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## The study of catalyst effects on the complexation of arenes with $\text{Cr}(\text{CO})_6$ . An overview \*

Milan Hudeček, Vladimír Gajda and Štefan Toma \*

*Department of Organic Chemistry, Comenius University, 842 15 Bratislava (Czechoslovakia)*

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### Abstract

New results from our thorough investigation of different catalytic effects on the rate and yields of complexation of arenes with  $\text{Cr}(\text{CO})_6$  are presented with a short review of the subject. With decalin as solvent the following substances were found to be the best catalysts: butyl acetate, ethyl formate, and dimethyl succinate. Butyl acetate proved to be the catalyst also in di-*n*-butyl ether. Special attention was paid to the complexation of naphthalene, and chlorobenzene. Some unsuccessful attempts at asymmetric induction of complexation are also described.

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### Introduction

The main problems connected with the direct complexation of arenes with  $\text{Cr}(\text{CO})_6$  are (i) long reaction times; (ii) sublimation of  $\text{Cr}(\text{CO})_6$  into the condenser; (iii) the separation of the product from a high boiling-point solvent, and (iv) decomposition of the product during complexation or isolation. The main goal of our work was to develop a method which would minimize or eliminate these problems.

### Discussion

In a previous paper [1] we described a special adapter which minimizes the problems with the sublimation of  $\text{Cr}(\text{CO})_6$  as well as those associated with  $\text{Mo}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$ . The apparatus was designed so that the course of the reaction could be followed volumetrically by measuring the CO evolved. The complexation of *N,N*-dimethylaniline was chosen as a test for finding a suitable solvent. Decalin due to its high boiling point proved to be the best, and 99.5% of the complex was isolated after 5.5 hours of reflux. The effects of dioxane and dibutylether as solvents were nearly equivalent (15.5% and 13.5% yield respectively of the complex after 5.5 hours of refluxing). The use of decalin as a solvent considerable reduced the time of

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\* Dedicated to Professor P.L. Pauson.

complexation e.g. 4–7 hours instead of 30–40 hours required for the Pauson–Mahaffy method [2]. The yields were either similar or higher, except in the cases of benzene, chloro- and fluorobenzene. The separation of the products was usually very simple, involving no more than freezing out at  $-18^{\circ}\text{C}$  or quick chromatography of the decalin solution on a  $\text{SiO}_2$  column. The cold reaction mixture should be filtered through kieselguhr immediately after complexation, to prevent autocatalytic decomposition.

During our investigation [1,3] we observed that our method could be successfully applied to many benzene derivatives and also to some polycyclic arenes but attempts at complexation of benzaldehyde, benzoic acid, nitrobenzene, thiophenol and chalcone failed. Complexation of benzene, chloro- and fluorobenzene met with failure too (no more than 8% of the complexes were isolated). On the other hand we observed fairly rapid complexation of benzophenone and esters of benzoic as well as phenylacetic acids. This, and the well known catalytic effect of acetone and other ketones on the ligand exchange reaction [4,5], as well as that of other coordinating ligands on solvolysis of  $\eta^6$ -arenetricarbonylchromium complexes [6] gave us a hint for studying certain substances as the catalyst for the complexation of arenes with  $\text{Cr}(\text{CO})_6$  [7]. The catalytic effects of butanone, butyl acetate, ethyl acetate, acetonitrile and dimethylacetamide were examined.

The highest rate of complexation of toluene was observed with dimethylacetamide as the catalyst, but decomposition of the product begun very early. Butyl acetate was found to be the best catalyst because the rate of complexation was high and we did not observe decomposition of the product during complexation. It seems that butyl acetate and other esters exhibit both a catalytic effect on complexation and some stabilizing effect on the product. Butyl acetate can be used not only as the catalyst but also as the solvent for complexation but due to its lower boiling point the rate of complexation is considerably lower. Typical examples of complexation of different arenes are given in Table 1. As can be seen the addition of two molar equivalents of butyl acetate into a solution of arene in decalin has a dramatic effect on the yields as well as on rate of complexation. ( $\eta^6$ -Benzene)tricarbonylchromium was prepared by our method in 97% yield after 5.5 h of reflux, while the Pauson–Mahaffy method produced 89% yield after 40 h of reflux. Likewise ( $\eta^6$ -toluene)tricarbonylchromium has been prepared by our method in 99% yield in 3 h time, while Fischer et al. [8] isolated only 53% of the complex after 13 h heating of a large excess of toluene with  $\text{Cr}(\text{CO})_6$  at  $245^{\circ}\text{C}$ . (The ratio arene:  $\text{Cr}(\text{CO})_6$  is 3:1 in our case.)

Complexation of naphthalene with  $\text{Cr}(\text{CO})_6$  in the presence of butyl acetate gave no ( $\eta^6$ -naphthalene)tricarbonylchromium after evolution of CO ceased, but some indirect evidence indicates the formation of bis( $\eta^6$ -naphthalene)chromium. In the first place, six equivalents of CO were evolved. Secondly the reaction mixture at the end of reaction was clear but green (( $\eta^6$ -naphthalene)tricarbonylchromium is red), and thirdly, the  $R_F$  value of the green product was only slightly lower than that of decalin, which is not the case with ( $\eta^6$ -naphthalene)tricarbonylchromium. For this reason it was not possible to isolate the green product in a pure state by column chromatography. The experiment was repeated, and after the evolution of CO ceased the reaction mixture was cooled and extracted with a 10% aqueous solution of HCl in which  $\text{NH}_4\text{PF}_6$  was dissolved. In this way 27% of a green solid [calculated on bis( $\eta^6$ -naphthalene)chromium $^+\text{PF}_6^-$ ] was isolated. Unfortunately the elemental

Table 1

The complexation of different arenes with  $\text{Cr}(\text{CO})_6$ 

No.	Arene	Described yield/time (%/h)	Decalin yield/time (%/h)	Catalyst <sup>a</sup>	Yield/time (%/h)
1	Benzene	89/42 [2]	3.5/4	A	97/5.5
2	Toluene	53/13 [8]	34/4.5	A	99/3
3	<i>o</i> -Xylene	44-81/15 [8,12,13]	—	A	98/2.5
4	Naphthalene	60/35 [15]	36/7	A	see text
				B	30/6
				C	50/4
5	Methyl benzoate	89/20 [2]	84/6.5	A	85/6
6	Ethyl benzoate	15/27 [14]	76/3.5	—	—
7	Methyl phenyl-acetate	—	83/4.5	A	96/2.5
8	Acetophenone	35/4.5 [12]	48/1.5	A	45/3.5
				C	86/3.5
9	Benzoic acid	0	0	A	27/1.5
10	Chlorobenzene	64/20 [2]	1/5	A	63/6
11	<i>N,N</i> -Dimethyl-aniline	85/19 [2]	99.5/5.5	—	—

<sup>a</sup> A: butyl acetate; B: ethyl acetate; C: ethyl formate.

analysis (Found: C, 32.89; H, 6.35; F, 7.56%) and the IR spectrum of the solid ( $\nu$  values in  $\text{cm}^{-1}$ : 790; 845; 1030; 1060; 1440; 1510 and 1580, all of them nearly of the same intensity) did not prove the proposed structure. It is worthy of note that according to the literature [9,10] the synthesis of bis( $\eta^6$ -naphthalene)chromium from naphthalene and  $\text{Cr}(\text{CO})_6$  has not been described and the oxidation of this complex to the cation is not possible because the complex is decomposed to  $\text{Cr}^{3+}$  salts [9].

As butyl acetate failed to catalyse the synthesis of ( $\eta^6$ -naphthalene)tricarbonylchromium we decided to examine other esters for the same purpose. Ethyl acetate yielded only 30% of the ( $\eta^6$ -naphthalene)tricarbonylchromium due to considerable decomposition of the complex. Ethyl formate demonstrated itself to be a good catalyst because no decomposition of the product was observed and 50% of the complex was isolated. The same ester proved to be a good catalyst for complexation of acetophenone (86%) but not as good in complexation of toluene (see Table 2). The scope and limits of ethyl formate as a catalyst for complexation of different arenes is now under study in our laboratory.

As it was mentioned earlier the complexation of chloro- and fluorobenzene caused problems [1] because only very low yields of the complex were isolated, and in all experiments ( $\eta^6$ -benzene)tricarbonylchromium, as well as ( $\eta^6$ -tetraline)tricarbonylchromium was produced. Using butyl acetate to catalyse complexation of chlorobenzene seems to solve the problem because 63% of the ( $\eta^6$ -chlorobenzene)tricarbonylchromium was isolated. Nevertheless again the presence of some ( $\eta^6$ -benzene)tricarbonylchromium, and ( $\eta^6$ -tetraline)tricarbonylchromium was observed. This indicated that reductive dehalogenation of the complex can take place and that decalin is the source of the hydrogen.

The complexation of chlorobenzene in a mixture of paraffin oil and n-heptane (b.p. 180°C) with ethyl formate as the catalyst has been attempted. No ( $\eta^6$ -

Table 2

The complexation of toluene with  $\text{Cr}(\text{CO})_6$  in boiling decalin with different catalysts

Catalyst	Yield/time (%/h)	Catalyst	Yield/time (%/h)
$\text{CH}_3\text{COOC}_4\text{H}_9$	97.5/4.5	$\text{CH}_3\text{COOC}_2\text{H}_5$	92/8.5
$\text{HCOOC}_2\text{H}_5$	70/5.5	$\text{CH}_3\text{COCH}_2\text{CH}_3$	72.5/6
$\text{CH}_3\text{CN}$	80.5/9	THF	85/7
$\text{HCOOC}_4\text{H}_9$	94/9.5	triacetylcellulose	37/3 <sup>a</sup>
$\text{CH}_3\text{CON}(\text{CH}_3)_2$	0	DMAP	0
$(\text{COOC}_2\text{H}_5)_2$	80/1.25	$\text{CH}_2(\text{COOCH}_3)_2$	75/1.75
$(\text{CH}_2\text{COOCH}_3)_2$	100/2.3	$\text{CH}_3\text{CONCH}(\text{COOC}_2\text{H}_5)_2$	74/0.75 <sup>b</sup>

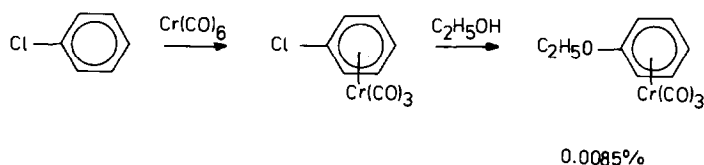
<sup>a</sup> 0.5 g of triacetylcellulose was used. <sup>b</sup> 3.1 mmol of the catalyst, instead of the usual 31 mmol was used.<sup>c</sup> When di-n-butyl ether was used as the solvent, and butyl acetate as a catalyst 87% of the complex was isolated after 12 h of reflux.

benzene)tricarbonylchromium was detected, and the yield of ( $\eta^6$ -chlorobenzene)tricarbonylchromium was rather low (30–50%), but a new complex (0.08%) was isolated. The analysis and  $^1\text{H-NMR}$  spectra confirmed its structure as ( $\eta^6$ -ethoxybenzene)tricarbonylchromium. A possible explanation for its formation lies in the fact that under the reaction conditions ( $\sim 180^\circ\text{C}$ ) the ethyl formate is at least partially decomposed to  $\text{CO}$  and  $\text{C}_2\text{H}_5\text{OH}$ , and a nucleophilic substitution is conceivable (Scheme 1).

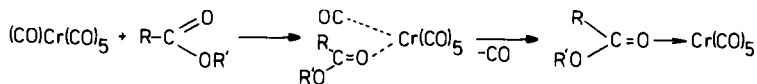
Another attempt at complexation of chlorobenzene was made in high boiling petroleum from which unsaturated hydrocarbons had been completely removed. Again only a small amount of ( $\eta^6$ -chlorobenzene)netricarbonylchromium was isolated together with some oily material which might be ( $\eta^6$ -alkoxybenzene)tricarbonylchromium (NMR). This means that during the extraction of the petroleum ether with concentrated  $\text{H}_2\text{SO}_4$  and its subsequent washing with water some  $\text{ROH}$  must be formed, which could act as a nucleophile. We assume therefore that the complexation of haloarenes should be possible in pure n-decane or in a mixture of high boiling n-alkanes.

As all esters we studied had some catalytic effect on complexation the question as to their mechanism of action arose. A dissociative mechanism of complexation is generally accepted [9,10], according to which the liberation of the first  $\text{CO}$  molecule from  $\text{Cr}(\text{CO})_6$  is the rate determining step, and the total rate of reaction is almost unaffected by the nature or concentration of arene. As the reaction rate is considerably increased by the presence of esters we assume participation of the ester in this stage of the reaction. The mechanism could be thus formulated (Scheme 2).

Our attempts to isolate  $(\text{RCOOR}')_n\text{Cr}(\text{CO})_{6-n}$  or to detect an intermediate by IR or  $^1\text{H-NMR}$  spectra failed. Some evolution of  $\text{CO}$  during the heating of  $\text{Cr}(\text{CO})_6$



Scheme 1.



Scheme 2.

with different esters was observed but the reaction terminated at a very low conversion. If our assumption is correct some catalytic effects should be observable also in the case of some other substances which could form a dative bond with Cr, and the diesters should be even better catalysts than the monoesters due to a hypothetical chelation effect, and/or their higher boiling point. The results of complexation with the help of different catalysts are summarised in Table 2. Surprisingly acetonitrile and THF are not very good catalysts under these conditions. It is difficult to say whether their poorer coordination properties are responsible for that result, because the rate of complexation depends very much on the reaction temperature. Their boiling points are much lower than that of decalin and this could have a considerable effect on the rate of reaction.

We were surprised that neither dimethylacetamide nor 4-dimethylaminopyridine (DMAP) can be used as the catalyst due to the rapid decomposition of the complex or  $\text{Cr}(\text{CO})_6$ , and we do not have any explanation for this fact. On the other hand all diesters are good catalysts, with reaction time being much shorter in these cases and the yields are high. Some lower yields than in the case of butyl acetate are probably caused by certain problems connected with the separation of the product from diesters and with decomposition of the complex. This difficulty could be reduced by the evaporation of diester at reduced pressure. A good example is the experiment with dimethyl succinate as the catalyst. The catalyst was evaporated at 0.1 mmHg, and 100% of ( $\eta^6$ -toluene)tricarbonylchromium was isolated. The catalytic effect of diethyl acetamidomalonate is also promising because the yield of complex was 70%, and reaction time was very short (0.75 h). Another advantage of this catalyst is that only 3.1 mmol of it was used while 31 mmol of butyl acetate was used in the analogous experiment. Some optimizing experiments with this catalyst would be desirable. To our surprise triacetylcellulose is not a good catalyst, and this may be caused by its lower solubility in decalin, but also some decomposition of the complex on its surface was observed. As can be seen from Table 2, acetic acid can be used as a catalyst of complexation, being especially good for complexation of ketones. Details are published elsewhere [11].

We have tried butyl acetate as a catalyst in other solvents. As can be seen from the footnote to Table 2, butyl acetate has a beneficial effect on complexation in di-*n*-butyl ether because 87% of the complex was isolated after 12 h of reflux while under Pauson–Mahaffy conditions such a yield was obtained after 40 h of reflux. Butyl acetate also has a noticeable, but small catalytic effect in dioxane, but no effect was observed in the mixture di-*n*-butyl ether/*n*-heptane 1 : 1.5.

There was some hope that with optically active esters some asymmetric induction of complexation of *o*-disubstituted benzenes could be observed. Unfortunate no asymmetric induction was observed during attempts to complex *o*-methalanisole or 2-(*o*-methoxyphenyl)-1,3-dioxolane with the help of 1-menthyl acetate, dimethyl L-tartrate, or L-methyl lactate as the catalysts.

## Experimental

All experiments were carried out under the conditions previously published [1,7]. The molar ratio arene:Cr(CO)<sub>6</sub>:catalyst was 3:1:3, if not stated otherwise. The volume of the reaction mixture was usually 100 ml, and 1 g of Cr(CO)<sub>6</sub> was the usual amount in one experiment.

All products showed the correct elemental analysis and <sup>1</sup>H-NMR spectra.

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