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An improved method for the synthesis of η^6-arenetricarbonylchromium complexes

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Abstract

A novel apparatus for the complexation of arenes with $Cr(CO)_6$ is described. This, and the modification of the reaction procedure shortens the reaction time, and improves the yields of η^6-arenetricarbonylchromium complexes. The method was tested for representative samples of arenes. The same method was used for complexation of arenes with $Mo(CO)_6$ and $W(CO)_6$. In all cases, except for $(\eta^6\text{-}C_6H_5X)Cr(CO)_3$ (X = F, Cl) and $(\eta^6\text{-}C_6H_5N(CH_3)_2)W(CO)_3$, fair to excellent yields of the complexes were obtained.

Several methods for the synthesis of η^6-arenetricarbonylchromium complexes are known, including those which require the use of $Cr(CO)_3(NH_3)_3$ [1], $Cr(CO)_3(CH_3CN)_3$ [2] and $Cr(CO)_3(Py)_3$ [3] as the complexation agents. However, the commonest procedure involves the direct heating of arene with $Cr(CO)_6$ in refluxing solvent, such as dioxane, decalin or di-n-buthyl ether [4,5]. This procedure was improved by Pauson and Mahaffy [6] who used di-n-buthyl ether with 10–20% of THF as the reaction medium. Though the yields of the complexes vary from modest to excellent, the most serious drawback of this method consists in some decomposition of the product owing to the prolonged heating of the reactants (up to several days). The photochemical synthesis of tricarbonylchromium complexes [7] usually gives lower yields of the products.

The main goal of this work was to find conditions which would shorten the reaction time and minimize the decomposition of the product complex during the heating.

Results and discussion

Our previous work with the (η^6-arene)tricarbonylchromium complexes [8,9] has shown that most of the problems associated with them are due to the adequate purity of the starting materials and the solvent used. The stability of the complex is

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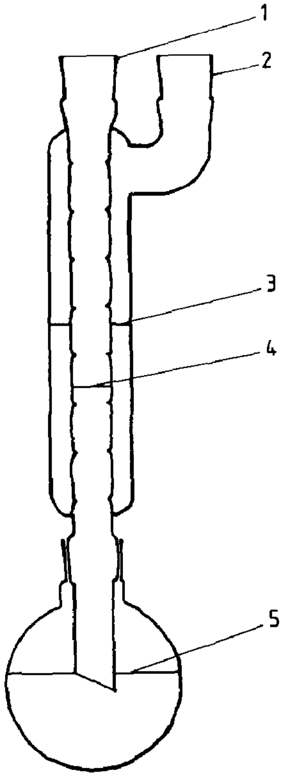

Fig. 1. The modified apparatus: 1,2 – ground joints, 3 – level of cooling liquid, 4 – level of the cooled part of the reaction mixture, 5 – level of the heated part of the reaction mixture.

very sensitive to impurities present in the reaction mixture and to traces of atmospheric oxygen over the mixture, since either can induce the autocatalytic decomposition of the complexes. Some of the problems, encountered during the preparation of complexes, are caused by the sublimation of the $Cr(CO)_6$ into the condenser during complexation.

It was necessary to devise a method which would prevent the sublimation of $Cr(CO)_6$ and minimize contact of the hot reaction mixture or the crude product with the air. First we concentrated on the purification of the starting materials and the solvent used (see Experimental). Then, to minimize sublimation by $Cr(CO)_6$ and contact of the the hot reaction mixture with the atmosphere, we devised a special adapter made from an ordinary Allinh condenser. It was converted as follows:

a) The lower part of the condenser was lengthened so that it was always immersed in the reaction mixture.

b) The inlet tube of the water jacket was sealed and the water outlet was replaced with a ground joint to which a reflux condenser could be attached (Fig. 1).

The apparatus for the complexation reactions consists of a reaction flask equipped with the adapter whose jacket is half-filled with a low boiling solvent such as acetone. Two condensers are attached to the adapter – one for carrying the CO liberated, and the second for the liquid in the jacket. During heating some of the reaction mixture is pushed into the adapter. Thus contact of the reaction mixture,

Table 1

Complexation data

No	Product	M.p. (°C)	Time (h)	Solvent	Yield (%)	Yield (%)	[Ref.]
1	$(\eta^6\text{-C}_6\text{H}_5\text{N(CH}_3)_2)\text{Cr(CO)}_3$	142–143	5.5	$(\text{n-Bu})_2\text{O}$	15.5		
2	$(\eta^6\text{-C}_6\text{H}_5\text{N(CH}_3)_2)\text{Cr(CO)}_3$	142–143	5.5	dioxan	13.5		
3	$(\eta^6\text{-C}_6\text{H}_5\text{N(CH}_3)_2)\text{Cr(CO)}_3$	142–143	5.5	decalin	99.5	85 (6)	
4	$(\eta^6\text{-C}_6\text{H}_5\text{N(CH}_3)_2)\text{Mo(CO)}_3$	> 120(dec.)	1	decalin	55	35	[10]
5	$(\eta^6\text{-Cd6H}_5\text{N(CH}_3)_2)\text{W(CO)}_3$	> 170(dec.)	4	decalin	1.5	82	[11]
6	$(\eta^6\text{-napthalene})\text{Cr(CO)}_3$	125–135	7	decalin	36		
7	$(\eta^6\text{-benzophenone})\text{Cr(CO)}_3$	92–93	2.5	decalin	45	55	[13]
8	$(\eta^6\text{-C}_6\text{H}_5\text{CH}_3)\text{Cr(CO)}_3$	82–84	4.5	decalin	34	53	[12]
9	$(\eta^6\text{-C}_6\text{H}_5\text{CO}_2\text{C}_2\text{H}_5)\text{Cr(CO)}_3$	57–58	3.5	decalin	76	15	[14]
10	$(\eta^6\text{-phenanthrene})\text{Cr(CO)}_3$	158 (dec.)	4	decalin	52		
11	$(\eta^6\text{-C}_6\text{H}_5\text{F})\text{Cr(CO)}_3$	126–128.5	3.5	decalin	8.1 [a]	90	[6]
12	$(\eta^6\text{-C}_6\text{H}_5\text{Cl})\text{Cr(CO)}_3$	78–87	5	decalin	1 [b]	64	[6]
13	$(\eta^6\text{-C}_6\text{H}_5\text{CO}_2\text{C}_2\text{H}_5)\text{Cr(CO)}_3$	57–58	25	$(\text{n-Bu})_2\text{O/THF}$	37	15	[14]
14	$(\eta^6\text{-C}_6\text{H}_5\text{CON(CH}_3)_2)\text{Cr(CO)}_3$	104–105.5	1	decalin	23		
15	$(\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{CO}_2\text{CH}_3)\text{Cr(CO)}_3$	77.5–78	4.5	decalin	83		
16	$(\eta^6\text{-C}_6\text{H}_5\text{CO}_2\text{CH}_3)\text{Cr(CO)}_3$	96–98	6.5	decalin	84	89	[6]

[a] 17% of $(\eta^6\text{-C}_6\text{H}_5)\text{Cr(CO)}_3$ was also isolated. [b] 6% of $(\eta^6\text{-C}_6\text{H}_5)\text{Cr(CO)}_3$ was also isolated.

which is at the boiling temperature of acetone (56 °C) with the atmosphere is restricted to a small area. The Cr(CO)_6 that sublimes on the walls is washed down from the adapter by warm solvent. The course of the reaction was followed volumetrically from the evolution of CO. The reaction is complete either when evolution of CO ceases, or when onset of decomposition is observed. On completion most of the product is frozen out (if decalin is the solvent), and the residue was chromatographed rapidly.

After preliminary experiments (Table 1, entries 1–3), decalin was found to be the best solvent, and the optimal molar ratio of arene to Cr(CO)_6 of 3.5 : 1 was used throughout the study. Vigorous boiling of the decalin (bath temperature about 240 °C) is preferable. Thus from the data listed in Table it is clear that our method can be used for the preparation of Mo(CO)_3, and of W(CO)_3 complexes (entries 4, 5); but the tungsten complex was prepared only in very low yield. Our method gives better product yields than the Pauson–Mahaffy procedure [6] in the case of (η^6-dimethylaminobenzene)-, and (η^6-ethoxycarbonylbenzene)tricarbonylchromium complexes, but much lower yields in the case of (η^6-(4-fluoro- or 4-chlorobenzene))tricarbonyl complexes (entries 11, 12). In these cases a reductive dehalogenation occurs because (η^6-benzene)tricarbonylchromium was isolated as the main product in 17 and 6% yields (entries 11 and 12, respectively). In all other cases the yields of the products are satisfactory, and the reaction time is much shorter (1–7 h) than with the Pauson method. We tested our adapter (entry 13) under conditions of the Pauson–Mahaffy procedure. The reaction time was only a little shorter (25 h), but our yield was more than double that of the Pauson–Mahaffy experiment.

There are methods which give better yields of the products than our's, but invariably prolonged heating with a large excess of arene is necessary, such as for (η^6-dimethylaminobenzene)Mo(CO)_3 (35%) [10], (η^6-dimethylaminobenzene)-

$W(CO)_3$ (82%) [11] or (η^6-toluene)$Cr(CO)_3$ (53%) [12], or an excess of $Cr(CO)_6$, such as for (η^6-benzophenone)$Cr(CO)_3$ (55%) [13].

Experimental

All solvents were carefully purified and dried. Special attention was paid to the purification of decalin. First, it was distilled from sodium, then stirred with 10 vol.% of conc. H_2SO_4 at 100 °C for 10 h. After separation it was refluxed during 8 h over sodium and then rectified under N_2. The solid arenes were purified either by sublimation (naphthalene, phenanthrene) or crystallization (benzophenone). The liquid arenes were purified by distillation, and $Cr(CO)_6$ was sublimed before use.

General procedure for complexation

A 3.5 : 1 mixture of the arene and $Cr(CO)_6$ in decalin (100 ml of decalin for 0.01 mol of $Cr(CO)_6$) was purged for 20 min with Ar, then evacuated for 20 min, and argon was again passed through it. This procedure was repeated 2–3 times. The reaction mixture was then refluxed till the evolution of CO had ceased or onset of decomposition was observed.

The mixture was cooled first to 20 °C, and then to −18 °C under argon. The crude product was filtered off, then dissolved in benzene and filtered through Kieselguhr. After concentration some light petroleum was added and the solution was left for crystallization at −18 °C. The residue which was insoluble in benzene yielded some $Cr(CO)_6$ by sublimation at 80 °C/10 mmHg. A second crop of product was isolated by chromatography of the decalin solution on a SiO_2 column. Decalin was eluted with petroleum ether, and the starting arenes were eluted either with petroleum ether/benzene 3 : 1 (naphthalene, phenanthrene) or petroleum ether/ethyl acetate 9.5 : 0.5 (*N,N*-dimethylaniline, benzophenone). The complexes were eluted with benzene/ethyl acetate 9.5 : 0.5. All products show the correct elemental analysis, and ^{1}H-NMR spectra. The yields given in Table 1 are based on the $Cr(CO)_6$ used up in the reaction.

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