.

Bis(η^6-hexaphenylbenzene)chromium (III) was characterized by elemental analysis in the form of the iodide of the corresponding cation of IIIb. In the IR spectrum of IIIb there are no bands characteristic of a C≡C bond but bands corresponding to the phenyl ring stretching vibrations are present. Attempts to record the mass spectrum of the complex were unsuccessful since the compound decomposes prior to the evaporation point.

Complexes I–III differ from one another in solubility (I has the highest solubility in petroleum ether and benzene whereas the solubility of III is lowest) and in stability towards oxidation and decomposition (III is the most stable to oxidation and does not decompose under irradiation in CH_2Cl_2 or under the action of $H_2O_2 + HCl$).

Thus, upon interaction of chromium atoms with diphenylacetylene π-coordination of chromium to a phenyl ring is accompanied by oligomerization of acetylene with the formation of hexaphenylbenzene both in the free state and in the form of a π-bonded complex.

Experimental

The reaction of diphenylacetylene with chromium vapour was carried out in the reactor described previously [4]. Purification and isolation of neutral bisarene-chromium complexes were carried out under an inert atmosphere. The solvents were distilled under argon. Al_2O_3 for chromatography of neutral compounds was prepared by heating under high vacuum at 140°C/2×10^{-4} Torr for 3 hours with subsequent water deactivation (10% by weight).

The mass spectra were recorded on an MS-30 mass spectrometer under the following conditions: inlet temperature 210–400°C, ionization chamber temperature 250°C, emission current 100 μA, ionizing voltage 70 eV.

Interaction of diphenylacetylene with chromium

Chromium metal (1 g, 0.019 g-at) was evaporated for 2 hours and a hot solution of diphenylacetylene (30 g) in 200 ml of decane was simultaneously introduced into the reactor. After completion of the reaction, the reactor was warmed up to room temperature and filled with argon. The reaction mixture was siphoned off into a Schlenk tube, and the solid residue was repeatedly extracted with benzene. Combined organic solutions were filtered, air was bubbled through the filtrate in the presence of water, and the aqueous fraction (A) was separated from organic layer (fraction B). The residue insoluble in benzene was extracted with hot water as long as the water solution became colorless (fraction C). Potassium iodide was then added to the combined aqueous fractions A and C and extraction was performed with CH_2Cl_2. After evaporation, a mixture (0.2 g) of iodides of bisarenechromium complexes was obtained containing, according to TLC (Al_2O_3, acetone : methanol = 7 : 1), two compounds with $R_f = 0.54$ and 0.14 (fraction AC).

A black residue left after extraction with hot water was extracted with methanol; 10 ml of aqueous solution of KI was added to the methanol solution which was then evaporated to dryness. Extraction of the residue with chloroform yielded 0.5 g of a solid violet product which, according to TLC (Al_2O_3, benzene : ethanol = 3 : 1) contained one compound ($R_f = 0.53$) (fraction D).

(a) Isolation of bis(η^6-diphenylacetylene)chromium I and (η^6-diphenylacetylene)(η^6-hexaphenylbenzene)chromium II. A mixture (0.2 g) of iodides of bisarenechromium complexes (fraction AC) was dissolved in 5 ml of MeOH and treated in a four-necked flask with $Na_2S_2O_4$ (0.7 g), KOH (0.25 g), and H_2O (30 ml) under a benzene layer. The colored benzene layer was separated and a new benzene portion was added to the reaction mixture; the operation was repeated until a benzene layer became colorless. After evaporation of benzene, an oily red product was obtained (0.16 g). Chromatography on Al_2O_3 gave 0.06 g of I as a yellow oil (elution with petroleum ether) and 0.07 g of II as a red powder (elution with 1/1 benzene : petroleum ether), m.p. 178°C (from hexane).

Mass spectrum of I (inlet temperature 210°C), m/e (rel.int,%) (ion): 408 (9.6) $(P)^+$, 230 (28.1) $(C_6H_5C_2C_6H_5Cr)^+$, 178 (100) $(C_6H_5C_2C_6H_5)^+$, 52 (53.1) $(Cr)^+$. The products of photochemical decomposition in CH_2Cl_2 contained diphenylacetylene as detected by GLC.

Neutral I was oxidized by bubbling air through a benzene solution in the presence of water. Potassium iodide was added to the aqueous solution and bis(η^6-diphenylacetylene)chromium iodide, Ib, was extracted with $CHCl_3$. After distillation of the solvent, Ib was isolated in the form of a red oil hardening upon grinding with petroleum ether; decomp. point 143°C. Found: C, 62.11; H, 3.79; Cr, 9.93; I, 23.94. $C_{28}H_{20}CrI$, calcd.: C, 62.80; H, 3.74; Cr, 9.72; I, 23.74%.

Mass spectrum of II (inlet temperature 350°C), m/e (rel. int.,%) (ion): 586 (23.3) $[(C_6H_5)_6C_6Cr]^+$, 534 (100) $[(C_6H_5)_6C_6]^+$, 178 (60.0) $(C_6H_5C_2C_6H_5)^+$, 52 (23.3) $(Cr)^+$.

IR spectrum of II (KBr): 2210 cm^{-1} (C≡C stretching vibrations), 690, 750, 800, 1440, 1520, 1600 cm^{-1} (phenyl groups).

The products of photochemical decomposition of II contain diphenylacetylene (detected by GLC) and hexaphenylbenzene (detected by TLC). II was oxidized to the corresponding cation and isolated in the form of the iodide IIb, m.p. 137–138°C (from MeOH); decomp. point 175°C.

(b) Isolation of bis(η^6-hexaphenylbenzene)chromium (III). Bis(η^6-hexaphenylbenzene)chromium iodide, IIIb, was obtained as dark-violet crystals (m.p. 299–300°C) from fraction D after chromatography on Al_2O_3 (elution with chloroform) and recrystallization from MeOH.

Found: C, 80.12; H, 5.12; Cr, 4.55; I, 10.18. $C_{84}H_{60}CrI$, calcd.: C, 80.83; H, 4.81; Cr, 4.17; I, 10.18%.

The IR spectrum of IIIb contains bands at 700, 760, 1440, 1500, and 1600 cm^{-1} corresponding to stretching vibrations of phenyl rings; no C≡C stretching vibrations are seen. Reduction of IIIb by the procedure similar to that described for Ib and IIb and subsequent extraction with benzene (ca. 250 ml) gave neutral bis(η^6-hexaphenylbenzene)chromium III; recrystallization from a benzene-hexane mixture yielded III in the form of a red powder, m.p. 251–254°C, decomp. point ca. 340°C.

(c) Investigation of the organic reaction products. The solution after removing organochromium products (fraction B) was evaporated and the residue was chromatographed on Al_2O_3. Unreacted diphenylacetylene (25 g) was eluted with petroleum ether. Elution with a petroleum ether-benzene mixture (1 : 1) gave 1,2,3,4-tetraphenyl-1,3-butadiene (V) (0.16 g), m.p. 180°C (from a hexane-benzene mixture). (Lit. m.p. 183–184 [7]). The mass spectrum of V contains the peak of the molecular ion (*m/e* 358).

A mixture of petroleum ether-benzene (1 : 5) eluted 0.22 g of hexaphenylbenzene (IV), m.p. 424°C (Lit. m.p. 426–427°C [8]). From the upper band 0.58 g of an oily yellow product was isolated whose structure was not determined (elution with benzene and then with ether).

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