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The chromiumtricarbonyl group as an electron acceptor in η^6-complexes of stilbene and its derivatives

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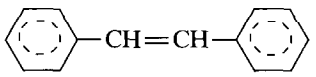
Abstract

The influence of nitro and chromiumtricarbonyl groups on susceptibility of stilbene and 4,4′-dimethoxystilbene to protophilic isotope hydrogen exchange were compared. Both groups assist in the reaction, but for the chromiumtricarbonyl substituent the simultaneous presence of an electron donor fragment (the methoxy group) in the stilbene ligand is necessary.

1. Introduction

Coordination of benzene and its derivatives to the chromiumtricarbonyl group leads to strong drawing off of electron density from arene ligands. The electron withdrawing effect of $Cr(CO)_3$ is juxtaposed with that of NO_2; it is displayed during ionization of suitable carbonic acids [1], and hydrolytic splitting of appropriate methylbenzoates [2].

However, changes in the properties of the stilbene row as a result of metal-coordination remain practically unstudied. It is interesting, therefore, to compare the behaviour of free ligands (**1**,**2**) and their chromiumtricarbonyl derivatives in a particular reaction. In addition, it seems important to compare the reactivities of complex **3** and 4-nitrostilbene (**5**), complex **4** and 4-nitro-4′-(*N*,*N*′-dimethylamino)stilbene (**6**).



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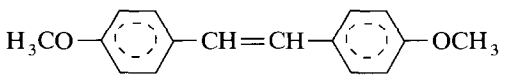

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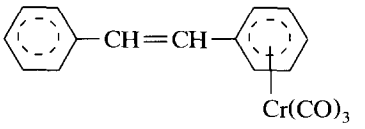

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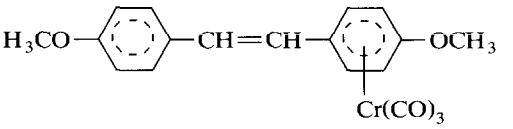

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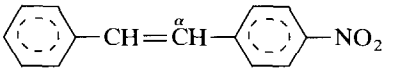

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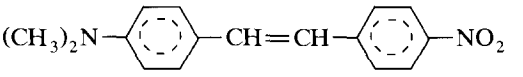

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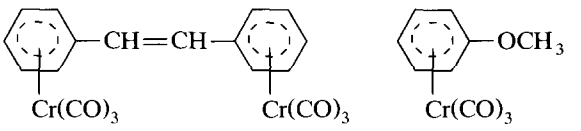

7 **8**

2. Protophilic isotope hydrogen exchange (PIHE)

This exchange reaction was chosen to compare the compounds mentioned above. The conditions of the

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reaction were maintained constant: ^{t}BuOD + ^{t}BuOK, 50°C, 8 h. In this reaction, as in many others, *cis* olefines appear to be more active than their *trans* isomers [3]. Therefore, stilbenes **1**–**5** and **7** were examined as *cis* form; stilbene **6** was prepared only in trans form.

Under the conditions indicated above, non-coordinated ligands **1** and **2** are not involved in PIHE entirely. Stilbene coordinated to one chromiumtricarbonyl (*i.e.* complex **3**) also does not enter into PIHE. The nearest non-metallic analogue of this complex, 4-nitrostilbene **5**, exchanges an α-proton very effectively (PIHE proceeds by 80%) [3]. Thus, a complete analogy between NO_2 and $Cr(CO)_3$ is not possible under the conditions of PIHE. The former group is a much stronger acceptor than the latter.

If the influence of one $Cr(CO)_3$ fragment is reinforced by the introduction of another $Cr(CO)_3$ fragment, the exchange does take place: the binuclear complex **7** is enriched by deuterium by 20% (15% corresponds to the exchange of olefinic protons and 5% to that of aromatic protons).

An unexpected activating effect is observed at the presence of methoxy groups in the mononuclear chromiumtricarbonyl complex **3**. In the case of η^6-chromiumtricarbonyl-4,4′-dimethoxystilbene (**4**), it is the mononuclear complex that undergoes PIHE. The total extent of the exchange amounts to 15% (10% for aromatic protons and 5% for olefinic protons); methoxy protons do not take part in PIHE. With hydrogen–deuterium exchange, complex **4** occupies an intermediate position between 4-nitrostilbene (**5**) and η^6-chromiumtricarbonyl anisole (**8**): in the case of stilbene **5**, hydrogen–deuterium exchange involves entirely the α-olefinic proton, and in the case of metallocomplex **8** it involves entirely aromatic protons [4].

As follows from the comparison of 4,4′-dimethoxystilbene (**2**) with its η^6-chromiumtricarbonyl complex **4**, the $Cr(CO)_3$ activates the stilbene system in the same manner as the nitro group does in compound **5**. The ethylenic bond is able to take part in PIHE. At the same time, the $Cr(CO)_3$ group, being coordinated to the anisyl ring altogether, activates this ring. The susceptibility of ring protons to PIHE, in the case of complex **4**, remains principally the same as that of complex **8**. In other words, chromiumtricarbonyl dimethoxystilbene has two reactive positions: the aromatic ring coordinated to the chromiumtricarbonyl group (analogous with the arenechromiumtricarbonyl complex **8**) and the ethylenic bond conjugated with the electron withdrawing group $Cr(CO)_3$.

Comparison of the stilbene complex **3** with the dimethoxystilbene complex **4**, leads to an unusual observation: instead of weakening the effect of the $Cr(CO)_3$ acceptor, the donor substituent OCH_3 strengthens it. This is in full accordance with previously published observations: the removal of electron density from the arene ligand onto the $Cr(CO)_3$ fragment proceeds more effectively when the arene ligand contains donor substituents [5]. Intensification of this removal is an effect specific to metallocomplexes: uncoordinated stilbene **6** contains NO_2 as acceptor and as $N(CH_3)_2$ as donor; unlike the nitrostilbene **5**, the "push–pull" stilbene **6** is completely insensitive to PIHE.

3. Experimental details

^{1}H NMR spectra were recorded using a Bruker WP-200 SY spectrometer (TMS as internal standard). Mass spectra were recorded with an MS-30 spectrometer (ionization potential 70 eV). TLC was performed with Silufol UV-254 plates (eluent hexane–ether 3 : 1). Physical constants and spectral characteristics of the substances were in accordance with literature data.

Chromiumtricarbonyl complexes of *cis*- and *trans*-4,4′-dimethoxystilbenes were prepared for the first time according to the following procedure.

A mixture of 500 mg (2 mmol) 4,4′-dimethoxystilbene, 470 mg (2.55 mmol) triammoniachromiumtricarbonyl and 12 ml dioxan was boiled for 4 h with stirring. During boiling all the stilbene was involved in complex formation (monitored by TLC). The mixture was cooled to 0°C, filtered, and the filtrate was evaporated. The residue was recrystallized twice from heptane–ether 1 : 2. Yellow crystalline η^6-4,4′-dimethoxystilbene chromium tricarbonyl (**4**) was obtained: 230 mg (0.6 mmol). Anal. Found: C, 60.92; H, 4.22; Cr, 13.95% (Molecular mass 376 (mass spectrometry)). $C_{19}H_{16}CrO_5$ calc.: C 60.80, H 4.29, Cr 13.83 (Molecular mass 376.3). Melting points: complex **4** in *cis* form 104°C, complex **4** in *trans* form 159°C.

3.1. Protophilic isotope hydrogen exchange

The experiments were conducted in an argon atmosphere. Metallic potassium (1.0 mg-atom) was dissolved in 5 ml t-butyl alcohol (98% deuterium in the hydroxy group) and heated up to 50°C. Chromiumtricarbonyl complexes of different stilbenes (1.0 mmol) were added, in small portions, into the solution. The mixture was stirred at the same temperature for 5 h. Then potassium t-butylate was separated by filtration and washed with absolute THF. The combined filtrate and washings were evaporated, and the dry residue was crystallized several times from benzene–ether 3 : 1. Chromiumtricarbonyl complexes of stilbenes were obtained (0.1 mmol) and identified according to melting points and mass and ^{1}H NMR spectra.

3.2. Determination of deuterium enrichment (combination of mass and ^1H NMR spectra)

3.2.1. Bis(chromiumtricarbonyl)stilbene

The complex (before and after hydrogen–deuterium exchange) was dissolved in $CDCl_3$ to obtain solutions of equal concentrations. ^1H NMR spectra of the solutions were compared. The degree of hydrogen–deuterium exchange was determined for the ethylenic bond (15%). From mass spectra, total enrichment of the complex amounted to 20% (5% referred to benzene rings).

3.2.2. Chromiumtricarbonyl-4,4'-dimethoxystilbene

Comparison of PMR spectra of equimolar solutions of the complex before and after hydrogen–deuterium exchange showed that the ethylenic bond was enriched by deuterium by 5%. According to the mass spectrum, the total deuterium enrichment of the complex was estimated as 15%. Deuterium was not involved in the methoxy group because its percentages in the molecular ion and in the fragment ion M^+-OCH_3 were equal. Fragment ions $(ArCH{=}CHAr)^+$ and $(ArC{\equiv}CAr)^+$ contained 15% and 10% deuterium respectively. In the latter, deuterium can only be included in a benzene ring; this is obviously the chromium-coordinated benzene ring—the literature analogue has already been quoted [4].

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