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η^6 -Chromiumtricarbonyl complexes of stilbene and 4,4'-dimethoxystilbene: slipping off the ligands enables *cis*–*trans* isomerization

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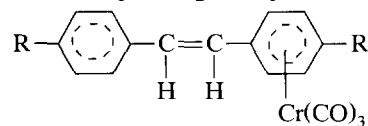
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Abstract

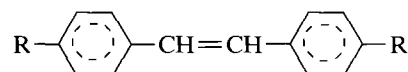
η^6 -Chromiumtricarbonyl complexes of stilbene and 4,4'-dimethoxystilbene (both in the *cis* form as ligands) were prepared. The complexes are stable as dry solids, but disintegrate during exposure at 25°C in argon, with liberation of the ligands. They are returned as a mixture of *cis*–*trans* isomers. The conversion of *cis*–*trans* types observed depends not on the spontaneous isomerization of a ligand in a complex, but on the interaction between the slipping ligand and chromium sesquioxide—the product of the transformation of the $\text{Cr}(\text{CO})_3$ fragment.

1. Introduction

In complexes with general formula **1**, the chromiumtricarbonyl group coordinated at the benzene ring influences the ethylenic bond. This group acts as an acceptor and draws off the electron density of the ethylenic bond. This effect resembles the removal of electron density in charge-transfer complexes under the influence of an external acceptor molecule. As shown for 4,4'-dimethoxystilbene, charge-transfer complexation provokes *cis*–*trans* conversion [1]. The conversion proceeds slowly and, for example with tetracyanoquinodimethane as an acceptor, takes several years (at 25°C). For this reason, the action of an internal acceptor, $\text{Cr}(\text{CO})_3$, is interesting, with respect to the *cis*–*trans* conversion of the stilbenoid ligand as a result of prolonged exposure.



1: R = H (**a**), OCH_3 (**b**)



2: R = H (**a**), OCH_3 (**b**)

2. Behaviour of complexes **1a** and **1b** during prolonged exposure in solution

Exposure of complexes **1a** and **1b** at 25°C in argon for two weeks results in the liberation of ligands **2a** and **2b** as a mixture of *cis* and *trans* forms. The degree of *cis*–*trans* conversion is 42% for complex **1a** and 31% for complex **1b**.

There are two possible causes of the stereoisomeric transformation: action of an internal acceptor which is developed during prolonged storage of the sample in solution, or action of an external oxidizer. The disintegration of complexes **1a** and **1b** during prolonged storage in argon proceeds slowly and is revealed by the formation of green turbidity. The liquid phase contains quantities of metal complexes which are gradually reduced. According to ¹H NMR spectra, the complexes retain the initial *cis* structure of coordinated stilbene until the very moment of decomposition. Hence, internal activation cannot be the cause of stereoisomeric interconversion of the ligands.

3. Action of external oxidizers

External oxidizers were used to check the suppression of external activation.

3.1. Oxidation using π -acids

π -Acids were used as model oxidizers which are unable to cause severe destructive changes in com-

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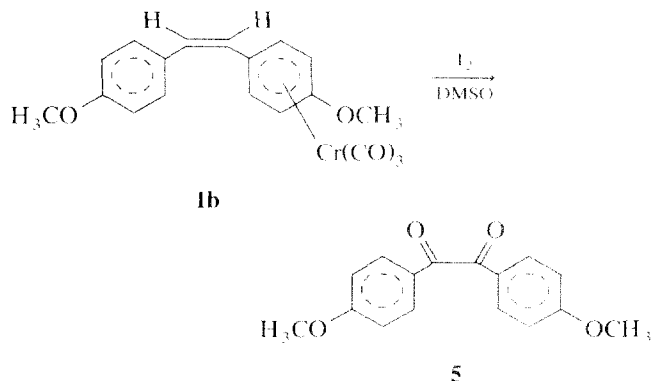
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plexes **1a** and **1b** and ligands **2a** and **2b**. *p*-Chloroanil (**3**) and *cis*- α,β -dinitrostilbene (**4**) were chosen as the model oxidizers.

In each case, the interaction between these oxidizers and complex **1b** or the *cis* form of ligand **2b** was studied; the proportion of reagents was equimolecular. Experimental conditions were, naturally, identical for complex **1b** and for ligand **2b**. In the case of oxidizer **3**, the mixtures were held for 15 h at 40°C in methylene chloride; the degree of conversion of stilbene **2b** was equal to 30%, and complex **1b** was returned without any changes. In the case of oxidizer **4**, the mixtures were held for two weeks at 20°C in benzene-*d*₆; the degree of conversion of stilbene **2b** reached 50%, and complex **1b** was not changed.

3.2. Oxidation using iodine

Iodine is a rather weak oxidizer and is commonly used to remove ligands from a central metal atom. Complex **1b** yielded 4,4'-dimethoxydibenzoyl (**5**) as a result of iodine treatment in DMSO:



The same diketone **5** was formed after iodine treatment of ligand **2b** in DMSO. The transformation of stilbene into dibenzoyl under these conditions is described in a recent work [2]. Iodine annihilates the indicator fragment, *i.e.* the ethylenic bond.

3.3. Oxidation using chromium sesquioxide

An oxidizer had to be chosen which cannot transform the ethylenic fragment into an α,β -dicetonic fragment. Decomposition of complexes **1a** and **1b** results in the formation of green turbidity. This suggests that chromium sesquioxide is an appropriate oxidizer (Cr_2O_3 , green colour). The formation of this oxide has also been used to mark the decomposition of other chromiumtricarbonyl complexes [3].

cis-Stilbenes **2a** and **2b** yield *trans* isomers after treatment with a suspension of chromium sesquioxide in benzene; the degrees of conversion are 39% and 28.5% respectively. These conversions are practically equal to those observed during the disintegration of chromiumtricarbonyl complexes **1a** and **1b** (see above).

4. Conclusion

With respect to π -acids **3** and **4**, complex **1b** and ligand **2b** behave differently: the metallocomplex **1b** appears to be stable configurationally, whereas ligand **2b** isomerizes to a marked extent. A reasonable explanation of this result is the strong electron acceptor effect of the chromiumtricarbonyl group on the π -system of the dimethoxystilbenic ligand in complex **1b**. This effect reduces the removal of electron density from complex **1b** onto the π -acids **3** and **4**, *i.e.* isomerization of the complex is hindered, compared with stilbene **2b**. The data obtained allow us to conclude that the introduction of chromium in the stereoinicator system of *cis*-4,4'-dimethoxystilbene increases its configurational stability. The liberation and configurational isomerization of ligands **2a** and **2b** take place during prolonged exposure of chromium complexes **1a** and **1b** in solution. Ligand isomerization is explained not by spontaneous rotation around the ethylenic bond in the body of the complex, but by complex destruction and posterior interaction between the liberated ligand and chromium sesquioxide (the product of transformation of the chromiumtricarbonyl fragment).

5. Experimental details

η^6 -Chromiumtricarbonyl complexes of stilbene (**1a**) and 4,4'-dimethoxystilbene (**1b**) were prepared by boiling suitable stilbene with triammoniumchromiumtricarbonyl in the molar proportion 2:2.55 for 4 h, in dioxan.

η^6 -Chromiumtricarbonyl-*cis*-stilbene (**1a**). Yield 40%, melting point 107°C. ^1H NMR (CDCl_3 , δ , ppm): 7.28 (s, 4H, Ar), 6.70 and 6.12 (q, 2H, CH=CH), 5.23 (s, 4H, ArCr).

η^6 -Chromiumtricarbonyl-*trans*-stilbene was prepared in the same manner. Yield 20%, melting point 134°C. ^1H NMR (CDCl_3 , δ , ppm): 7.35 (s, 4H, Ar), 6.50 and 6.32 (q, 2H, CH=CH), 5.45 (s, 4H, ArCr).

η^6 -Chromiumtricarbonyl-*cis*-4,4'-dimethoxystilbene (**1b**) was obtained using the reaction mentioned above. Yield 30%, melting point 103°C. ^1H NMR (C_6D_6 , δ , ppm): 7.10 and 6.70 (AA'BB', 4H, Ar), 6.30 and 5.70 (q, 2H, CH=CH), 5.10 and 4.33 (AA'BB', 4H, ArCr), 3.30 (s, 3H, OCH_3 of Ar), 2.90 (3H, OCH_3 of ArCr).

η^6 -Chromiumtricarbonyl-*trans*-4,4'-dimethoxystilbene was prepared in the same manner. Yield 17%, melting point 157°C. ^1H NMR ($(\text{CD}_3)_2\text{CO}$, δ , ppm): 7.15 and 6.95 (AA'BB', 4H, Ar), 7.25 and 6.72 (q, 2H, CH=CH), 6.20 and 5.60 (AA'BB', 4H, ArCr), 3.84 (s, 3H, OCH_3 of Ar), 3.80 (s, 3H, OCH_3 of ArCr).

The complexes and the free ligands, returned after the reactions, were identified using ^1H NMR spectroscopy.

As was established previously [4], *cis*- and *trans*-stilbenes can be identified qualitatively from ^1H NMR spectra of their mixtures. In the present work, the degree of conversion was determined quantitatively by comparison between integral intensities of appropriate signals. In order to check the results, artificial mixtures were prepared by weighing, and then the proportion of components was determined from the ^1H NMR spectra. For different mixtures, the *cis*:*trans* proportions were 25:1, 10:1, 17:1 (by weight) and 24:1, 11.5:1, 15.7:1 (by comparison of ^1H NMR integral intensities).

In the case of 4,4'-dimethoxystilbene (**2b**), *cis* and *trans* isomers can be clearly distinguished by chemical shifts of methoxyl protons, *cf.* δ (ppm): 3.80 and 3.83 in $(\text{CD}_3)_2\text{CO}$; 3.80 and 3.84 in CDCl_3 ; 3.29 and 3.33 in C_6D_6 . Proton integral intensities of methoxyls were compared for *cis* and *trans* isomers. This relation was adopted as the relation of isomers in the mixtures. The isomers were separated, in parallel with ^1H NMR, by means of TLC (Silufol UV-254 plates, eluent hexane-ether 2:1, development in UV light, $R_f(\textit{cis})$ 0.46, dark band and $R_f(\textit{trans})$ 0.38, band with blue reflection). The bands were separated mechanically, then extracted with benzene, the extracts were evaporated, and the remains were weighed. The relation of *cis*:*trans* isomers in mixtures was 1.9:1, 2.6:1 according to TLC, and 2:1, 2.8:1 according to ^1H NMR.

The oxidation of stilbenes was conducted in argon.

5.1. Oxidation with *p*-chloroanil (**3**)

A solution of *cis*-4,4'-dimethoxystilbene (*cis*-**2b**, 5 mmol) and *p*-chloroanil (**3**, 5 mmol) in 10 ml CD_2Cl_2 was heated at 40°C for 15 h. The solution was first violet coloured and then green. According to analysis, a mixture of *cis*- and *trans*-**2b** was formed, the degree of conversion being 30%.

5.2. Oxidation with *cis*- α,β -dinitrostilbene (**4**)

A solution of *cis*-**2b** (0.1 mmol) and *cis*-**4** (0.1 mmol) in 4 ml C_6D_6 was held at 20°C for 80 h. The solution

was then evaporated, and the remains were analysed by ^1H NMR and TLC. As established, *Cis*-**2b** was transformed into *trans*-**2b** by 50% (^1H NMR) or 53% (TLC). *cis*-*trans* conversion of oxidizer **4** was not observed. This was concluded on the basis of absence of the spot of *trans*-**4** in the thin-layer chromatogram or ^1H NMR signals of *ortho*-protons of the benzene ring of *trans*-**4** with chemical shifts of 7.41 and 7.37 ppm. These signals are quite different from all other signals of *cis* or *trans*-**4** in the region of 6.99–6.68 ppm.

5.3. Oxidation with iodine

A solution of *cis*-**2a** or *cis*-**2b** (1.5 mmol) and iodine (1.5 mmol) in 16 ml DMSO was held at 155°C for 10 h. The resulting mixture was poured into a 1% aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (40 ml). Yellow crystals (yield 90%–95%) were deposited: dibenzoyl melting point 93°C (literature melting point 94°C [2]), 4,4'-dimethoxydibenzoyl melting point 127°C (literature melting point 128°C [5]). In the latter case the product was characterized by elemental analysis and ^1H NMR. Found: C 71.09%, H 5.08%. $\text{C}_{16}\text{H}_{14}\text{O}_4$ calculated: C 71.19%, H 5.19%. ^1H NMR spectrum (C_6D_6 , δ , ppm): 8.00 and 6.50 (H, Ar), 3.07 (H, OCH_3).

5.4. Oxidation with chromium sesquioxide

A solution of *cis*-**2a** or *cis*-**2b** (1.5 mmol) in 10 ml C_6D_6 was stirred with Cr_2O_3 (3 mmol) at 20°C for 6 h. After filtration, the resulting solution was evaporated and the rest was analysed by ^1H NMR. The degree of conversion was found to be 39% for *cis*-**2a** and 28.5% for *cis*-**2b**.

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