Reactions of benzene derivatives containing $C\equiv N$ and $C\equiv CH$ groups with atomic chromium

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Reactions of benzonitrile and phenylacetylene with atomic chromium were studied. Products of the trimerization and polymerization of the initial aromatic compounds form in considerable amounts along with bisarenechromium complexes. Mechanisms of the reactions were suggested. The possibility of increasing the yields of the bisarenechromium complexes was considered.

Key words: chromium, benzonitrile, phenylacetylene, reactions; bisarenechromium complexes, cryochemical synthesis; cyclotrimerization, polymerization.

Substituted bisarenechromium complexes (BAC), which became accessible due to the development of cryochemical synthesis, can be efficiently used for the preparation of binuclear bisarenechromium complexes linked by $-Ph_2P-Ni(CO)_2-Ph_2P$ type bridges.[1,2] Developments in this direction depends essentially on the accessibility of the initial substituted BAC.

It is difficult to draw a conclusion on the dependence of the yield of BAC on the nature or number of the substituents in the arene ligands from the published data available presently. For example, the yield of dibenzenechromium varies from 13 [3] to 60%,[4] and that of bis(ethylbenzene)chromium changes from 31 [3] to 52%.[5] The technical parameters of the installations used for cryochemical syntheses are very important factors. The use of an apparatus with a rotating reaction chamber for preparation of bis(diphenylmethane)chromium made it possible to increase the yield of the product to 58%.[6] (The yield was 22% with the use of a stationary reactor.[7]) The effects of the experimental conditions have been poorly studied. Several works[8,9] should be mentioned that consider ways to optimize low-temperature cocondensation by taking into account the apparatus design, the choice of the necessary degree of isolation of metal atoms in the organic matrix, and other factors of cryosynthesis. In some cases, a low yield is explained by side processes (dioxygenation, polymerization, *etc.*). The problem of the behavior of an atomic metal under conditions of competing reactions with several reaction centers in the molecule of an organic compound has not been studied well. The solution of this problem is difficult, because the complicated processes occurring both under the conditions of low-temperature synthesis (77 K) and in the subsequent isolation of the products have not been sufficiently studied. This is due to the fact that the reaction products always contain a considerable amount of ultradisperse metal particles along with the initial aromatic compounds and the organometallic compounds formed. The high reactivity of these metal particles can substantially change the composition of the final products due to various processes occurring after the end of the low-temperature synthesis.[10] All these factors can exert a noticeable effect on the yield of BAC and should be studied in detail.

It seemed reasonable to study reactions of atomic chromium with aromatic compounds containing such reactive groups as $C\equiv N$ and $C\equiv CH$ in the benzene ring. These compounds were chosen due to the wide synthetic possibilities of chromium π-complexes containing benzonitrile and phenylacetylene as ligands, and the fact that a detailed understanding of the processes occurring would make it possible to establish the factors responsible for the yield of these complexes.

Results and Discussion

An unsuccessful attempt to synthesize bis(benzonitrile)chromium by the reaction of atomic chromium with benzonitrile has been previously reported.[3] In this reaction the elimination of the cyanide group under the action of the atomic metal was observed.

We succeeded in obtaining bis(benzonitrile)chromium[11] by the condensation of benzonitrile and chromium vapor followed by purification of the product by column chromatography on Al_2O_3. The reaction is accompanied by the cyclotrimerization of benzonitrile to 1,3,5-triphenyltriazine. The yield of bis(benzonitrile)chromium $(PhCN)_2Cr$ is not greater than 10% (calculated from the amount of evaporated metal) and

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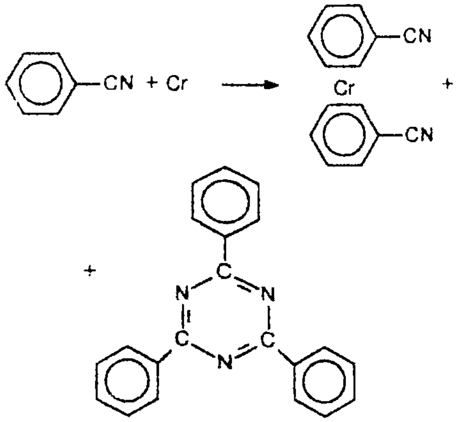
depends slightly on the molar ratios of atomic chromium and benzonitrile. Bis(benzonitrile)chromium is stable in air for a long time, because the two electron-withdrawing substituents stabilize the complex to oxidation. The low yield of $(PhCN)_2Cr$ can likely be associated with the side process of cyclotrimerization (due to the attack of atomic chromium on the C≡N bond) and with specific features of the subsequent preparative isolation of the complex. In fact, the formation of triphenyltriazine in amounts close to the yield of $(PhCN)_2Cr$ was observed in all experiments (Scheme 1).

Scheme 1

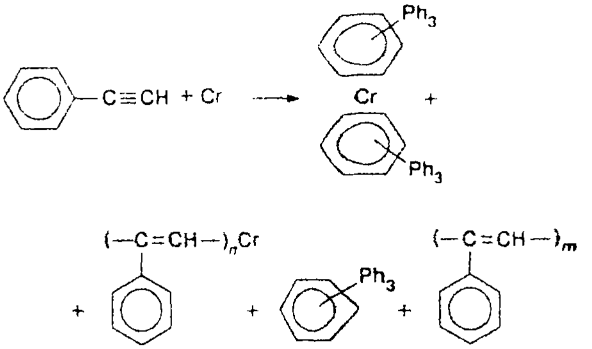


Prolonged storage of cryosynthesis product, which always is a mixture of benzonitrile, organometallic complex, and ultradisperse chromium that has not reacted, results in an increase in the fraction of cyclotrimerization products. The yield of BAC also decreases when the excess benzonitrile is distilled from the product of cryosynthesis, if the unreacted chromium has not been removed from the reaction mixture. The participation of ultradisperse chromium as an initiator of decomposition of $(PhCN)_2Cr$ has been mentioned previously.[3] The authors of this work synthesized several bisarene-chromium complexes using sublimation to separate the products.[3] However, no benzonitrile complex was obtained.

Because of the destabilizing role of ultradisperse metal particles, which are almost always present in products of cryochemical syntheses, an approach that helps avoid or substantially decrease their action is recommended: to remove or separate, as soon as possible, the unreacted metal that cannot be removed by traditional filtration methods. In several cases, products of reactions of aromatic compounds with atomic metals are stable colloidal solutions that can be coagulated by variation of the dielectric permeability of the medium. For example, a black metal precipitates when a nonpolar solvent (pentane) is added. A similar effect can also be achieved by the injection of air oxygen in the system, if it is known that the complexes synthesized are rather stable. Using this procedure, the yield of $(PhCN)_2Cr$ can be increased 1.8—2.3 times over that of the procedure used previously.[11] The $(PhCN)_2Cr$ complex was isolated by sublimation at 10^{-5} Torr and -80 °C after removal of the ultradisperse metal and triphenyltriazine from the products of the synthesis.

The reaction of phenylacetylene with atomic chromium differs substantially from the reaction with benzonitrile. No complexes containing η^6-coordinated phenylacetylene as a ligand are observed. Mixtures of isomeric 1,2,4- and 1,3,5-triphenylbenzenes and their π-complexes with chromium are isolated from the reaction products (Scheme 2).[12]

Scheme 2



A specific feature of this reaction is the formation of considerable amounts of organic and organochromium polymeric products. This testifies that the initial arylacetylene undergoes various transformations that occur under the action of atomic metal or of the compounds that appear due to low-temperature cocondensation.

After BAC was separated from the products of the reaction of phenylacetylene with chromium vapor, 1,2,4- and 1,3,5-triphenylbenzenes along with organic and chromium-containing polymers were extracted with benzene.

Compounds containing 0.1—7.6% Cr were obtained by precipitation of the polymers obtained from the benzene solution using methanol. Analysis showed that the content of chromium in the products depends on the ratio of the reagents used and the time from the moment of thawing of the matrix to the beginning of isolation of the products.

Increasing the amount of evaporated chromium at a constant volume of phenylacetylene results in an increase in the fraction of polymerization products in the reaction mixture. This is also favored by an increase in the duration of the exposure of the products of the synthesis at room temperature until the moment of isolation of the individual compounds.

It is noteworthy that the main mass of the polymer obtained in the synthesis (>80%) contains <1% Cr. After repeated reprecipitation of the polymeric products containing the metal, the fraction of the latter increases (for example, from 4.6 to 6.43%).

The composition of the organic polymer corresponds to that of polyphenylacetylene (PPA) $(C_8H_6)_n$. The molecular weight of this polymer determined by ebullioscopy is equal to 800—2000. The molecular weight of the chromium-containing polymers varies from 1200 to 2000 but, unlike organic polymers, their molecular-weight distribution is always narrower regardless of the percentage content of the metal.

For physicochemical studies, we obtained samples of organic and chromium-containing (6.43% Cr) polymers. Their properties were compared to those of PPA synthesized by thermally initiated block polymerization of phenylacetylene.

Analysis of the IR spectra of organic and chromium-containing polymers obtained by cocondensation of phenylacetylene and chromium vapor showed that they are absolutely identical to the spectra of PPA synthesized by the procedure described previously.[13]

For chromium-containing polymers, it is of interest to elucidate the nature of the bond between the metal and the polymeric matrix. The IR spectra of the chromium-containing polymers obtained contain no bands corresponding to vibrations of the chromium—aromatic ring (400—500 cm^{-1}), which are typical of all BAC, including π-complexes with macromolecular ligands.[14]

The ESR spectra of the chromium-containing polymers isolated in air contain a broad signal corresponding to $g = 2.0024$, which is close to the g-factor of a free electron (2.0023). The spectrum contains no signals of paramagnetic $(arene)_2Cr^+$ cations, whose g-factor depends slightly on the nature of the substituent and is equal to 1.986. The signal corresponding to the paramagnetic Cr^{3+} species ($g = 1.9796$) is also not observed. The g-factor remains almost unchanged (2.0027) after treatment of the metal-containing products with a benzene-methanolic solution of potassium iodide or iodine. The product containing 6.43% Cr prepared in an argon atmosphere turned out to be diamagnetic.

The ^1H NMR spectrum of a solution of the chromium-containing polymer (6.43% Cr) in $CDCl_3$ (Fig. 1) contains a broad signal at 6—8 ppm. The shape of the spectrum in this region is identical to the ^1H NMR spectrum of pure PPA (in $CDCl_3$).[15] The multiplet mentioned is assigned to the aromatic and olefinic protons of the polymer. The ^1H NMR spectra of PPA and of the chromium-containing polymer also contain a weak signal at 3.40 ppm assigned to the ≡CH ethynyl protons and are probably caused by the existence of an insignificant admixture of the initial phenylacetylene in the polymer (for a solution of PhC≡CH in $CDCl_3$, δ(≡CH) is equal to 3.40).

The ^{13}C NMR spectra of solutions of PPA and of the chromium-containing polymer in $CDCl_3$ are also similar and contain broadened signals of aromatic and olefinic carbon atoms in the region of 125—130 ppm. Individual sharp signals with chemical shifts at 129.9, 128.8, 127.8, and 127.3 ppm are seen against the background of these compounds. In addition, the ^{13}C NMR spectra of these compounds contain a broadened signal at 141.3 ppm with lower intensity. It is assigned, as the procedure of polarization transfer (DEPT) shows, to the *ipso*-C atoms of the aromatic rings.

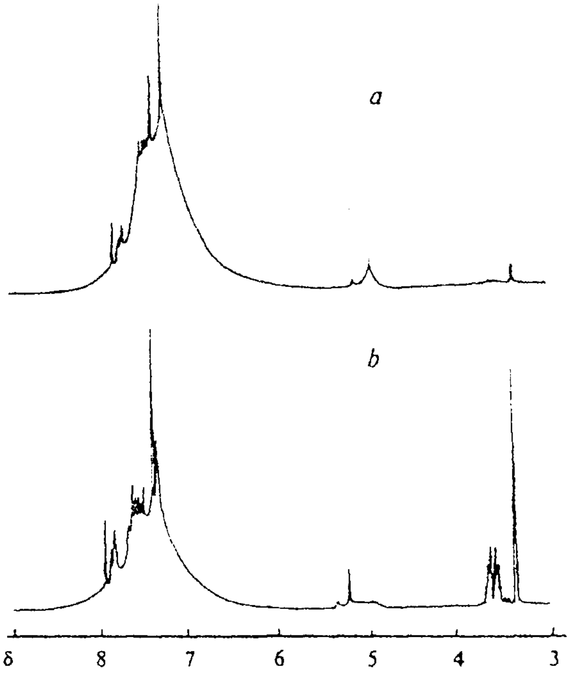


Fig. 1. ^1H NMR spectra of polyphenylacetylene (*a*) and metal-containing (6.43% Cr) polymer obtained by cryochemical synthesis (*b*) in $CDCl_3$.

It follows from the spectral data that the structure of the chromium-containing polymeric product isolated is similar to that of PPA (both obtained by us and described previously[13,15]). The ^1H and ^{13}C NMR spectra of chromium-containing polyphenylacetylene contain no signals assigned to protons or to C atoms of polymeric phenyl groups coordinated to the Cr atom (the bisarene π-complex type), which, by analogy with bisarenechromium complexes,[3] should lie at considerably higher fields than those of the initial PPA.

Various structural and physicochemical properties of PPA under various conditions of polymerization of phenylacetylene and for different types of the catalyst used have been studied previously.[13,15] In this connection, it was of interest to study the properties of the organic and organochromium polymeric compounds obtained and to compare them with the available published data.

The properties of the metallopolymers isolated with different contents of chromium were compared with the parameters of pure PPA with a molecular weight close to that of chromium-containing polymers.

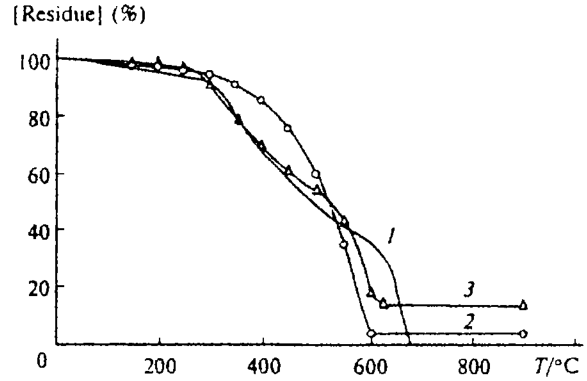


Fig. 2. Dynamic thermogravimetric analysis of polyphenylacetylene in air: *1*, pure PPA; *2*, PPA containing 1.31% Cr; and *3*, PPA containing 6.43% Cr.

Analysis of the dynamic thermogravimetric tests of the samples performed in air (Fig. 2) showed that increasing the content of chromium in polyphenylacetylene up to 1.31 or 6.43% does not result in a substantial increase in the thermal stability of the polymer in air. At the same time, at the temperature of the complete thermal destruction of pure PPA (680 °C), its chromium-containing analogs have a carbon residue (3 and 14%, respectively) that approximately adequately reflects the percentage content of the metal in the products.

Thermomechanical studies of the same samples (Fig. 3) testify that both pure PPA and metallopolymers are thermally pliable. Pure PPA is a solid substance that transforms into the viscous-flow state at 95—100 °C. The inclusion of a metal in the polymer increases the temperature of the transition to the viscous-flow state. For example, for the product containing 1.31% Cr, it increases to 115—125 °C, and for the sample with 6.43% Cr, it increases to 225—235 °C.

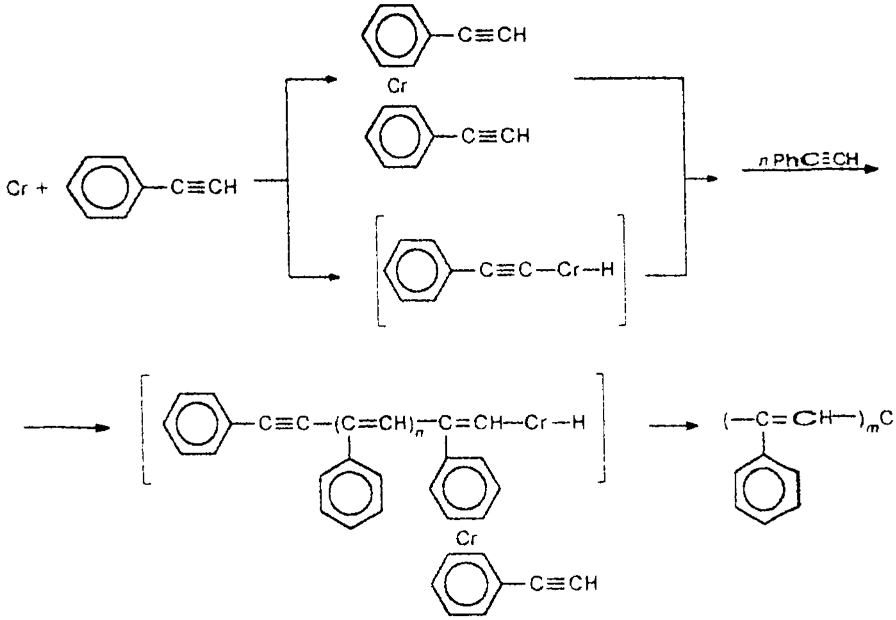
It can be assumed on the basis of the results of the studies performed that the organic component of the organochromium polymer is PPA. An unambiguous conclusion on the nature of the Cr—PPA chemical bond cannot be drawn from the data of ^{1}H NMR, ESR, and IR spectroscopies. A structure of the bisarene complex type is highly improbable. Perhaps, these products are similar to compounds containing metallic clusters in polymeric matrices.[16]

It can be assumed that the polymerization of phenylacetylene under the action of chromium occurs *via* oxidative addition to form the chromium hydridoacetylenide ligand followed by the insertion of phenylacetylene molecules into the carbon—metal σ-bond (Scheme 3).

The participation of the acetylenes formed in the synthesis of BAC in the catalytic cyclooligomerization and polymerization is rather improbable. For example, it has been established that bisarenemolybdenum complexes catalyze cyclotrimerization and polymerization of phenylacetylene, while their bisarenechromium analogs are inactive under these conditions.[17]

The increase in the yield of polymerization products as the duration of exposure of the reaction mixture at 20 °C increases can also be caused by the presence of ultradisperse chromium in the system. It has been mentioned previously[18] that the reaction of phenylacetylene with nickel results in the formation of nickel-containing PPA along with triphenylbenzene and triphenylcyclooctatetraene.

Scheme 3



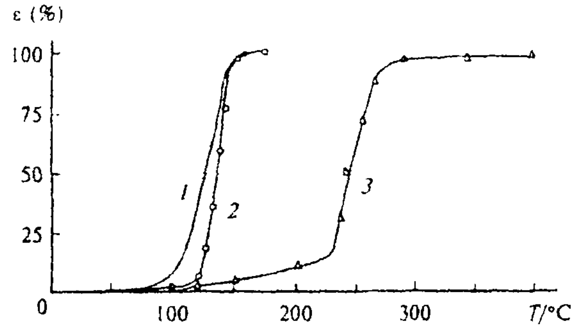


Fig. 3. Thermomechanical curves for polyphenylacetylene: *1*, pure PPA; *2*, PPA containing 1.31% Cr; and *3*, PPA containing 6.43% Cr.

Experimental

Organic reagents and solvents were purified by known procedures.[19] Solvents freshly distilled in a flow of argon were used. The purity of the chromium used was not lower than 99.9%.

The reactions of organic compounds with chromium vapor were performed in a reactor at $p = 10^{-4}$ Torr and $T = 77$ K. A W-resistive evaporator was used for the preparation of the metal in the vapor state. An organic compound was continuously injected into the reactor, while the flow rate was controlled by a fine-adjusting valve. All procedures to isolate products were carried out in an atmosphere of purified argon.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker WR-200SY instrument. ESR spectra were recorded on an ERS-200 instrument. IR spectra were recorded on a spectrometer in pellets with KBr. Thermomechanical compression curves were obtained for pellets 4.5 mm in diameter and 2 mm thick. The pressure on a punch (44 mm in diameter) was equal to 0.8 MPa. The temperature was increased at a rate of 70 °C h^{-1}. The dynamic thermogravimetric analysis in air was performed on a MOM derivatograph (Hungary) (the rate of the temperature increase was 5 °C min^{-1}).

Number-average molecular weights were determined by ebullioscopy in $CHCl_3$ and C_6H_6.

Bis(benzonitrile)chromium. Chromium (0.7 g, 0.013 g-at) was cocondensed with PhCN (60 mL). After the end of the synthesis, the cocondensate was frozen out and siphoned from the reactor to a Schlenk flask in an argon atmosphere, pentane (30 mL) was added, and the mixture obtained was filtered on a column (d = 40 mm, $h_{Al_2O_3}$ = 20 mm, 1% H_2O, C_6H_6). After evaporation of the solution, a dense oily substance remained, which was repeatedly chromatographed on a column (d = 25 mm, $h_{Al_2O_3}$ = 200 mm, 1% H_2O, C_6H_6—petroleum ether (1 : 1) as the eluent, dark-yellow band). The evaporation of the solvents gave a viscous brown liquid.

After recrystallization from benzene, $(PhCN)_2Cr$ (0.73 g, 21%) was isolated as brown crystals with decomp.p. 205 °C (Ref. 11: decomp.p. 205—206 °C). Found (%): C, 65.52; H, 3.82; Cr, 20.72. $C_{14}H_{10}N_2Cr$. Calculated (%): C, 65.12; H, 3.88; Cr, 20.16.

1,3,5-Triphenyltriazine was isolated from the eluate: m.p. 234 °C (from a pentane—benzene mixture) (Ref. 20: m.p. 233—235 °C).

Reaction of phenylacetylene with chromium. Conditions for the isolation and analysis of the reaction products are presented in Ref. 12. Changing the conditions of isolation of the products did not result in a noticeable increase in the yield of $(Ph_3C_6H_3)_2Cr$ or in the formation of other chromium complexes, but exerted a substantial effect on the degree of polymerization of phenylacetylene. The introduction of pentane into the reaction mixture immediately after synthesis decreased the yields of products of oligomerization. One of the samples of chromium-containing polyphenylacetylene was prepared and studied under conditions excluding contact with air.

Phenylacetylene (120 mL) was cocondensed with chromium (1.4 g, 0.027 g-at). The product of the interaction (grayish-brown liquid) was siphoned into a Schlenck flask in an argon atmosphere. The freshly prepared product is pyrophoric in air. After separation of chromium π-complexes and products of cyclotrimerization, a brown powder was obtained. Found (%): C, 82.73; H, 5.60; Cr, 6.43. A crimson-colored substance was isolated from the mother liquor. Found (%): C, 93.61; H, 5.33. C_8H_6. Calculated (%): C, 94.12; H, 5.88.

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